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Reactive extraction for synthesizing long chain ester butyl hexanoate intensified by deep eutectic solvent

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ABSTRACT

Butyl hexanoate (BuHE) is an important long-chain ester that is widely used in the food, beverage and cosmetic industries. In this work, reactive extraction concept was proposed to intensify the BuHE formation in a biphasic system, in which deep eutectic solvent (DES) comprising 2-methylimidazole (2-MIm) and *p*-toluenesulfonic acid (PTSA) was used as dual solvent-catalyst. First, the effect of 2-MIm to PTSA molar ratio on esterification was investigated to determine the optimum DES of [2-MIm:2PTSA], which was characterized by FT-IR and TGA. Then, the liquid–liquid equilibrium (LLE) and esterification experiments were carried out to confirm the extraction and catalytic effect of [2-MIm:2PTSA], respectively. Afterwards, the pseudo-homogeneous kinetic model was employed to describe the esterification kinetics. Finally, the intensification mechanism of reactive extraction for BuHE formation was proposed according to the experiments and interaction effect analysis.

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1. Introduction

Butyl hexanoate (BuHE, C₁₀H₂₀O₂), an important long-chain ester derived from hexanoic acid (HeAc) and *n*-butanol (BuOH), is an essential ingredient of fruit flavor used in the food, beverage, and cosmetic industries [1–5]. It is conventionally synthesized by the Fischer esterification [6] with mineral acid (e.g. sulfuric acid) as homogenous catalyst [7], which suffers from equipment corrosion, difficult recycling and side reactions. Moreover, esterification is strongly limited by chemical equilibrium, and thus *in-situ* separating the products from reaction system is necessary.

To address the above problems and improve the reactants conversion, process intensification is expected to shift the chemical equilibrium towards the right [8]. For short-chain esters such as methyl acetate and butyl acetate, reactive distillation is effective owing to the large difference in boiling points of products ester and water [9–11]. However, for long-chain ester system including BuHE, the complex thermodynamics makes it difficult to properly match the reaction and distillation conditions [12,13]. Therefore, another intensification technology of reactive extraction is proposed for long-chain ester formation, with the benefit of thermodynamic nature of immiscibility between ester and water [14–

16]. Of central importance is the selection of a suitable solvent playing the dual role of extractant and catalyst, to not only efficiently catalyze the esterification but also strongly repel the product ester out of the reaction system.

Deep eutectic solvents (DESS) have been recently thrust into limelight as neoteric solvents, which refer to the mixtures of hydrogen bond acceptor (HBA) and hydrogen bond donors (HBD) in a certain stoichiometric ratio [17,18]. The complex HB network accounts for the charge delocalization inside DES system [19–21] that leads to the much lower melting points than that of the counterparts [22–24]. This spectrum of solvents shares the similar physicochemical properties with ionic liquids (ILs) of nonflammability, negligible vapor pressure, wide liquid range and designability [25–29]. However, DESSs show the superiority over ILs with respect to low cost, simple preparation, easy control and reasonable biodegradability, which render them as the new generation of ILs to employ in diverse fields including extraction, reaction, gas adsorption and electrodeposition [30–33].

Taking the acid-catalyzed reaction mechanism of esterification into account, the DES is desired to possess strong acidity [34–36]. For esterification, the PTSA-based DESSs have been reported to exhibit good catalytic performance. Hayyan *et al.* [37] found that DES consisting of PTSA and allyltriphenylphosphonium bromide could catalyze the esterification of crude palm oil (LGCP) containing free fatty acids, to reduce the content of free fatty acids. Taysun

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et al. [28] investigated the catalytic activities of three benzyl trimethyl ammonium chloride (BTMAC)-based acidic DESs for the esterification between acetic acid and butanol, in which the DES [BTMAC:PTSA] revealed the highest conversion. Li *et al.* [38] studied the esterification of ethanol and lauric acid catalyzed by three DESs based on benzyltrimethylammonium chloride (BAC) and PTSA, and the DES [BAC:3PTSA] showed the best catalytic results.

However, the aforementioned DESs contain environment-polluting and hazardous halogens that possibly cause environmental concerns and affect the product quality [39,40]. In addition, the halogen gases emit when preparing these DESs by the heating method, suggesting that the halogen anion could react with the sulfonic acid group to destroy the initial DESs structure [15]. Moreover, the above reports only focused on the catalysis effect of DES, but ignored the solvent effect. Qin *et al.* [15] proposed the acid-base tunable halogen-free DESs consisting of imidazole and PTSA to promote the isobutyl isobutyrate formation, and analyzed the solvent and catalysis effects of DES. However, the deep insights into the reaction mechanism of DES-based esterification are still rarely reported, and it is essential to investigate the intensification effect of DES as dual solvent-catalyst.

In this contribution, we prepared the halogen-free DES by PTSA and 2-methylimidazole (2-MIm) to intensify BuHE formation in the proposed reactive extraction process. The thermodynamic features and catalysis effect of DES were studied by LLE and esterification experiments, and the important parameters were optimized. The pseudo-homogeneous model was employed to correlate the experimental data. Finally, the intensification mechanism for the reactive extraction process was proposed.

