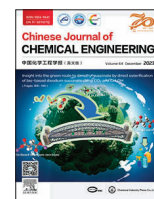




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Full Length Article

Separation of fuel additives based on mechanism analysis and thermodynamic phase behavior

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ABSTRACT

tert-butanol and ethyl acetate, as fuel additives and oxygenated fuels, can improve fuels quality and reduce exhaust emissions. Therefore, the recovery of these compounds from azeotropic systems is of great significance. Ionic liquids (ILs) are promising green solvents for separating azeotropic systems. In this study, an efficient extraction strategy based on 1-butyl-3-methylimidazolium acetate ([Bmim][AC]) is proposed. The mechanism by which ILs enable the separation of binary alcohol-ester azeotropes was revealed by evaluating the lowest conformational energy through combining an independent gradient model based on the Hirshfeld partition (IGMH) and frontier molecular orbitals, to preliminarily screen the extractants. The range of extractants was further reduced by a vapor–liquid phase equilibrium (VLE) experiment, and a modeling method for separating the alcohol–ester system and recovering the solvent using [Bmim][AC] and 1-ethyl-3-methyl-3-imidazolium acetate ([Emim][AC]) is established. Under the optimal operating conditions, the use of [Bmim][AC] can reduce the total annual cost (TAC) per year by 17.78%, and the emissions of CO₂, SO₂, and NO can be reduced by 10.86%. In this study, a comprehensive method for screening extractants is proposed, and the simulation process is optimized in combination with the economic and environmental impact. The results have important guiding significance for realizing efficient, energy-saving, and green azeotropic separation systems in industry.

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1. Introduction

With the reduction in oil resources and the increase in pollutant emissions, reducing fuel consumption and improving emissions have become the top priorities in internal combustion engine research [1]. In addition to improving the engine, the addition of oxygen-containing fuels and additives is a practical and feasible measure for improving fuel quality and reducing exhaust emissions [2,3].

As an environmentally friendly compound, ethyl acetate is a potential oxygen-containing biofuel with a low kinematic viscosity, good cold-flow characteristics, and high miscibility with VOs and fossil diesel, which can increase the safety of fuel treatment and transportation and improve engine performance in winter [4–6]. *tert*-butanol is a versatile chemical product and intermediate that can be used not only as a synthetic intermediate, antioxidant, and solvent, but also as a fuel additive instead of methyl *tert*-butanol [7,8]. Mixing oxygen-containing fuel with fuel can improve

the impact resistance and reduce tail-gas emissions [9,10]. However, ethyl acetate and *tert*-butanol form an azeotropic mixture under atmospheric pressure, which is difficult to separate; therefore, it is important to achieve efficient separation of the azeotropic system to obtain valuable substances.

Distillation is one of the most commonly used and well-studied separation technologies in industry for treating and separating azeotropic mixed solvents [11,12]. However, it is often very difficult or impossible to separate certain azeotropic systems using ordinary rectification methods, making it necessary to consider the use of special rectification methods such as pressure swing distillation [13,14], extractive distillation [15,16], and reaction distillation [17,18] to achieve the separation requirements, where extractive distillation is the most effective and widely used technique. In terms of extraction, ILs have excellent extraction properties [19]. Chao *et al.* [20] used 1-nonylimidazolium thiocyanate ([C₉Im][SCN]) as an extractor to isolate the components of *n*-hexane/methyl cyclopentane azeotropic systems using computer-aided molecular design; process simulation studies provided valuable guidance for the separation of other alkane-naphthene mixtures. Yan *et al.* [21] used different ILs as extractants to separate ethyl acetate–methanol azeotropic systems. Considering the

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overall benefits of the extraction and distillation processes, it was found that 1-ethyl-3-methylimidazolium diethyl phosphate ([Emim][DEP]) was superior to other solvents, enabling reduction of the costs and energy consumption compared to conventional extraction and distillation processes. Yan *et al.* [22] used [Bmim][AC] as an extractant to separate water/isopropanol/ethyl acetate azeotropic systems, and applied thermal integration technology to optimize the process and reduce energy consumption. ILs are excellent options for separating azeotropic systems.

In the separation of an azeotropic system, the internal action and synergistic extraction mechanisms of the mixture must be clearly understood. Quantum chemistry is suitable for studying the interactions between molecules and can be used to conduct fine theoretical research on systems at the molecular and atomic levels. Quantum chemistry can also be used to accurately and statically study the properties, characteristics, and reactions of a single or a small number of molecules [23–25]. Through energy analysis, Zhao *et al.* [26] found that methanol undergoes strong interactions with 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]), which has greater selectivity for CO₂, revealing the separation mechanism at the molecular level. Zhang *et al.* [27] compared the Gibbs free energy and potential energy data with the experimental results, verified the consistency of the quantitative calculation and experimental parameters, and predicted the formation of water. As an important means of analysis, quantum chemistry occupies an important position in the interpretation of chemical phenomena.

