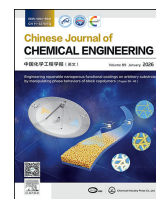




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Full Length Article

Ionic liquids screened by COSMO-RS for phase equilibrium separation of 2-methylfuran and methanol: Thermodynamic and mechanistic analysis

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ABSTRACT

Separation of 2-methylfuran (2-MF) and methanol (MeOH) azeotropes is a key challenge in biofuel production because of the efficiency and sustainability issues of conventional methods. In this study, ionic liquids (ILs) were introduced as green solvents for separation of 2-MF/MeOH through liquid–liquid equilibrium (LLE) experiment. Three ILs, namely 1-ethyl-3-methylimidazole dihydrogen phosphate ([EMIM][H₂PO₄]), 1-propyl-3-methylimidazole dihydrogen phosphate ([PMIM][H₂PO₄]) and 1-butyl-3-methylimidazole dihydrogen phosphate ([BMIM][H₂PO₄]), were screened out from 425 candidates using the conductor-like screening model for real solvents (COSMO-RS). Then, the ternary LLE data of 2-MF (1) + MeOH(2) + ILs(3) were determined at 30 °C and 101.32 kPa. Results confirmed [EMIM][H₂PO₄] as the best performer, achieving a selectivity of 343.86 and a distribution coefficient of 36.66 for MeOH—significantly higher than [PMIM][H₂PO₄] and [BMIM][H₂PO₄]. The accuracy of the LLE data was verified by Othmer–Tobias and Hand equations ($R^2 > 0.90$). The non-random two liquid model was used to correlate the experimental data (RMSE < 2%). Besides, the combination of electrostatic surfaces potential, independent gradient model based on Hirshfeld partition, mean square displacement and radial distribution functions revealed strong electrostatic interactions between [H₂PO₄][−] and MeOH. Interaction energy analysis further emphasizes the mechanism of MeOH separation from a mixture of 2-MF and MeOH by ILs. This work provides a multiscale strategy for the separation of 2-MF and MeOH azeotropes, highlighting the potential of ILs to improve biofuel purification while reducing energy and environmental costs.

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1. Introduction

As a critical solution to fossil fuel-induced environmental crises, bioenergy has gained prominence in carbon neutrality strategies due to its technological readiness and infrastructure adaptability [1,2]. Within advanced biorefinery frameworks, biomass resources (lignocellulose, energy crops, algae, etc.) are transformed into value-added products through platform chemicals [3,4]. Notably, furfural—a pivotal platform compound for second-generation biofuels—is synthesized via hemicellulose hydrolysis–dehydration [5–7]. Its catalytic conversion pathways,

particularly hydrogenation processes, generate high-performance derivatives like 2-methylfuran (2-MF), a gasoline-compatible biofuel with exceptional properties (octane number: 103, freezing point: 22 °C) and excellent compatibility with conventional gasoline [8–10]. Currently, 2-MF is produced partly by catalytic hydrogenation of furfural over a metal catalyst with methanol (MeOH) as both solvent and hydrogen donor [11–13]. However, the presence of MeOH can form an azeotrope with the product 2-MF, which poses a major challenge to industrial separation, directly affecting product purity and process economics [14,15]. Current research focuses on catalyst optimization, the critical separation bottleneck of 2-MF–MeOH azeotrope remains unaddressed [16,17]. Systematic investigation into azeotrope-breaking techniques is urgently required to establish an industrially viable production protocol.