2. Experimental

2.1. Reagents and chemicals

2-methylimidazole (2-MIm) ($\geq 98\%$), *p*-toluenesulfonic acid (PTSA) ($\geq 99\%$) and decane ($\geq 99\%$) were purchased from Adamas Beta Co. (Shanghai, China). Hexanoic acid (HeAc) ($\geq 99\%$), butyl hexanoate (BuHE) ($\geq 98\%$), *n*-butanol (BuOH) ($\geq 99\%$) and heptane were purchased from Aladdin Biochemical Technology Co. (Shanghai, China). All the chemicals were directly used as received without further purification.

2.2. DES preparation and characterization

2-MIm and PTSA in different molar ratios were weighted on a Sartorius BSA224S-CW balance with the precision of ± 0.0001 g. After that, the mixtures were heated and magnetically stirred at 353.15 K and 800 $\text{r}\cdot\text{min}^{-1}$ to form homogenous liquids. The temperature was controlled by Huber Ministat 230 with a fluctuation of ± 0.1 K (Offenburg, Germany). The DES melting point was measured by differential scanning calorimetry of Pyris Diamond DSC (Massachusetts, USA). The thermal stability of DES was determined by Thermogravimetric Analysis using PerkinElmer TGA-4000 (Massachusetts, USA). The pH of the aqueous DES ($0.10 \text{ mol}\cdot\text{L}^{-1}$) was measured by pH meter of Mettler Toledo FE20 (Zurich, Switzerland), and the DES density was obtained using the digital density meter of Anton Par DMA-4500M (Glaz, Austria). The IR spectra of 2-MIm, PTSA and DES were run on the spectrometer of PerkinElmer Spectrum 100 (Massachusetts, USA) using KBr discs.

2.3. Liquid-liquid equilibrium (LLE) determination

The LLE experiments of {BuHE + HeAc + [2-MIm:2PTSA]} and {BuHE + BuOH + [2-MIm:2PTSA]} were performed in 25 cm^3 vials with screw caps. The specific mass of HeAc or BuOH, BuHE and

DES [2-MIm:2PTSA] were introduced into the vials within the magnetic stirrers, after which the mixtures were vigorously stirred for 12 h and then settled for 12 h in the oil bath at 353.15 K. The samples were carefully taken out from both phases using syringes. The content of HeAc, BuOH and BuHE were detected by gas chromatograph of 7890 GC (California, USA) equipped with a flame ionization detector and a PEG-20M column, where heptane and decane were used as the internal standard substance of HeAc (BuOH) and BuHE, respectively. The DES content was determined according to the law of mass conservation.

2.4. Esterification experiment

The esterification reactions were performed in a 100 cm^3 round bottom flask, as described by the following typical process: specific amounts of BuOH and DES were charged into the flask at the desired temperature, and then the preheated HeAc was added at vigorous stirring of 1000 $\text{r}\cdot\text{min}^{-1}$. Liquid samples of 0.30 cm^3 were withdrawn at interval times of 5, 10, 30, 60, 90, 120, 180, 240, 300 min, and were quickly cooled down to avoid the further reaction. The HeAc conversion can be calculated from the initial and final HeAc concentration. All experiments and analyses were repeated at least three times to ensure reproducibility.

3. Results and Discussion

3.1. DES selection and characterization

3.1.1. DES selection

The DESs at different 2-MIm to PTSA molar ratios were investigated and compared to catalyze the BuHE formation. As shown in Fig. 1, when the molar ratio of 2-MIm to PTSA is 1:1, the *n*-butanol conversion was only 24.60 %, and the reaction system was homogenous. Further increasing PTSA content to 1:1.2, the conversion significantly increased to 74.54 %, and favorable phase splitting occurred. A maximum conversion of 85.17 % was reached at 1:2, after which the conversion slightly decreased. The DES contents in the upper phase were as well determined to evaluate the solvent loss, which were lower than 0.30 % to suggest a strong repulsion between DES and BuHE. As a result, 1:2 was chosen as the optimal molar ratio, and DES [2-MIm:2PTSA] was selected for further study.

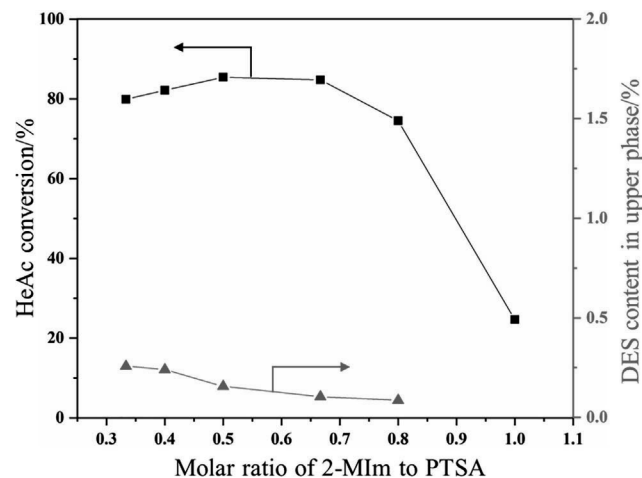


Fig. 1. The DES content in the upper phase and HeAc conversion at different 2-MIm to PTSA molar ratios of 1:1, 1:1.25, 1:1.5, 1:2.5, 1:3. (from right to left; 353.15 K, 5 h, BuOH to HeAc = 1:1, and 20% (mass) DES dosage).