In this study, a method combining quantum chemistry and experiments for screening extractants is developed, and the extractive distillation process is simulated. The binding capacity between the ILs and *tert*-butanol/ethyl acetate molecules is analyzed using quantum chemical methods including intermolecular structure optimization and parameter analysis, with the lowest conformational energy, hirshfeld partition (IGMH) and frontier molecular orbital. The results show that system separation can be achieved if the extractant undergoes attractive interactions with *tert*-butanol and repulsive interactions with ethyl acetate. After preliminarily screening the extractants, VLE experiments are used to determine whether [Bmim][AC] or [Emim][AC] has the better extraction effect. Finally, combined with Aspen Plus V11, the process of separating *tert*-butanol–ethyl acetate by extractive distillation is designed and optimized, proving that ILs can be used as extractants for separating azeotropic systems. The results have a guiding role in the use of ILs for the clean and efficient separation of azeotropic systems.

2. Materials and Methods

2.1. Intermolecular structure optimization and parameter analysis

In the process of building a molecular model, there is no guarantee that the initial molecular configuration will have the lowest energy, thus, the initial configuration must be optimized. If the initial configuration of the complex is generated by artificial placement, some configurations with energy minima on the potential energy surface are ignored; therefore, these configurations should be generated randomly. The ideal complex design is screened after a series of iterative searches for a randomly generated configuration [28,29]. Herein, the structure of each molecule was initially optimized using Gaussian software [30]. The initial configuration of the complex was then generated at random using the genmer program of the Molclus [31] software. The basic configuration is initially optimized using Molecular Orbital PACKage (MOPAC) [32] software by utilizing a computationally effective semi-empirical approach. After optimizing the initial configuration, the

optimized configuration is sorted, screened, and the duplicated structures are removed according to the energy and geometric parameters of the configuration. The B3LYP function was implemented in Gaussian [30] software at the 6-311G* level to optimize the configuration and obtain the configuration with the lowest energy.

In this study, [Bmim][AC], 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]), [Emim][AC], [Emim][BF₄], 1-ethyl-3-methylimidazolium hexafluorophosphate ([Emim][PF₆]), 1-hexyl-3-methylimidazolium acetate ([Hmim][AC]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF₄]), and 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF₆]) were respectively selected and optimized with *tert*-butanol and ethyl acetate by using Gaussian [30]. The optimization results are shown in Fig. S1 in Supplementary Material, and the structural parameters are listed in Table S3.

2.2. Lowest conformational energy

After gradual screening of the composite configuration, the stable configuration of each molecule and the stable interaction between the entrainer and *tert*-butanol and ethyl acetate were determined to obtain the minimum conformational energy of each molecule and the lowest conformational energy between the entrainment agent and *tert*-butanol and ethyl acetates to calculate the energy difference of the complex [33,34].

$$\Delta E = E_{AB} - E_A - E_B \quad (1)$$

The lowest conformational energies of components A and B and the binary systems are indicated by E_A , E_B , and E_{AB} , respectively. By calculating the energy difference of the complex, the stable performance of the complex can be judged and the force of the entrainment on the components can be determined.

2.3. Independent gradient model based on Hirshfeld partition

The IGMH [35] method uses the Hirshfeld atomic space division method to divide the electron density of each atom from the actual electron density of the system, considering the actual electronic structure and chemical environment, while the δg (the difference between the Independent gradient model based on Hirshfeld partition (IGMH) and the atomic electron density gradient)/inter/intra isosurface of the IGMH method is relatively thin and attractive, which can purely show the characteristics of the interaction region. Herein, the lowest conformation of the complex can be divided into two fragments using the Multiwfn [36] software, and the box is defined by extending a certain distance around the central molecule (i.e., the grid distribution area); a lattice spacing of 0.15 Bohr is specified, and the lattice data is exported after the calculation. Finally, the Visual Molecular Dynamics (VMD) [37] software is used to draw the IGMI isosurface figure.

2.4. Frontier molecular orbital

The frontier molecular orbital contains the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and is one of the key pieces of information in theoretical quantum chemistry calculations [38]. The HOMO is mainly related to the electron-donating ability and the LUMO is mainly related to the electron-receiving capacity of the molecule. The energy difference of the leading orbitals is expressed as ΔE ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), which can be used to determine the energy of the composite. The smaller the calculated value of ΔE , the smaller the energy level difference between the electron donor and the

electron receptor, the stronger the orbital action, and the easier the electron transfer.

2.5. Experiment

At atmospheric pressure, *tert*-butanol-ethyl acetate formed an azeotropic system. To combine theory and practice and identify the best solvent, the solvent selected by screening was used as the extractant, and ternary phase equilibrium experiments were performed at atmospheric pressure [39,40]. Table S1 lists the evaluated solvents, and Table S2 lists the chromatographic characteristics.