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Extensive techniques including distillation, adsorption, membrane separation, and liquid–liquid equilibrium (LLE) have explored for the separation of azeotropic mixtures [18–21]. Notably, LLE has emerged as a promising approach owing to its operational feasibility under moderate conditions, cost-effectiveness, and excellent scalability for industrial applications [22,23]. Nevertheless, conventional LLE processes are frequently hampered by the inherent limitations of extractants, particularly their volatility, toxicity, and challenges in regeneration, thereby underscoring the critical need for sustainable alternatives [24]. The advent of ionic liquid (IL) as novel green solvents has revolutionized LLE processes, offering remarkable advantages over traditional systems, such as negligible vapor pressure, exceptional thermal stability, remarkable recyclability, effectively addressing the limitations associated with conventional extractants [25–28]. Significant research efforts have been directed towards utilizing ILs for breaking various industrially relevant azeotropes, including alcohol/ether mixtures. In 2021, Wang *et al.* [29] effective separation of methyl *tert*-butyl ether and MeOH using different ILs and determination of their ternary LLE data. In 2023, Zhu *et al.* [30] chose different molar ratios of water and 1-ethyl-2,3-dimethylimidazole ethyl sulfate mixed solvents for the separation of ethanol and methyl *tert*-butyl ether. These studies demonstrate the potential of ILs to separate alcohol–ether azeotropes. However, the application of ILs to separate challenging MeOH/2-MF azeotropes has not been systematically explored or reported to our knowledge. Therefore, the present study addresses this major research gap by pioneering investigations. Furthermore, the structural versatility of IL, achieved through strategic combination of various cations and anions, enables precise customization of their extraction performance, facilitating highly efficient and selective separation of target compound.

In order to obtain IL with excellent separation properties and to reduce experimental trial, error and labor waste, appropriate IL screening tools and experimental simulation methods should be used. In recent years, conductor-like screening model for real solvents (COSMO-RS) provides an efficient quantum chemical approach to predict the thermodynamic properties and solvent–solvent interactions of ILs and azeotropes, which enables rapid screening of specific target compounds with optimal extraction performance [31,32]. The COSMO-RS model can guide the rational design of task-specific ILs by predicting the effects of modifications and combinations of anionic and cationic structures on extraction efficiencies. This will accelerate the development of green extraction technologies by reducing trial and error.

In this study, three phosphate ILs with different carbon chain lengths, namely 1-ethyl-3-methylimidazole dihydrogen phosphate ([EMIM][H₂PO₄]), 1-propyl-3-methylimidazole dihydrogen phosphate ([PMIM][H₂PO₄]) and 1-butyl-3-methylimidazole dihydrogen phosphate ([BMIM][H₂PO₄]), were screened for LLE experiments of the azeotropes 2-MF–MeOH by using the COSMO-RS model. The ternary LLE data of 2-MF(1) + MeOH(2) + IL(3) were further determined and validated by Othmer–Tobias and Hand equations. The non-random two liquid (NRTL) model was used to correlate the experimental data. In addition, the electrostatic surfaces potential (ESP) and independent gradient model based on Hirshfeld partition (IGMH) analysis of components were analyzed by quantum chemical calculations to confirm the interaction sites. Then, the interaction type was analyzed by molecular dynamics calculations, which further verified the separation mechanism. All results showed that the screened ILs possess outstanding separation ability of 2-MF–MeOH, which presented a new thought and technical support for the efficient separation of biomass fuels.

2. Experiment and Calculation Methods

2.1. Materials and experiment

The reagents used in this experiment, including 2-MF and MeOH were analytically pure reagents, purchased and used directly without purification. Three ILs [EMIM][H₂PO₄], [PMIM][H₂PO₄] and [BMIM][H₂PO₄] were dried in a vacuum drying oven at 85 °C for 12 h before the phase equilibrium experiments. The details of reagents are listed in Table S1 (in Supplementary Material).