3.1.2. DES characterization

In Fig. 2(a), the FTIR spectra of [2-MIm:2PTSA], PTSA and 2-MIm were recorded. For PTSA, the peaks at 1170 cm^{-1} and 1130 cm^{-1} were attributed to the anti-symmetric and symmetrical stretching vibration of S = O, respectively. With respect to 2-MIm, the stretching vibration of N-H on the imidazole ring were observed at 3180 cm^{-1} , and the peak at 1590 cm^{-1} reflected the vibration of imidazole ring skeleton; moreover, the absorption peak at 1150 cm^{-1} was ascribed to the stretching vibration of the imidazole ring. Compared PTSA to [2-MIm: 2PTSA], the stretching vibration of OH was red-shifted from 3450 cm^{-1} to 3440 cm^{-1} ; while compared 2-MIm to [2-MIm:2PTSA], the peak of NH changed from 3180 cm^{-1} to 3160 cm^{-1} . All the above changes proved that hydrogen bond was formed between 2-MIm and PTSA to produce DES [2-MIm:2PTSA].

The melting point of [2-MIm:2PTSA] was determined as 289.15 K , which was much lower than those of 2-MIm (415.15 K) and PTSA (377.15 K) to justify the DES formation. Moreover, the TGA curves were depicted in Fig. 2(b) to evaluate the DES thermal stability. The mass loss of [2-MIm:2PTSA] before 423.15 K was around 9% , which was ascribed to the decrease of water content. After that, the DES mass almost kept constant until 503.15 K , where a significant mass loss appeared to reflect the decomposition of DES. Therefore, [2-MIm:2PTSA] can remain stable until

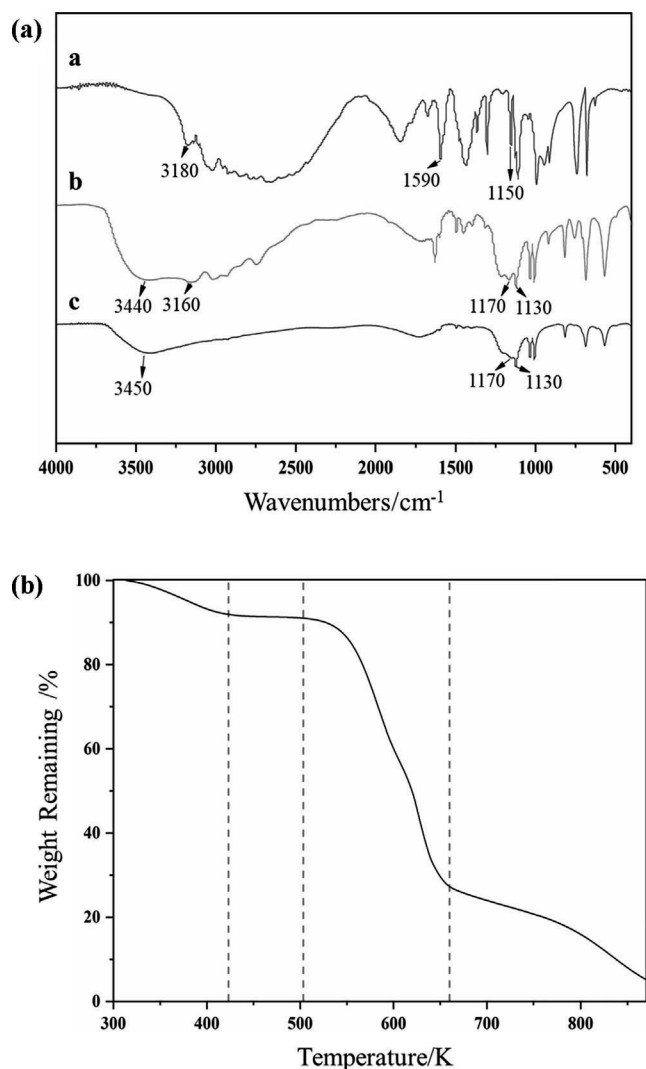


Fig. 2. (a) FTIR spectra of (1) 2-methylimidazole, (2) [2-MIm:2PTSA] and (3) PTSA, respectively; (b) TGA curves of [2-MIm:2PTSA].

503.15 K , which was much higher than that of the BuHE esterification temperature. The density of [2-MIm:2PTSA] was $1.27\text{ g}\cdot\text{cm}^{-3}$ at 298.15 K ; and the pH of $0.10\text{ mol}\cdot\text{L}^{-1}$ aqueous DES solution was 0.61, suggesting the strong acidity of [2-MIm:2PTSA].