2.6. Process simulation

Aspen Plus V11 was used to simulate the extraction and distillation process for separating *tert*-butanol from ethyl acetate. The optimal extractant was selected through molecular simulations and phase equilibrium experiments. The feed rate of the raw material was 100 kmol·h⁻¹, and the *tert*-butanol and ethyl acetate were fed into the system according to the azeotropic point, that is, *tert*-butanol 0.168 (molar fraction, the same below), ethyl acetate 0.832, where the ILs are defined based on the UNIFAC-Lei [41,42] model; the parameters related to the definition were listed in Tables S7–S9. Owing to the abuse and widespread use of ILs, residual ILs in wastewater have gradually become an important ecological health and environmental impact problem, causing direct or indirect harm to human health and the environment [43,44]. Therefore, a double-column process (extractive distillation column and solvent recovery column) was established and the influence of the process parameters was preliminarily mastered, enabling separation of components and recycling of the extractants. Assuming that the payback factor is three years, the optimal process parameters of the extractive distillation process were determined using a sequential iterative optimization process, supplemented by sensitivity analysis, with the lowest TAC [45] as the goal. Finally, the environmental impact analysis of the gas emissions was performed to bolster the economic analysis.

3. Results and Discussion

3.1. Intermolecular structure optimization and parameter analysis

In general, hydrogen bonding occurs if the distance between the donor and acceptor is less than the distance of the van der Waals force and greater than the bonding distance, and the angle

between the acceptor, donor, and atoms connecting the donor is greater than 90° [11,46]. Fig. S2 shows the configuration of all the solvents used to form complexes with *tert*-butanol/ethyl acetate, and Table S3 shows the relevant structural parameters of all the complexes. The data in Table S3 showed that the nine ILs formed hydrogen bonds with the system. For example, in the *tert*-butanol-[Bmim][AC] configuration, atom 12 is O, atom 18 is H, the bond length between the two atoms is 1.66493×10^{-10} m, and $\angle(12, 44, 36)$ is 172.3766°. Because the van der Waals radius of the H atom is 1.2×10^{-10} m and that the O atom is 1.52×10^{-10} m, the maximum distance of the van der Waals force of the H···O bond is 2.72×10^{-10} m, and the H—O bond distance is 0.95×10^{-10} m. This also suggests that the distance between the donor and the acceptor of the complex is less than the distance of the van der Waals force and greater than the bonding distance, and the angle between the acceptor, donor, and the atoms connected to the donor is greater than 90°. Therefore, this H···O interaction may form a hydrogen bond. In the ethyl acetate-[Bmim][BF₄] configuration, atom 29 is F, atom 42 is H, the bond length of the two atoms is 2.26098×10^{-10} m, and $\angle(29, 42, 36)$ is 149.4225°. If the van der Waals radius of the H atom is 1.2×10^{-10} m and the van der Waals radius of the F atom is 1.47×10^{-10} m, the maximum distance of the van der Waals force of the H—F bond is 2.67×10^{-10} m, and the H—F bond distance is 0.96×10^{-10} m. Therefore, the complex satisfies the conditions required for hydrogen bond formation.

3.2. Lowest conformational energy

When the interaction energy difference (ΔE) between the solvent and *tert*-butanol or ethyl acetate is greater, the extraction effect of the solvent is better and the selectivity is higher. The greater the absolute value of ΔE , the stronger the binding ability between the ILs and azeotropic components, and the more stable the configuration of the complex. Table 1 listed the lowest conformational energies of *tert*-butanol, ethyl acetate, and the solvents, as well as the lowest conformational energy and calculated energy difference between the forming system and the complex formed by the solvents. As shown in Table 1, the absolute value of ΔE for the most stable form of all the ILs and *tert*-butanol was greater than that for the most stable form of the ILs and ethyl acetate. Therefore, the interaction between all ILs and *tert*-butanol is stronger than that between the ILs and ethyl acetate, for example:

$$\Delta E_{\text{tert-butanol-[Bmim][Ac]}} = -0.9170 \text{ eV}$$

$$\Delta E_{\text{ethyl acetate-[Bmim][Ac]}} = -0.7184 \text{ eV}$$

Table 1

Lowest conformational energy of *tert*-butanol, ethyl acetate, and solvents, and lowest conformational energy and energy difference for the formation of complexes

System	E_A/eV	E_B/eV	E_{AB}/eV	$\Delta E/\text{eV}$
<i>tert</i> -butanol-[Bmim][AC]	-6359.0076	-17739.2205	-24099.1451	-0.9170
<i>tert</i> -butanol-[Bmim][BF ₄]	-6359.0076	-23071.9529	-29431.8230	-0.8625
<i>tert</i> -butanol-[Bmim][PF ₆]	-6359.0076	-37116.8149	-43476.7477	-0.9252
<i>tert</i> -butanol-[Emim][AC]	-6359.0076	-15598.8316	-21959.1862	-1.3470
<i>tert</i> -butanol-[Emim][BF ₄]	-6359.0076	-20932.0565	-27292.0247	-0.9606
<i>tert</i> -butanol-[Emim][PF ₆]	-6359.0076	-34976.9131	-41336.8078	-0.8871
<i>tert</i> -butanol-[Hmim][AC]	-6359.0076	-19879.3536	-26239.0061	-0.6449
<i>tert</i> -butanol-[Hmim][BF ₄]	-6359.0076	-25211.9363	-31571.7928	-0.8490
<i>tert</i> -butanol-[Hmim][PF ₆]	-6359.0076	-39256.7820	-45616.6413	-0.8517
ethylacetate-[Bmim][AC]	-8373.5628	-17739.2205	-26113.5016	-0.7184
ethylacetate-[Bmim][BF ₄]	-8373.5628	-23071.9529	-31446.2476	-0.7320
ethylacetate-[Bmim][PF ₆]	-8373.5628	-37116.8149	-45491.1668	-0.7891
ethylacetate-[Emim][AC]	-8373.5628	-15598.8316	-23973.3414	-0.9470
ethylacetate-[Emim][BF ₄]	-8373.5628	-20932.0565	-29306.4492	-0.8299
ethylacetate-[Emim][PF ₆]	-8373.5628	-34976.9131	-43351.3195	-0.8436
ethylacetate-[Hmim][AC]	-8373.5628	-19879.3536	-28253.4823	-0.5660
ethylacetate-[Hmim][BF ₄]	-8373.5628	-25211.9363	-33586.2637	-0.7646
ethylacetate-[Hmim][PF ₆]	-8373.5628	-39256.7820	-47631.1094	-0.7646