The experiments were performed according to reported literature methods [33]. 2-MF and MeOH contents were analyzed using a gas chromatograph (GC-7980A, Agilent, USA) with flame ionization detector. The detection conditions were as follows: the carrier gas was N₂, the temperatures of the gasification chamber and column were 100 °C, and the temperature of the FID detector was 160 °C. The mass difference method was used to analyses the ILs. Each sample was analyzed three times to ensure the accuracy of the experiment. Distribution coefficients (β) and selectivity (S) were used to assess the ILs' separation performance for 2-MF and MeOH with specific Eqs. (1) and (2):

$$\beta = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \quad (1)$$

$$S = \frac{(x_2^{\text{II}} / x_1^{\text{II}})}{(x_2^{\text{I}} / x_1^{\text{I}})} \quad (2)$$

in the above equation, the subscripts I and II refer to raffinate and extracted phases, x stands for mole fraction, while 2-MF and MeOH are represented by 1 and 2, respectively.

2.2. COSMO-RS screening

COSMO-RS was employed to systematically evaluate the thermodynamic properties of ILs through combinatorial analysis of various cationic and anionic structures. The molecular structures of 2-MF, MeOH, along with a library of 25 cations and 17 anions, were geometrically optimized and subsequently imported into the COSMOtherm 2023 software package. The infinite dilution activity coefficients (γ^∞) of 2-MF and MeOH in the designed ILs were calculated to assess their extraction capacity and selectivity by Eqs. (3) and (4). Furthermore, the σ -profiles, which represent the probability distribution of the molecular surface charge density, were generated to yield detailed reflections of the molecular interactions and solvation properties in the IL systems.

$$\text{Capacity} = 1 / \gamma_{\text{solute}}^\infty \quad (3)$$

$$\text{Selectivity} = \gamma_{\text{MeOH}}^\infty / \gamma_{\text{2-MF}}^\infty \quad (4)$$

2.3. Quantum chemical calculations

Structural optimization and energy calculations were performed for each component using Gaussian 09 software at the B3LYP function set and the 6-311G (d, p) level [34]. The optimization was completed using Multiwfn [35] and VMD software [36] for wavefunction analysis and visualization of the image output, which in turn led to the analysis of the ESP and IGMH. The interaction energy (E) between ILs and 2-MF/MeOH was calculated by Eq. (5), and the energy was correlated to the basis set superposition error (BSSE) by the counterpoise method to reduce the basis set overlap error:

$$\Delta E_{A-B} = E_{A+B} - E_A - E_B + E_{BSSE} \quad (5)$$

2.4. Molecular dynamic simulation

Molecular dynamics (MD) simulations of the IL–2-MF–MeOH system were performed using GROMACS [37]. The relevant files for simulations having been generated using Sobot program based on general Amber force field (GAFF) and restrained electrostatic potential charges. The construction of a 50 nm × 50 nm × 80 nm crystal box was facilitated by PACKMOL program [38], with the mixture of 2-MF and MeOH positioned centrally and the IL situated on opposing sides. The MD simulation follows the steps below: (1) the system underwent 50000 steps of energy minimization using the steepest descent algorithm; (2) a 1 ns isothermal-isobaric (NPT) equilibration using both the V-rescale and Berendsen thermostats; (3) a 50 ns production simulation was conducted under the V-rescale thermostat and Parrinello–Rahman barostat. The total energy of this system fluctuated smoothly within 50 ns, thus meeting the convergence criteria. Mean square displacement (MSD) and radial distribution functions (RDF) were calculated by trajectory analysis to reveal the interaction mechanism of separating 2-MF–MeOH by ILs.

3. Results and Discussion

3.1. Preliminary screening of ILs

The structural differences of anions and cations in ILs have a significant effect on their separation performance as extractants. To optimize the separation of the azeotrope 2-MF from MeOH, 25 imidazole/pyridine cations and 17 anions in Table S2 were imported into the COSMO-RS database and systematically combined to construct a library of candidate extractants in the present study. The selection of extractants is based on two key parameters, namely their capacity and selectivity for azeotropes. The higher the selectivity character, the better the extraction results. A better equilibrium is more likely to be obtained under the condition that the capacity of the IL to MeOH is > 2, while the capacity of the IL to 2-MF is < 0.7. By analyzing the data in Fig. S1 and Table S3–S5, it was found that although anions such as [OH][−], [AC][−], [Lac][−], [Cl][−], [Br][−], and [I][−] exhibited high capacity and excellent selectivity to MeOH, they also maintained relatively high capacity to 2-MF, resulting in the inability to achieve an effective phase separation process. Among the remaining anions in Fig. 1(a), [H₂PO₄][−]-based ILs possesses the highest selectivity for MeOH, which is a better anion candidate. For cations, the short-chain [EIM]⁺, [MIM]⁺, [BIM]⁺

