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Long-Chain Ester Formation Intensified by Bifunctional Solvents and Reactive Extraction

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Highlights

- An innovative intensified reactive extraction process is proposed.
- Ionic liquid [BMIm][HSO_4] and deep eutectic solvent as dual catalyst and solvent are used.
- Formation of isobutyl isobutyrate is taken as example.
- LLE and reactive extraction process performance are determined experimentally.

1. Introduction

Long-chain esters are widely applied as solvent, additive and raw materials. For instance, isobutyl isobutyrate (IBIBE), one of long-chain esters formed by fatty acids and alcohols, is an important additive and intermediate in the food and pharmaceutical industries. IBIBE is conventionally synthesized by the Fischer esterification of isobutyric acid (IBAc) with isobutanol (IBOH).[1] However, this traditional process suffers from problems of recycling liquid catalyst hydrogen sulfate, severe corrosion due to the strong acidity of catalyst, and produced acidic waste.[2-3] In addition, esterification is an equilibrium-limited reaction; the unconverted reactants will come out with the product. Due to the complex thermodynamics of the reaction system, azeotropes of {IBAc + IBIBE}, {IBIBE + H_2O}, {IBOH + IBE +H_2O} and liquid phase splitting can be generated, which makes it very difficult to separate the reaction mixture effectively by employing an ordinary distillation. To address these serious problems, an innovative intensified reactive extraction process employing ionic liquids (ILs) as dual catalyst and solvent is proposed in this work.

2. Method

The proposed reactive extraction process with dual catalyst and solvent is illustrated in Fig. 1. As long-chain esters are not miscible with water, they will split into the IL phase and ester phase once formed by chemical reaction, which can remove water and ester simultaneously with IL as solvent. The proposed new concept makes full use of thermodynamic features of the esterification system, thus the conversion significantly enhanced by the integration of reaction and extraction. [BMIm][HSO_4], one of the typical Brønsted acidic ILs with easy commercial access, is employed for IBIBE formation.

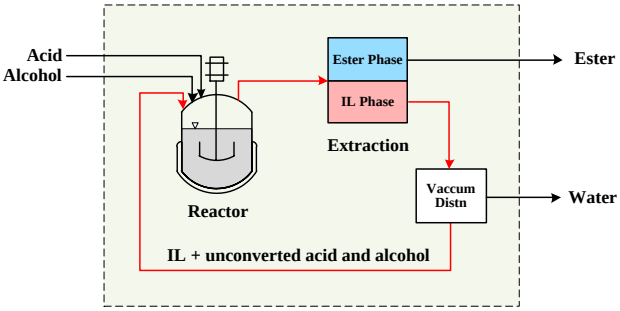

Fig. 1. Long-chain ester formation intensified by reactive extraction.

All experiments of LLE, kinetics and extraction process were carried out. Samples from the IL phase (lower layer) and ester phase (upper layer) were analyzed by a gas chromatograph equipped with a flame ionization detector and a PEG-20 M column using an internal standard method where decane was the internal standard substance.

3. Results and discussion

Considering the forward reaction between IBAc and IBOH and reverse reaction between IBIBE and H_2O, the thermodynamics properties of this reactive extraction process using ternary systems involving no reaction and quinary system which reaches both chemical and physical equilibrium are syudied.

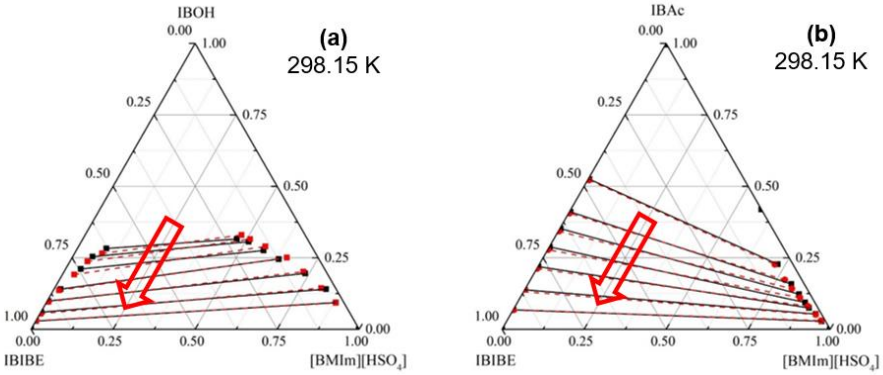

Fig. 2. Experimental and calculated LLE data for the ternary systems

From Fig. 2, IBIBE and IL are almost immiscible, indicating that [BMIm][HSO_4] is a proper extractant to remove IBIBE from the system by phase splitting. With the comparison of phase region, the solubility of IBOH in IL is higher than IBAc, suggesting that it is important to select a proper reactant ratio. All the obtained LLE data of the ternary and quinary systems were correlated by the NRTL model. NRTL model can predict LLE of the ester system, and it can be used for the activity-based reaction kinetics.

Based on the proposed reactive extraction process with ionic liquid as dual catalyst and solvent, the process parameters are optimized as following: T = 353.15 K, IBAc/IBOH = 1:1 (mol), IL dosage = 20 wt%, the overall conversion of IBAc can reach 99.7% and the purity of ester can be as high as 98.6%, which can be further enhanced by downstream separation.

In addition, deep eutectic solvent formed by imidazolium and PTSA is also analyzed as dual catalyst and solvent for IBIB formation, which demonstrates very promising intensification effect for long chain ester formation by using reactive extraction process.