Therefore, the industrial separation of azeotropic systems of *tert*-butanol and ethyl acetate can be realized by combining the solvent with *tert*-butanol owing to the stronger force between the solvent and *tert*-butanol. The covalent bond formed between the azeotropic component and the extractant through the H atom and the atom with strong electronegativity led to interactions between the molecules. Combining Table S3 and Fig. S2, it can be seen that the azeotropic system and the evaluated extractants are bonded *via* two main modes: (a) the O atom of *tert*-butanol with H atom of imidazole cation forms a covalent bond O...H bond with the H atom of the imidazole cation; (b) the H on the hydroxyl group of *tert*-butanol forms H...O or H...F with the O or F atoms of [AC]⁺, [BF₄]⁻, and [PF₆]⁻. The energy differences between [Bmim][AC], [Bmim][BF₄], [Bmim][PF₆], [Emim][AC], [Emim][BF₄], [Emim][PF₆], [Hmim][AC], [Hmim][BF₄], [Hmim][PF₆] and *tert*-butanol were calculated as -0.9170, -0.8626, -0.9252, -1.3470, -0.9606, -0.8871, -0.6449, -0.8490, and -0.8517 eV, respectively. The greater the absolute value of ΔE , the stronger the ability of ILs to bind *tert*-butanol. Consequently, the binding capacity of the nine ILs to *tert*-butanol followed the order: [Emim][AC] > [Emim][BF₄] > [Bmim][PF₆] > [Bmim][AC] > [Emim][PF₆] > [Bmim][BF₄] > [Hmim][PF₆] > [Hmim][BF₄] > [Hmim][AC].

3.3. Independent gradient model based on Hirshfeld partition

The IGMH isofacial was plotted using Multiwfn [36] and VMD [37], as shown in Fig. 1. Blue represents strong attractive interactions such as hydrogen and halogen bonds, green represents van der Waals forces, and red represents the potential resistance effect, that is, strong repulsive forces [33]. The darker the blue color of the isosurface, the stronger the attraction and a strong hydrogen bond can be formed. The redder the color of the isosurface, the stronger the intermolecular repulsion.

Fig. 1(a, a') demonstrates that when [Bmim][AC] was used as the extractant, [Bmim][AC] had three and two binding sites for *tert*-butanol and ethyl acetate, respectively. In the optimal configuration of the complex of *tert*-butanol and [Bmim][AC], the first binding site was located between the H atom of the hydroxyl group of *tert*-butanol and the O atom of [AC]⁺. The color of this isosurface was dark blue, indicating a strong hydrogen bonding effect. The second binding site is located between the O atom on the hydroxyl group of *tert*-butanol and the H atom of [Bmim]⁺. The color of the isosurface is between blue and green, indicating that the hydrogen bonding effect is weak. The third binding site is located between the H atom of the hydroxyl group of *tert*-butanol and the C atom of [Bmim]⁺. The isosurface is green, indicating the existence of weak van der Waals forces. For the optimal complex configuration of ethyl acetate and [Bmim][AC], the two sites were located between the O atom of the ester group of ethyl acetate and the C atom of the imidazole cation, and between the H atom of the ester group of ethyl acetate and the O atom of [AC]⁺. The isosurface color of these two binding sites was green, which proved that there was only a weak van der Waals effect between the molecules. Therefore, there is a strong hydrogen bond between [Bmim][AC] and *tert*-butanol, which is a strong attraction, and the interaction with ethyl acetate is weak. Therefore, [Bmim][AC] can separate azeotropic components by interacting with *tert*-butyl alcohol. The isosurfaces between [Bmim][BF₄], [Bmim][PF₆], [Emim][PF₆], [Hmim][AC], [Hmim][BF₄], [Hmim][PF₆] and *tert*-butanol/ethyl acetate were all green, basically without blue (Fig. 1), indicating that the intermolecular forces between these six ILs and *tert*-butanol/ethyl acetate are weak, and there is basically no difference in the strength of the interaction. This indicates that the six ILs cannot achieve azeotropic separation by interacting with one of the azeotropic components and not attracting the other.