3.2. Liquid-liquid equilibrium

The LLE of {DES + HeAc + BuHE} and {DES + BuOH + BuHE} were investigated to demonstrate the extraction effect of DES [2-MIm:2PTSA] on esterification system. The Othmer-Tobias equation was used to verify the reliability and consistency of the LLE data, which was expressed as:

$$\ln\left(\frac{1-w_2^R}{w_2^R}\right) = a + b \ln\left(\frac{1-w_3^E}{w_3^E}\right) \quad (1)$$

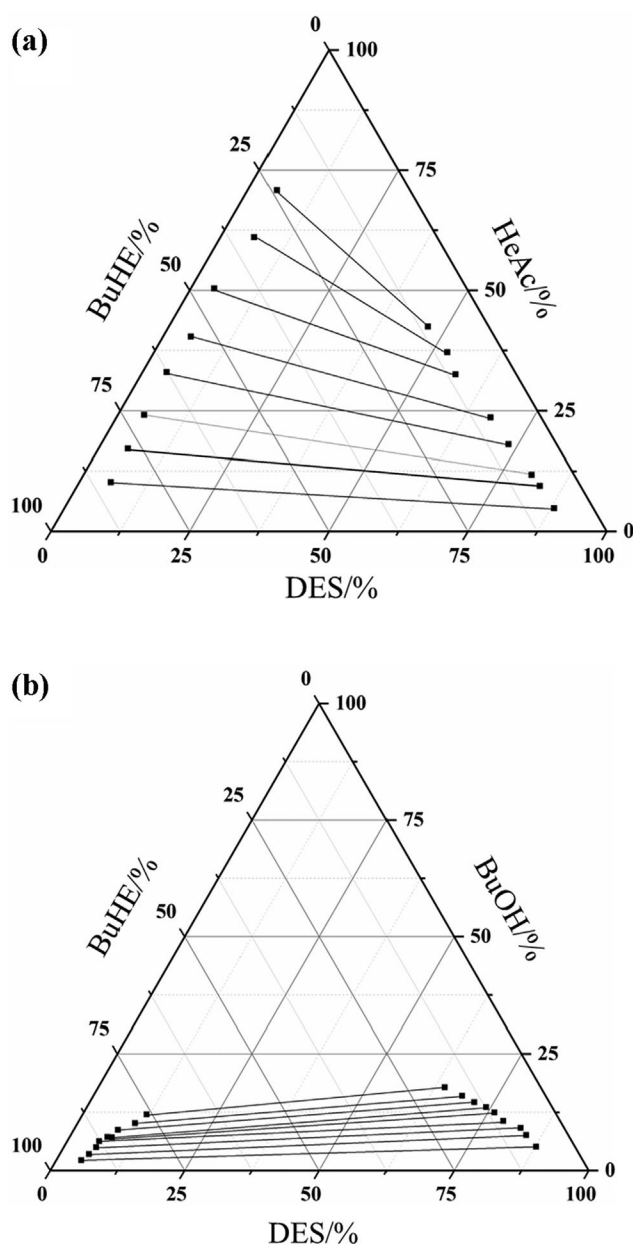


Fig. 3. Mass-based LLE for ternary systems of (a) {BuHE + HeAc + DES} and (b) {BuHE + n-BuOH + DES} at 353.15 K and 101.3 kPa (stirring time 12 h, settling time 12 h).

where w_2^R and w_2^E denoted the mass fraction of BuHE in the raffinate and DES in the extract, respectively. Accordingly, the linear regression coefficients of R^2 were 0.98 and 0.97 for {DES + HeAc + BuHE} and {DES + BuOH + BuHE}, respectively, suggesting the reliability of the experimental data.

From Fig. 3(a), the negative slope of tie lines suggested that HeAc had a stronger affinity for BuHE than DES. On the contrary, BuOH was more soluble in DES than in BuHE, since a positive slope of tie lines was observed in Fig. 3(b). In addition, the large immiscible gap in Fig. 3(a) indicated that changing HeAc dosage had a relatively small impact on the phase splitting; while the variation of BuOH dosage could obviously influence the phase splitting due to the small immiscible gap in Fig. 3(b). Moreover, the poor miscibility between DES and ester could reflect the strong repulsion between each other.

Based on the above analysis, firstly both BuOH and HeAc could dissolve into DES to form a homogenous state, which was helpful to the sufficient contacts between reactants and catalyst to accelerate the esterification. As the reaction went on, the product BuHE could be automatically removed from the reaction system. Simultaneously, DES could attract BuOH and HeAc from the ester phase into the DES phase to be converted.

The initial reactants molar ratio was very important for the esterification process, to cause different phase states after reaction [41]. The excess HeAc could promote the phase splitting to *in-situ*

remove BuHE from the DES phase, which was advantageous to shift the chemical equilibrium towards the right. However, excess HeAc enriched in the ester phase to increase the separation cost. By contrast, BuOH was more distributed in the DES phase, whereas excess BuOH may lead to the disappearance of phase splitting and a final homogenous phase state, which was not beneficial for shifting the chemical equilibrium and separating the product BuHE. Therefore, an appropriate reactants molar ratio was momentous for the reactive extraction process.

3.3. Esterification experiments

In this section, the influence of important reaction parameters including DES dosage, reaction temperature and initial reactants ratio were studied, to reveal the catalysis effect of DES and identify the optimal reaction conditions.