4. Conclusions

Ionic liquid [BMIm][HSO_4] and deep eutectic solvent formed by imidazolium and PTSA are used as dual solvent and catalyst for the long-chain ester formation. LLE data for isobutyl isobutyrate systems were determined experimentally and fitted by the NRTL model. The effect of IL dosage, reaction temperature and reactant molar ratio on the reaction have been studied. An intensified reactive extraction process for isobutyl isobutyrate formation was proposed and experimentally validated. The proposed reactive extraction concept are applicable for general long-chain ester formation.

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Keywords
Liquid-liquid equilibria, Isobutyl isobutyrate, Ionic liquid/Deep eutectic solvent, Reactive extraction

Dr. Hongye Cheng (Male, born in 1985) received his doctorate in Chemical Engineering from the East China University of Science and Technology (ECUST) in 2013. From Sep. 2011 to Sep. 2012, he worked as a joint Ph.D. student at the Norwegian University of Science and Technology (NTNU) under the supervision of Prof. Per-Olof Åstrand and Prof. De Chen. Due to his achievements, he was awarded *National Scholarship* in 2013 and *Excellent Doctoral Dissertation of ECUST* in 2015. After working as a postdoctoral fellow at the ECUST with Prof. Zhiwen Qi (2013-2016), he became an Assistant Professor of Chemical Engineering at the State Key Laboratory of Chemical Engineering at ECUST in Shanghai (2016-now).

Dr. Hongye Cheng has published more than 30 papers. His current research interests include ionic liquid intensified reaction processes, computer-aided solvent design and screening, molecular simulation of carbon-supported Pt catalyst. He focuses on long chain ester formation with the intensification of dual functional solvent of ionic liquid and deep eutectic solvent. For this purpose, he designs the suitable solvent structure relying on the liquid-liquid equilibrium, and further outlines the suitable windows of operation parameters.

In recent years, he has conducted or participated in 7 projects funded by National Natural Science Foundation of China, Ministry of Education, Shanghai Scientific and Technological Commission, and China Postdoctoral Science Foundation.

Selected Publications:

1. Lei Qin, Qian Zeng, Jingjing Zhang, Hongye Cheng*, Lifang Chen, Zhiwen Qi. Integrated process for extracting vitamin E with high purity from the methylated oil deodorizer distillate. ***Separation and Purification Technology***. 2017, DOI: 10.1016/j.seppur.2017.05.031.
2. Lei Qin, Jiangsheng Li, Hongye Cheng, Lifang Chen, Zhiwen Qi*, Weikang Yuan. Association extraction for vitamin E recovery from deodorizer distillate by in situ formation of deep eutectic solvent. ***AIChE Journal***, 2017, 63(6):2212-2220.
3. Qian Zeng, Jinwei Zhang, Hongye Cheng*, Lifang Chen, Zhiwen Qi. Corrosion properties of steel in 1-butyl-3-methylimidazolium hydrogen sulfate ionic liquid systems for desulfurization application. ***RSC Advances***, 2017, 7, 48526 - 48536
4. Hongye Cheng, Jinwei Zhang, Zhiwen Qi*. Effects of Interaction with Sulfur Compounds and Free Volume in Imidazolium-based Ionic Liquid on Desulfurization: A Molecular Dynamics Study. ***Molecular Simulation***. 2017, DOI: 10.1080/08927022.2017.1337273
5. Jianan Zhang, Daili Peng, Zhen Song, Hongye Cheng, Lifang Chen, and Zhiwen Qi*. COSMO-descriptor based computer-aided ionic liquid design for separation processes. Part I: Modified group contribution methodology for predicting surface charge density profile of ionic liquids. ***Chemical Engineering Science***, 2017, 162:355-363.
6. Jianan Zhang, Lei Qin, Daili Peng, Hongye Cheng, Lifang Chen, and Zhiwen Qi*. COSMO-descriptor based computer-aided ionic liquid design for separation processes. Part II: Task-specific design for extraction process. ***Chemical Engineering Science***, 2017, 162:364-374.
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8. Hongye Cheng, Yian Zhu*, De Chen, Per-Olof Åstrand, Ping Li, Zhiwen Qi, Xinggui Zhou. Evolution of Carbon Nanofiber-Supported Pt Nanoparticles of Different Particle Sizes: A Molecular Dynamics Study. ***J. Phys. Chem. C***. 2014, 118, 23711-23722.
9. Hongye Cheng, Yian Zhu*, Per-Olof Åstrand, De Chen, Ping Li, Xinggui Zhou. Evolution of Pt Nanoparticles Supported on Fishbone-Type Carbon Nanofibers with Cone-Helix Structures: A Molecular Dynamics Study. ***J. Phys. Chem. C***. 2013, 117, 14261-14271
10. Hongye Cheng, Per-Olof Åstrand*, De Chen, Yian Zhu, Xinggui Zhou, Ping Li. Adsorption of a Single Pt Atom on Polyaromatic Hydrocarbons from First-Principle Calculations. ***Chem. Phys. Lett***. 2013, 575, 76-80,.
11. Hongye Cheng, Yian Zhu*, Zhijun Sui, Xinggui Zhou, De Chen. Modeling of Fishbone-Type Carbon Nanofibers with Cone-Helix Structures. ***Carbon***. 2012, 50(12), 4359-4372.

Selected talks/lectures

1. Evaluating the Performance of Deep Eutectic Solvents for Extractive Desulfurization of Fuel by the COSMO-RS. The 9th Sino-US Joint Conference of Chemical Engineering. Beijing, China. Oct. 15-19, 2017.
2. An association extraction process for vitamin E recovery from the methylated oil deodorizer distillate by in-situ formation of deep eutectic solvent. The 3rd International Conference on Ionic Liquids in Separation and Purification Technology. Kuala Lumpur, Malaysia. Jan. 8-11, 2017.

Awards

1. National Scholarship (2013)
2. Excellent Doctoral Dissertation of ECUST (2015)