To separate the azeotropic system effectively, the selected solvent must significantly affect the interactions between *tert*-butanol and ethyl acetate. In other words, the ILs should exhibit strong and weak interactions with esters, respectively. Therefore, [Bmim][BF₄], [Bmim][PF₆], [Emim][PF₆], [Hmim][AC], [Hmim][BF₄] and [Hmim][PF₆] could not be used as extractants in this system. The color of the isosurface between the binding sites of [Bmim][AC], [Emim][AC] and [Emim][BF₄] with *tert*-butanol was dark blue, indicating the presence of strong hydrogen bonds. In comparison, the color of the isosurface with ethyl acetate is green, indicating a weak force. Therefore, [Bmim][AC], [Emim][AC] and [Emim][BF₄] exhibited poor attraction to ethyl acetate, but strong attraction to *tert*-butanol. These ILs are effective for the separation of *tert*-butanol and ethyl acetate and thus can be used as extractants for this system.

3.4. Frontier molecular orbital

The HOMO and LUMO values reflect the capacity of a molecule to provide and receive electrons; the larger the HOMO value, the easier it is to lose electrons, and the larger the LUMO value, the easier it is to receive electrons [38]. Conversely, the smaller the energy difference between the HOMO and LUMO, the more prone the electrons are to transitions. The stronger the chemical reactivity, the greater the action of the complex, and *vice versa*. The energies of the HOMO and LUMO of the nine complexes composed of the solvent and *tert*-butanol were determined using Gaussian [30] software, and the energy difference was calculated (Table 2).

Among the complexes formed by the ILs and *tert*-butanol, the energy difference between the HOMO and LUMO orbitals followed the order: [Hmim][PF₆] > [Bmim][PF₆] > [Emim][BF₄] > [Hmim][BF₄] > [Hmim][AC] > [Emim][PF₆] > [Bmim][BF₄] > [Bmim][AC] > [Emim][AC], with values of 6.3054, 6.3026, 6.3013, 6.1256, 5.9634, 5.8493, 5.7201, 4.8475 and 4.5376 eV, respectively. The energy gap reflects the chemical activity of the molecule, whereas the HOMO and LUMO energy gaps indicate the occurrence of charge-transfer interactions within the molecule [47]. A larger HOMO-LUMO gap indicates low stability, whereas a smaller gap indicates strong molecular stability. Therefore, the sequence of the effect of the ILs on *tert*-butanol is as follows: [Emim][AC] > [Bmim][AC] > [Bmim][BF₄] > [Emim][PF₆] > [Hmim][AC] > [Hmim][BF₄] > [Emim][BF₄] > [Bmim][PF₆] > [Hmim][PF₆].

To provide a more accurate analysis of the LUMO-HOMO orbitals between each ILs and *tert*-butanol, the Gaussian [30] and VMD [37] were used to visualize the trajectories of the orbitals (Fig. 2). In the *tert*-butanol - [Emim][AC] system, the HOMO electron cloud is mainly distributed on [AC]⁺, whereas the LUMO electron cloud is mainly concentrated on the imidazole ring, indicating that when the HOMO transitions to the LUMO, electrons are mainly transferred from [AC]⁺ to the imidazole ring through electronic transfer between the molecules. In the *tert*-butanol - [Bmim][AC] system, the HOMO and LUMO electron cloud are concentrated on [AC]⁺, the hydroxyl of *tert*-butanol and [Bmim]⁺, respectively. Therefore, electron transfer occurs between the oxygen atom on the hydroxyl group of [AC]⁺ and *tert*-butanol and the imidazole ring. Similarly, in the *tert*-butanol - [Emim][BF₄] system, the HOMO electron cloud is mainly localized on the imidazole ring, whereas the LUMO electron cloud is mainly concentrated on the *tert*-butanol, which indicates that when the HOMO transition to the LUMO, electron transfer between the molecules mainly occurs on the imidazole ring and *tert*-butanol.

Intermolecular structure optimization showed that all the selected solvents could form hydrogen bonds with the components of the system and can prospectively be used as extractants to separate the components of the system. Analysis of the lowest conformational energy revealed that all solvents had strong effects on