3.3.1. Effect of DES dosage

The effect of DES dosage ranging from 0 to 30% (mass) (based on the initial total mass of BuOH and HeAc) was illustrated in Fig. 4(a), with the fixed reaction temperature and BuOH to HeAc molar ratio of 353.15 K and 1, respectively. In the absence of DES, the HeAc conversion grew very slowly over time and only 4.98 % conversion was reached at 300 min. However, the introduce of DES significantly increased the reaction rate and HeAc conversion, which

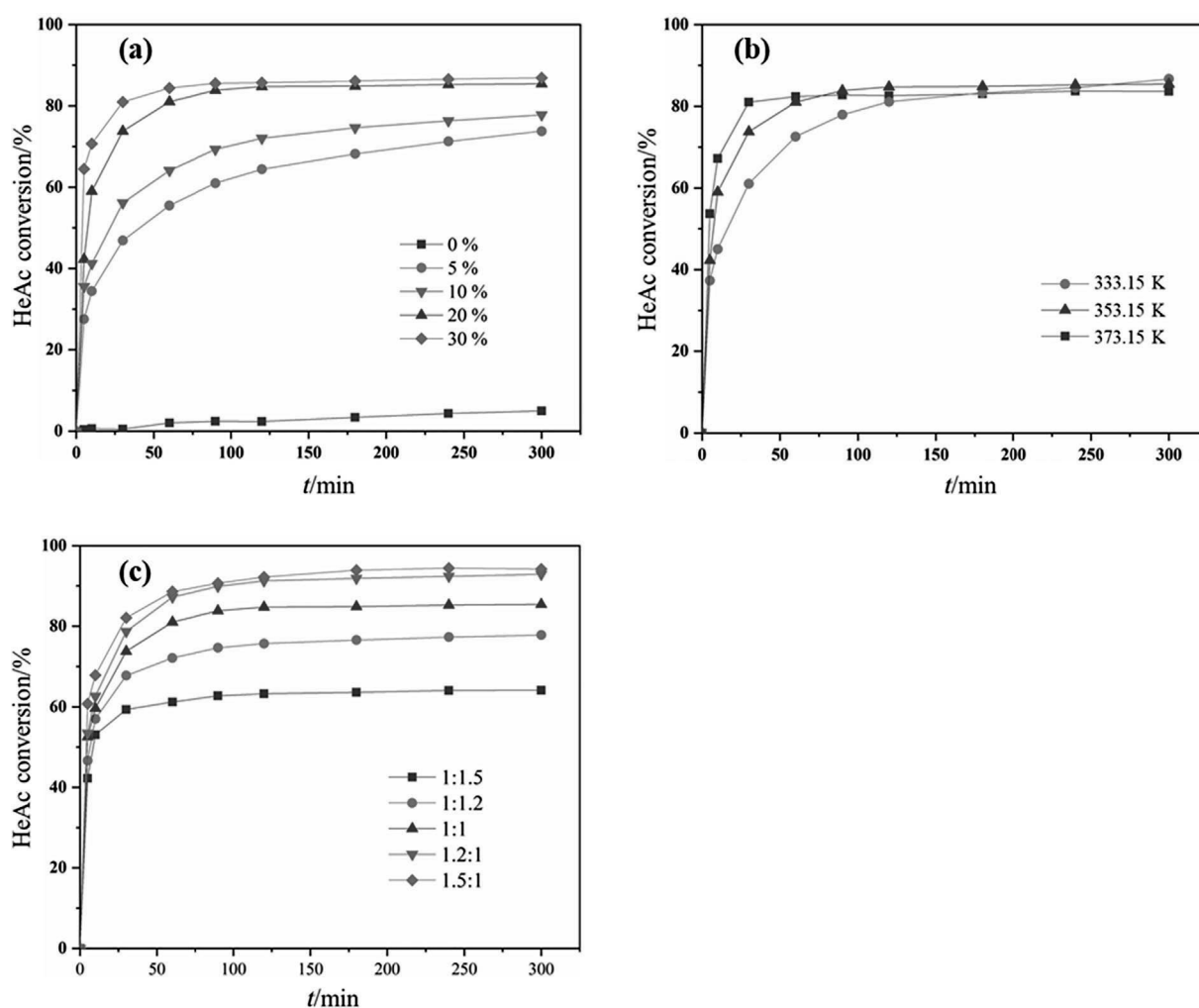


Fig. 4. Effect of (a) DES dosage (353.15 K, BuOH to HeAc = 1:1), (b) reaction temperature (20% (mass) DES dosage, BuOH to HeAc = 1:1) and (c) initial molar ratio of BuOH to HeAc (353.15 K, 20% (mass) DES dosage) on HeAc conversion as a function of time.

reflected the good catalysis effect of [2-MIm:2PTSA]. Moreover, the reaction rate and HeAc conversion showed a positive correlation with DES dosage. The HeAc conversion obviously improved in the range of 5%–20% (mass) DES; while it changed slightly further increasing DES dosage to 30% (mass). As a result, 20% (mass) DES was selected given both the HeAc conversion and DES cost, and the equilibrium conversion could reach 84.77 % at 120 min.