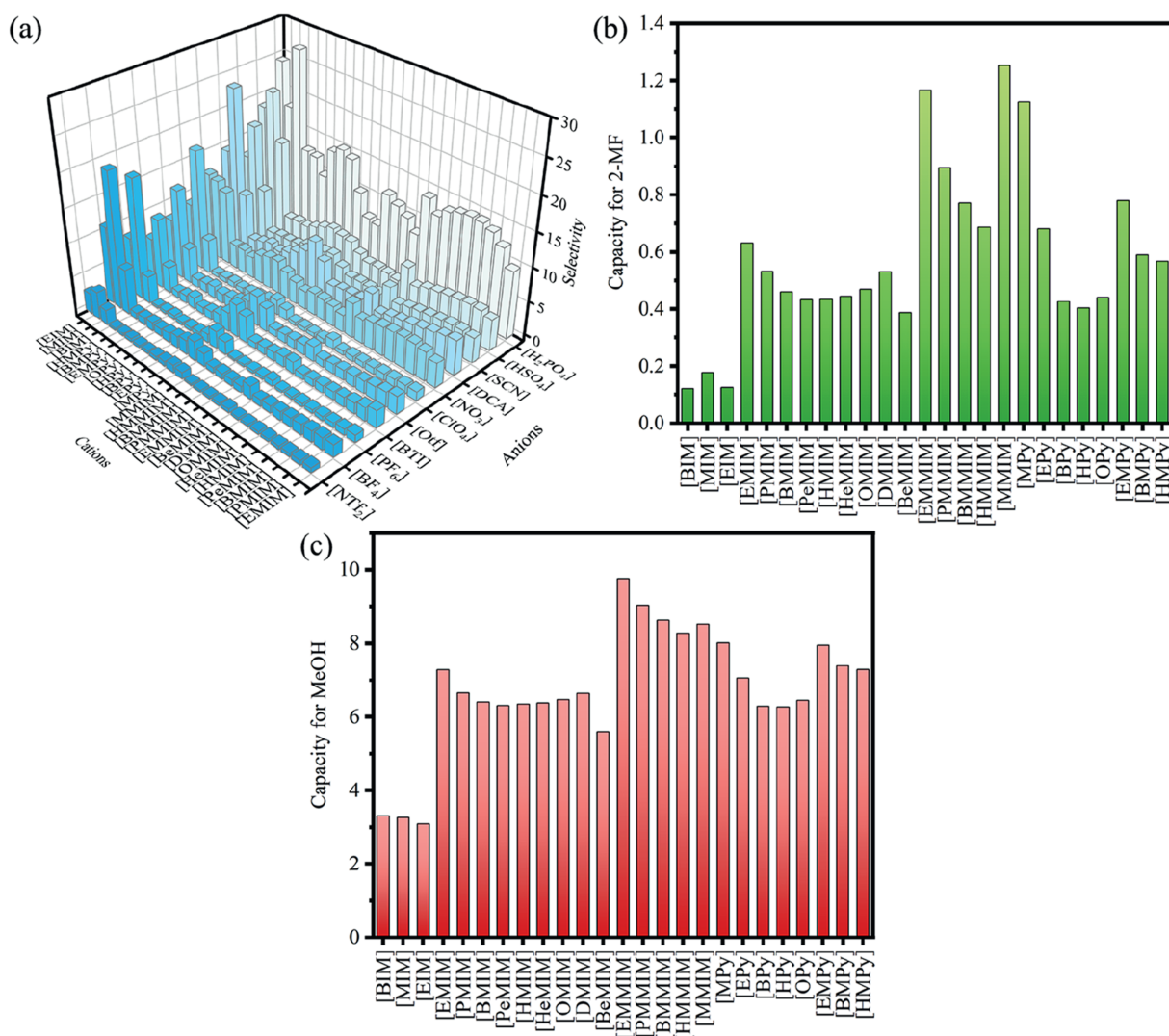


Fig. 1. (a) Infinite dilution selectivity of MeOH in different ILs. Infinite dilution capacity of [H₂PO₄]-based ILs for (b) 2-MF and (c) MeOH.

were excluded because of their low capacity for MeOH despite their high selectivity for MeOH. In Fig. 1(b)–(c), long-chain cations such as [EMIM]⁺, [PMIM]⁺, etc. were excluded because their capacity to 2-MF was larger, thus leaving only short-chain imidazole/pyridine cations, which have similar capacity to MeOH and 2-MF. Under the same conditions, imidazole-based ILs are less expensive than pyridine-based ILs. Therefore, under comprehensive consideration, [EMIM][H₂PO₄], [PMIM][H₂PO₄] and [BMIM][H₂PO₄] were selected as extractants for the separation of 2-MF and MeOH azeotropes.

The σ -profile helps verify the ability of COSMO-RS-screened ILs to separate azeotropes. This capability arises because the σ -profile reflects intermolecular interaction properties through charge distribution characteristics. The σ -profile can be classified into three characteristic zones based on the charge density distribution: hydrogen-bonding donor region (HBD: $\sigma < -0.82 \text{ e} \cdot \text{nm}^{-2}$), hydrogen-bonding acceptor region (HBA: $\sigma > 0.82 \text{ e} \cdot \text{nm}^{-2}$), and non-polar region ($-0.82 \text{ e} \cdot \text{nm}^{-2} < \sigma < 0.82 \text{ e} \cdot \text{nm}^{-2}$) [39]. As shown in Fig. 2(a), the σ -profiles of MeOH and 2-MF are distributed in all three regions, but the peak intensities of MeOH are significantly higher than