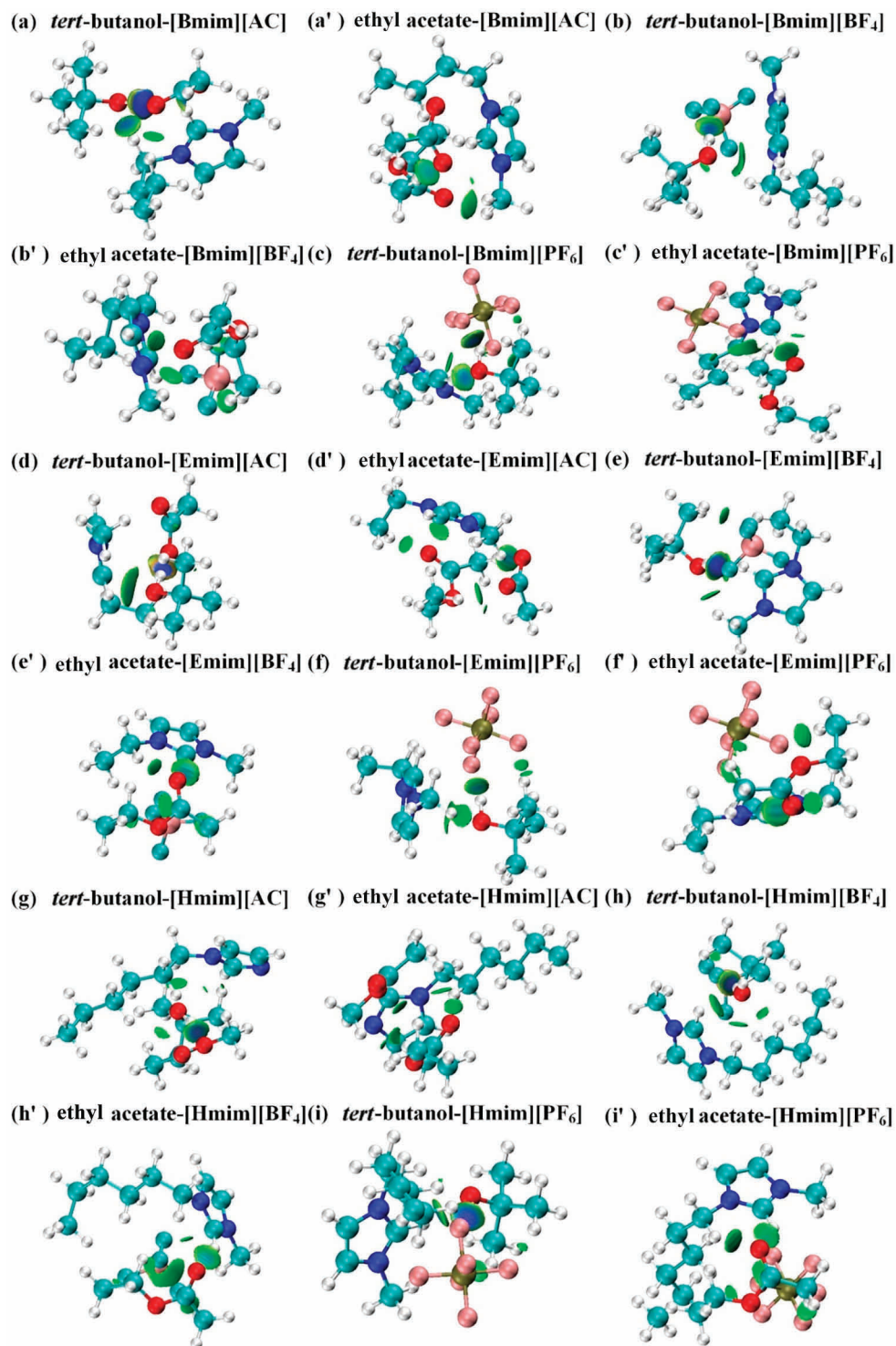


Fig. 1. IGMH isosurface of *tert*-butanol/ethyl acetate and solvents.

tert-butanol and weak effects on ethyl acetate. Therefore, azeotropes can be separated in combination with *tert*-butanol during the separation process. The images obtained through IGMH clearly showed that [Bmim][AC], [Emim][AC] and [Emim][BF₄] can meet the key condition of ensuring strong interaction with *tert*-butanol and weak interaction with ethyl acetate. Finally, strong binding between the above solvents and *tert*-butanol was verified by the frontier molecular orbitals from both numerical and image analyses. Therefore, [Bmim][AC], [Emim][AC] and [Emim][BF₄] are

expected to be the best solvents for *tert*-butanol-ethyl acetate azeotropic system.

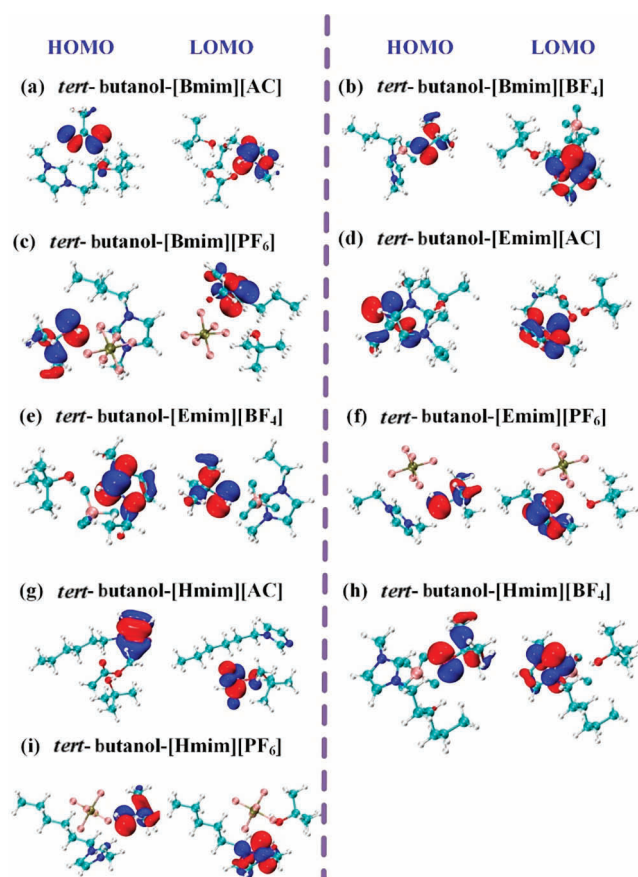
3.5. Experiment

To select the best solvent and reduce the separation cost and time, VLE experiments were carried out on the basis of the quantum chemistry calculation results. Before starting the experiment, the airtightness of the device was checked, and a ternary mixed