3.3.2. Effect of reaction temperature

At the condition of 20% (mass) DES dosage and BuOH to HeAc molar ratio of 1, the effect of temperature was investigated varying from 333.15 K to 373.15 K. As displayed in Fig. 4(b), the temperature affected not only the reaction rate but also the equilibrium conversion, and the reaction rate increased with temperature. For example, the esterification at 333.15 K had not reached the chemical equilibrium at 300 min; while raising the temperature to 353.15 and 373.15 K, the reaction could attain equilibrium within 120 min. The equilibrium HeAc conversion showed a slightly negative correlation with temperature, manifesting that BuHE esterification was exothermic. Considering both the reaction rate and equilibrium conversion, 353.15 K was determined as the optimal temperature.

3.3.3. Effect of initial reactants molar ratio

With 20% (mass) DES dosage and 353.15 K, the effect of initial BuOH to HeAc molar ratio was studied from 1:1.5 to 1.5:1. As can be seen from Fig. 4(c), changing reactants molar ratio from 1:1.5 to 1.2:1 could remarkably increase the HeAc conversion from 63.23 % to 91.27 % at 120 min, after which it raised very slightly to 92.23 % with the further addition of BuOH. From the LLE point of view, HeAc was more soluble in the ester phase according to the analysis of Section 3.2; moreover, the boiling points of HeAc (478.15 K) and BuHE (481.15 K) were high and close, making it difficult to separate HeAc from ester. Therefore, to facilitate the HeAc conversion and reduce the HeAc content, excess BuOH (boiling point: 390.15 K) was necessary. To sum up, 1.2:1 of BuOH to HeAc molar ratio was confirmed as the optimal condition.

3.4. Chemical equilibrium

The equilibrium constant for the esterification is described as follows [42,43]:

$$K_{eq} = \frac{c_{Ce}c_{De}}{c_{Ae}c_{Be}} \quad (2)$$

where K_{eq} is the chemical equilibrium constant, and c_{Ae} , c_{Be} , c_{Ce} , c_{De} represent the concentrations of HeAc, BuOH, ester and water at the chemical equilibrium state ($\text{mol}\cdot\text{L}^{-1}$), respectively. The standard reaction enthalpy can be calculated from the Vant' Hoff equation:

$$\ln(K_{eq}) = \frac{-\Delta_r H^0}{RT} + C \quad (3)$$

where C is a constant.

The relationship plot of $\ln K_{eq}$ and T^{-1} was depicted in Fig. 5(a), and the equilibrium constant can be expressed as:

$$\ln K_{eq} = \frac{1477.96}{T} - 0.6753 \quad (4)$$

According to Eqs. (2) and (3), $\Delta_r H^0$ was determined as $-12.29 \text{ kJ}\cdot\text{mol}^{-1}$, indicating that the esterification was exothermic.

3.5. Kinetic modelling

The pseudo-homogeneous (PH) model was widely applied in the reaction system including one or more reactants/solvents with

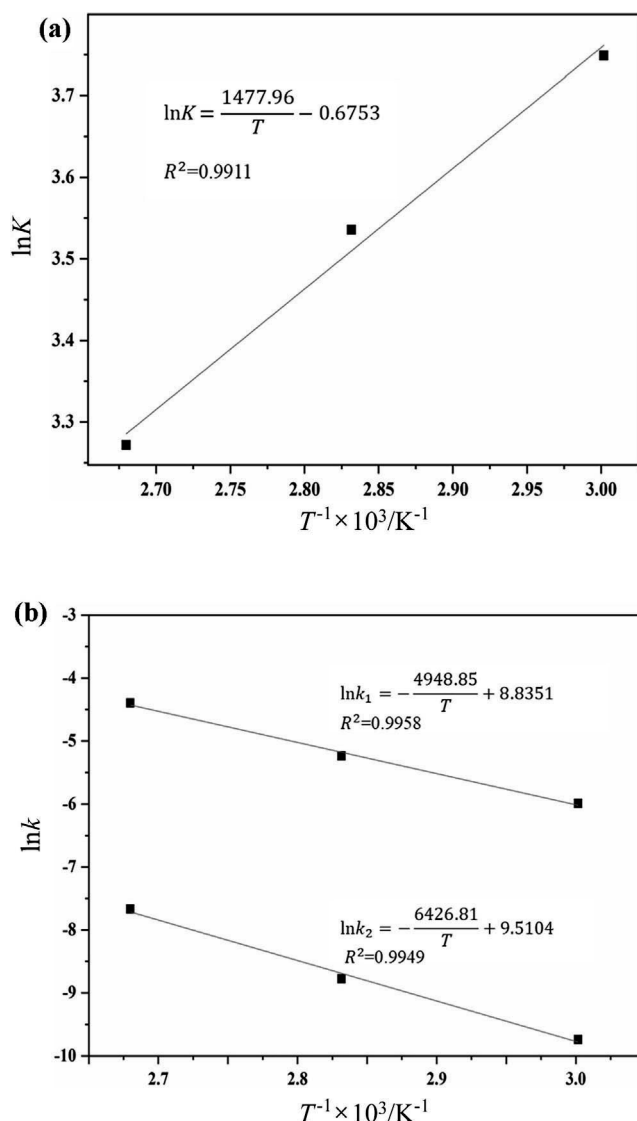


Fig. 5. The relationship between (a) $\ln K$ and $1000/T$ (b) $\ln k_i$ and $1000/T$.