those of 2-MF in both the HBA and HBD regions, suggesting that MeOH has a stronger hydrogen bonding ability than 2-MF. Further analysis of the σ -profiles of the three selected ILs revealed that their cations are mainly distributed in the HBD region and the nonpolar region, and the peak intensities in the HBD region show a decreasing trend of [EMIM]⁺ > [PMIM]⁺ > [BMIM]⁺ (Fig. 2 (b)). The anion [H₂PO₄][−], on the other hand, is simultaneously distributed in three regions and shows dual hydrogen bonding properties, acting as both a hydrogen bond donor and acceptor [40–42]. The above σ -profile analysis results indicate that the selected ILs are prone to form a hydrogen bond interaction with MeOH than with 2-MF, and this selective interaction mechanism offers a theory basis for realizing effective removal MeOH from azeotrope.

3.2. Experiment section

3.2.1. Thermal stability of ILs

ILs with excellent thermal stability will enable regeneration and recycling of IL. Because the content of ILs in this study was measured by differential gravimetry (vacuum drying at 85 °C), the thermal stability of the ILs is also an important factor in the

accuracy of the LLE results. The three ILs were thermally stabilized at room temperature by ramping up to 900 °C at 10 °C·min^{−1}. As shown in Fig. 3, the decomposition temperatures of the three ILs were basically similar, with a gradual decomposition at 243 °C, which is suitable for the determination of ILs content by differential gravimetry and can be recovered subsequently in LLE process.