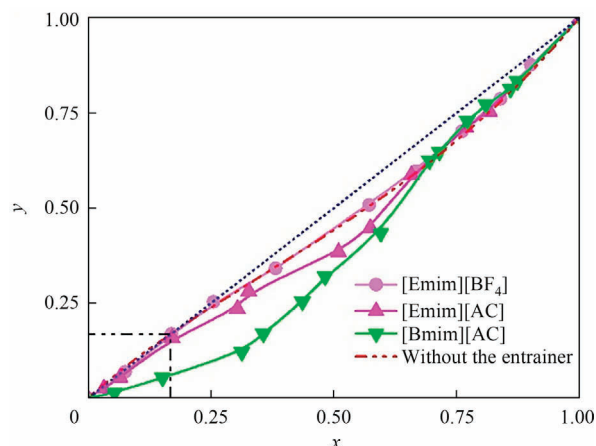
Table 2

Energy and the energy difference between the HOMO and LUMO orbitals of the complex formed by solvents and *tert*-butanol

Type	$E_{\text{LUMO}}/\text{eV}$	$E_{\text{HOMO}}/\text{eV}$	$\Delta E/\text{eV}$
<i>tert</i> -butanol-[Bmim][AC]	-5.4415	-0.5940	4.8475
<i>tert</i> -butanol-[Bmim][BF ₄]	-6.5187	-0.7986	5.7201
<i>tert</i> -butanol-[Bmim][PF ₆]	-7.1034	-0.8008	6.3026
<i>tert</i> -butanol-[Emim][AC]	-5.1555	-0.6179	4.5376
<i>tert</i> -butanol-[Emim][BF ₄]	-6.9467	-0.6454	6.3013
<i>tert</i> -butanol-[Emim][PF ₆]	-6.7377	-0.8884	5.8493
<i>tert</i> -butanol-[Hmim][AC]	-5.9756	-0.0122	5.9634
<i>tert</i> -butanol-[Hmim][BF ₄]	-7.0071	-0.8815	6.1256
<i>tert</i> -butanol-[Hmim][PF ₆]	-7.0988	-0.7934	6.3054

**Fig. 2.** HOMO and LUMO of the complex formed by solvents and *tert*-butanol.

solution with a solvent mass fraction of 0.2 was poured into the VLE kettle, and the heating power supply and cooling water were connected. To prevent the liquid from boiling, the heating pressure was adjusted to slowly boil the liquid in the kettle. If the temperature remained constant for at least 15 min, the system was considered to be in equilibrium. After equilibration, samples from both sides of the steam and liquid were collected, the sample mass, internal standard mass, and temperature were recorded, and chromatographic analysis was performed. The final results obtained through mathematical analysis of the experimental data were listed in Tables S4–S6. The *x*-*y* plot was shown in Fig. 3. According to previous reports, *tert*-butanol (1) - ethyl acetate (2) exists in an azeotropic state at $x_1 = 0.168$ [48]. It can be clearly seen that the addition of [Bmim][AC] and [Emim][AC] resulted in the absence of intersection points between the azeotropic composition and the diagonal, and the degree of deviation greatly increases, indicating that the azeotropic state of the system was broken. This effect

**Fig. 3.** The *x*-*y* figure of *tert*-butanol-ethyl acetate-ILs.

is favorable, and these ILs were considered the optimal solvents for separation for further analysis.

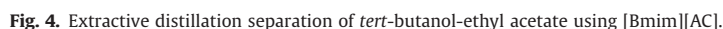
3.6. Process simulation

The extraction and distillation processes for the separation of *tert*-butanol-ethyl acetate using [Bmim][AC] and [Emim][AC] were simulated using Aspen Plus V11. The simulation processes were shown in Figs. 4 and 5, respectively. Raw materials entered from the bottom of the extractive distillation column T1, and the extractant entered from the top of the column. Ethyl acetate with a mole fraction greater than 0.999 was extracted from the column top at stream D1, and the mixture of *tert*-butanol and ILs flowed out from the bottom of the distillation column B2 and into the solvent recovery column T2. Finally, the qualified *tert*-butanol product was obtained from the top of column T2, and the extractant was bottom of the column through column B2.