strong polarity [44,45], which was used to describe the BuHE formation as follows:

$$r_A = k_1 c_A c_B - k_2 c_C c_D = k_1 \left(c_A c_B - \frac{1}{K_{eq}} c_C c_D \right) \quad (5)$$

k_1 , k_2 are the kinetic constants of the forward and backward reactions, respectively, which can be obtained from the Arrhenius equation:

$$k_i = k_{i,0} e^{\frac{-E_{a,i}}{RT}} \quad (6)$$

where $k_{i,0}$ and $E_{a,i}$ are the pre-exponential factor and activation energy, respectively. The relationship between k_1 , k_2 and K_{eq} can be expressed as

$$K_{eq} = k_1/k_2 \quad (7)$$

The kinetic parameters were fitted using the experimental data by the least squares method, which were summarized in Tables 1 and 2.

The Arrhenius plot of $\ln k_i$ versus T^{-1} was illustrated in Fig. 5(b). Based on the obtained kinetic parameters, the reaction rate equation can be expressed as:

Table 1

Kinetic parameters of the pseudo-homogeneous model at 333.15 K, 353.15 K and 373.15 K, respectively

T/K	$k_1/\text{mol}\cdot\text{min}^{-1}$	Standard error/ $\text{mol}\cdot\text{min}^{-1}$	RMSD
333.15	2.50×10^{-3}	8.36×10^{-5}	0.0238
353.15	5.31×10^{-3}	1.12×10^{-4}	0.0215
373.15	1.23×10^{-2}	2.53×10^{-4}	0.0441

Table 2The pre-exponential factors $k_{i,0}$ and activation energy $E_{a,i}$

	$k_{i,0}/\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$	$E_{a,i}/\text{J}\cdot\text{mol}^{-1}$
The forward reaction	6.87×10^3	4.11×10^4
The inverse reaction	1.35×10^4	5.34×10^4

$$r = 6.87 \times 10^3 \exp\left(-\frac{4.11 \times 10^4}{RT}\right) C_A C_B - 1.35 \times 10^4 \exp\left(-\frac{5.34 \times 10^4}{RT}\right) C_C C_D \quad (8)$$

The comparison between the experimental data and the calculated values by the PH model was shown in Fig. 6. The root mean square deviation (RMSD) can be calculated as follows:

$$\text{RMSD} = \sqrt{\sum_{i=1}^N (x_{\text{HeAc,cal},i} - x_{\text{HeAc,exp},i})^2 / N} \quad (9)$$

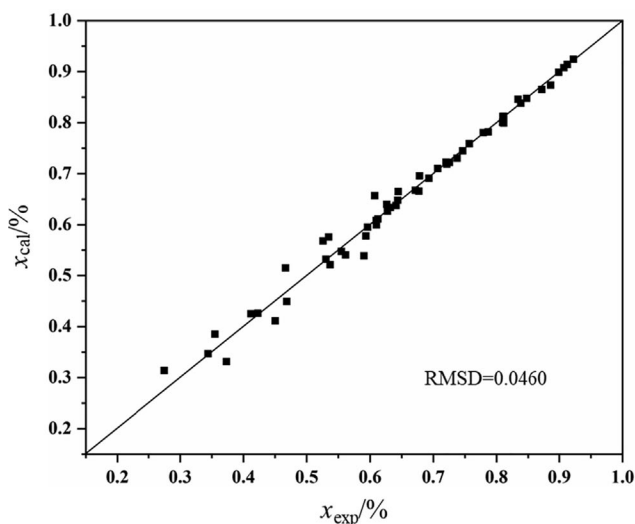
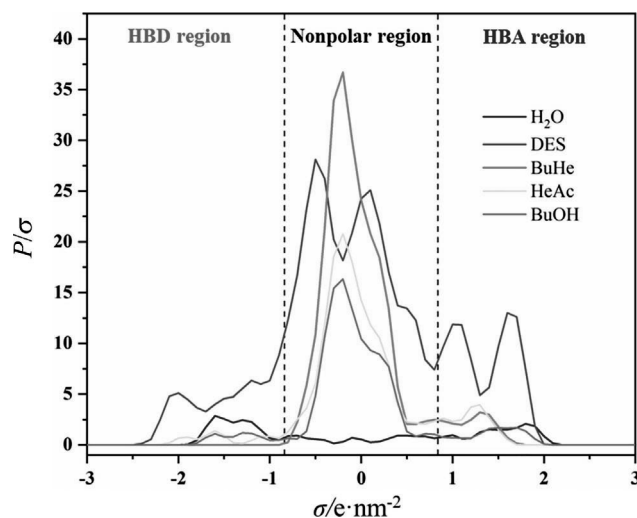
The RMSD was only 4.60%, reflecting a good representation of the esterification kinetic behavior using the PH model.

3.6. Intensification mechanism of reactive extraction

3.6.1. Interaction effect analysis by COSMO-RS

The qualitative understanding of the intermolecular interaction for the esterification system is available according to the COSMO-RS theory. The σ -profile plot was divided into three regions, including the nonpolar region ($-0.84 \text{ e}\cdot\text{nm}^{-2} < \sigma < 0.84 \text{ e}\cdot\text{nm}^{-2}$), the HBD region ($\sigma < -0.84 \text{ e}\cdot\text{nm}^{-2}$), and the HBA region ($\sigma > 0.84 \text{ e}\cdot\text{nm}^{-2}$). The σ -profiles of HeAc, BuOH, BuHE, H₂O, and DES were shown in Fig. 7.

For BuHE, the σ -profile mostly distributed in the nonpolar region. Only a weak peak existed in the HBA region, while no peak

**Fig. 6.** Comparison between the calculated and experimental HeAc conversion.**Fig. 7.** σ -Profiles of HeAc, BuOH, BuHE, H₂O, and DES, respectively.

appeared in the HBD region. Thus, BuHE is supposed to present very weak polarity and strongly repel the strong polar components. On the contrast, the σ -profiles of H₂O and DES have broad distributions in the polar regions, suggesting their strong polarity as both HBA and HBD. Therefore, from the *like dissolve like* rule, there should be strong repulsion between DES/H₂O and BuHE, but strong affinity of water towards DES.

Regarding the σ -profiles of HeAc and BuOH, the similar distributions of them were found in both polar and nonpolar regions, reflecting the strong interaction with each other to bring about a good miscibility. Moreover, peaks appeared in both HBA and HBD regions to suggest their ability acting as both HBA and HBD. Consequently, they can interact with DES through hydrogen bonds. HeAc and BuOH can likewise interact with BuHE through van der Waals forces, due to the peaks in the nonpolar region.

3.6.2. Intensification mechanism of reactive extraction

Based on the experimental results and σ -profile analysis, the intensification mechanism for such a reactive extraction process was proposed in Fig. 8. At the beginning of esterification, HeAc, BuOH and DES were miscible with each other to bring about a homogenous state, which could promote the sufficient contacts of them. With the catalysis effect of DES, the products of BuHE and water continually produced. Owing to the solvent effect of DES, the DES will force BuHE and water into different phases. BuHE was *in-situ* repelled out of the reaction system into the ester phase, while water enriched in the DES phase. As a result, favorable phase splitting occurred to push the reaction towards the right.

Meanwhile, BuHE could attract the reactants of HeAc, BuOH into the ester phase. However, DES will extract them back into the DES phase to convert, accordingly reaching the high conversion. Once the reaction was complete to reach the final phase and chemical equilibrium, two phases were obtained. The product BuHE mainly stayed in the ester phase, while water and DES remained in the DES phase. As a consequence, the esterification of HeAc with BuOH was promoted and intensified with DES [2-MIm:2PTSA] as dual solvent-catalyst.

4. Conclusions

The reactive extraction was proposed to promote the BuHE formation, with the halogen-free DES [2-MIm:2PTSA] as dual solvent-catalyst. First, the effect of 2-MIm to PTSA molar ratios was investigated to confirm the optimal DES of [2-MIm:2PTSA], which was

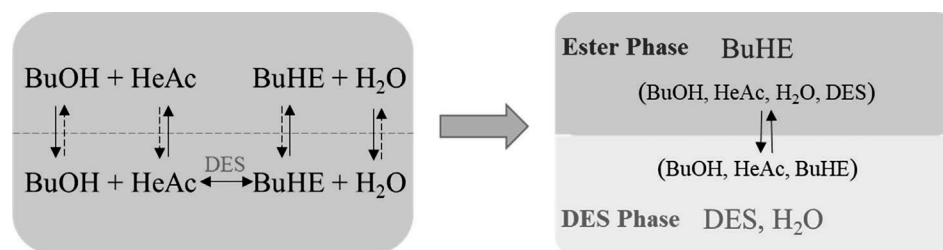


Fig. 8. The intensification mechanism for the reactive extraction process.

characterized by FT-IR and TGA to analyze the formation mechanism and thermal stability, respectively. Afterwards, the LLE experiments of two ternary systems of {BuHE + HeAc + [2-MIm:2PTSA]} and {BuHE + BuOH + [2-MIm:2PTSA]} were performed to affirm the solvent effect of [2-MIm:2PTSA]. It concluded that DES showed a strong repulsion to BuHE, and reactants of HeAc and BuOH reflected a contrary distribution in DES and ester. Moreover, the esterification experiments were carried out to determine the catalysis effect, and the reaction parameters were optimized to obtain a high HeAc conversion of 91.27 %, at the condition of 1.2:1 BuOH to HeAc, 353.15 K and 20% (mass) DES dosage. In addition, the pseudo-homogeneous model was used to successfully describe the kinetic behavior of esterification by correlating the experimental data, with a small RMSD of 4.60 %. Finally, based on the experimental results and the interaction effect analysis by COSMO-RS, the intensification mechanism of reactive extraction was proposed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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