The molar purity of the product after using the two processes to separate the *tert*-butanol-ethyl acetate system was 0.999. Combined with sensitivity analysis, based on the sequential iterative algorithm, the process was optimized with the goal function of minimum TAC, so that the simulation parameters reached the optimum. The TAC calculation formulas were listed in Table S10, and the sequential iterative optimization of the separation process was shown in Fig. S3. The simulation parameters were listed in Table 3. When [Bmim][AC] was used as the extractant, the TAC was 3.602×10^6 USD·a⁻¹ and the emissions of CO₂, SO₂ and NO were 4243.34, 127.66 and 63.83 kg·a⁻¹, respectively. When [Emim][AC] was used as the extractant, the TAC was 4.381×10^6 USD·a⁻¹ and the emissions of CO₂, SO₂ and NO were 4760.23, 143.21 and 71.60 kg·a⁻¹, respectively. The final results show that compared with [Emim][AC] distillation for separating *tert*-butanol-ethyl acetate azeotrope, [Bmim][AC] extractive distillation significantly reduced the TAC and acid gas emissions. The [Bmim][AC] extractive distillation process reduced the emissions of CO₂, SO₂ and NO by 10.86%, and the TAC by 17.78%. The above economic and environmental performance analyses and evaluations showed that the process has excellent economic and environmental performance. This study has important reference significance for realizing energy saving, consumption reduction and green and efficient separation of *tert*-butanol-ethyl acetate azeotrope in industry.

4. Conclusions

The microscopic mechanisms of separation *tert*-butanol-ethyl acetate azeotropic systems using nine ILs ([Bmim][AC], [Bmim][BF₄], [Bmim][PF₆], [Emim][AC], [Emim][BF₄], [Emim][PF₆],



Parameters	[Bmim][AC]	[Emim][AC]
NT1	58	56
NF1	43	42
NEF1	2	2
NT2	5	5
NF2	2	2
TAC/USD·a ⁻¹	3.602 × 10 ⁶	4.381 × 10 ⁶
Saving TAC/%	17.78	—
CO ₂ /kg·a ⁻¹	4243.34	4760.23
SO ₂ /kg·a ⁻¹	127.66	143.21
NO/kg·a ⁻¹	63.83	71.60
Saving XO _x /%	10.86	—

[Hmim][AC], [Hmim][BF₄] and [Hmim][PF₆]) were researched by quantum chemistry analysis. Analysis of the lowest conformational energies of the nine ILs and *tert*-butanol/ethyl acetate revealed strong interactions between the extractants and *tert*-butanol. The weak interaction between the azeotrope and extractant was analyzed intuitively using IGMH, and the conformation with the lowest energy was further verified. Furthermore, the frontier molecular orbital method was used to check the ability of the molecules to combine together to form complexes, as well as to preliminarily screen the solvents, providing a molecular basis for analysis of the separation mechanism. VLE experimental analysis revealed that [Bmim][AC] and [Emim][AC] exhibited the best separation effect on *tert*-butanol-ethyl acetate. Through process com-

parison, it was found that the use of [Bmim][AC] can reduce the TAC by 17.78%, and the emissions of CO₂, SO₂ and NO can be reduced by 10.86%. Therefore, this work provides theoretical guidance for the selection of extractants in industry and is of great significance for promoting clean, energy-saving and efficient separation of azeotropes.

CRediT Authorship Contribution Statement

Mengjin Zhou: Conceptualization, Methodology, Investigation, Writing – original draft. Yanli Zhang: Validation, Data curation, Visualization, Software, Writing – review & editing. Ke Xue: Validation, Formal analysis. Haixia Li: Data curation, Visualization, Software. Zhaoyou Zhu: Validation, Formal analysis. Peizhe Cui: Supervision. Yinglong Wang: Writing – review & editing, Funding acquisition. Jingwei Yang: Writing – review & editing.

Data Availability

Data will be made available on request.

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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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2023.05.015>.

Nomenclature

[Bmim][AC]	1-butyl-3-methylimidazolium acetate
[Bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[Bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[C ₉ Im][SCN]	1-nonylimidazolium thiocyanate
[Emim][AC]	1-ethyl-3-methylimidazole acetate
[Emim][BF ₄]	1-ethyl-3-methylimidazolium tetrafluoroborate
[Emim][PF ₆]	1-ethyl-3-methylimidazolium hexafluorophosphate
[Emim][DEP]	1-ethyl-3-methylimidazolium diethyl phosphate
E _A	lowest conformational energies of component A
E _B	lowest conformational energies of component B
E _{AB}	lowest conformational energies of binary systems
ΔE	lowest conformational energy
E _{HOMO}	energy of HOMO orbitals
E _{LOMO}	energy of LOMO orbitals
ΔE _{LOMO-HOMO}	energy difference of the leading orbitals
[Hmim][AC]	1-hexyl-3-methylimidazolium acetate
[Hmim][BF ₄]	1-hexyl-3-methylimidazolium tetrafluoroborate
[Hmim][PF ₆]	1-hexyl-3-methylimidazolium hexafluorophosphate
HOMO	the highest occupied molecular orbital
ILs	ionic liquids
IGMH	independent gradient model based on Hirshfeld partition
LUMO	lowest unoccupied molecular orbital
TAC	total annual cost
VLE	vapour-liquid phase equilibrium
x	molar fraction of components in the liquid phase

y	molar fraction of components in the vapor phase
α	relative volatility
ω	mass fraction of components

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