3.2.2. Experimental data

The separation performance of the three phosphorus-based ILs was evaluated by a ternary phase diagram analysis system under 30 °C and 101.32 kPa. Repeat each experiment at least three times. As shown in Table 1, the selectivity of [EMIM][H₂PO₄], [PMIM][H₂PO₄] and [BMIM][H₂PO₄] for MeOH was exceeding 1, confirming that the ILs are capable of achieving azeotropic separation of 2-MF and MeOH. During phase equilibrium, the line connecting the coordinates of the two liquid phases is often referred to as the “conjugate line”. Once the system is in equilibrium, the two liquid layers are called conjugate phases. In Fig. 4, the three-phase diagram shows that there is a large unmixed-phase region in the system. Experimental results indicated that the studied systems had the LLE phase behavior of type I. It shows that there is a wide

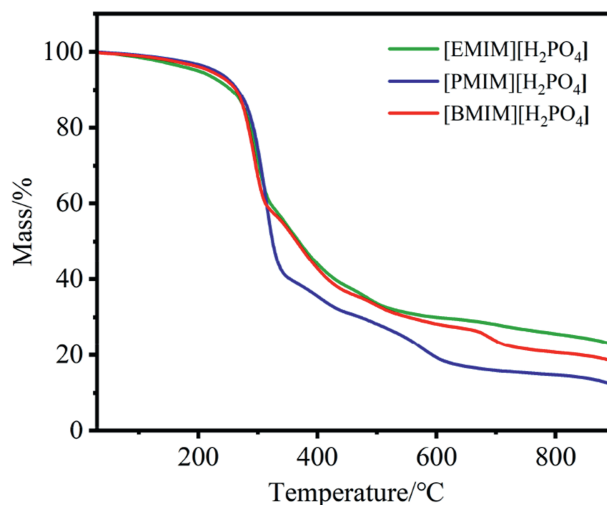


Fig. 3. Thermal stability of three ILs.

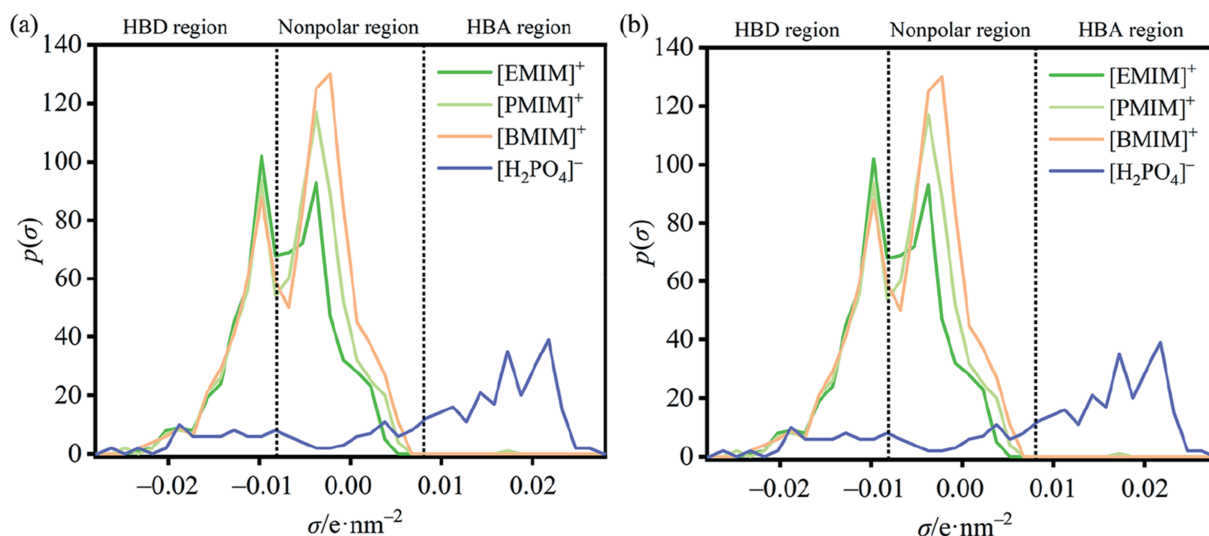
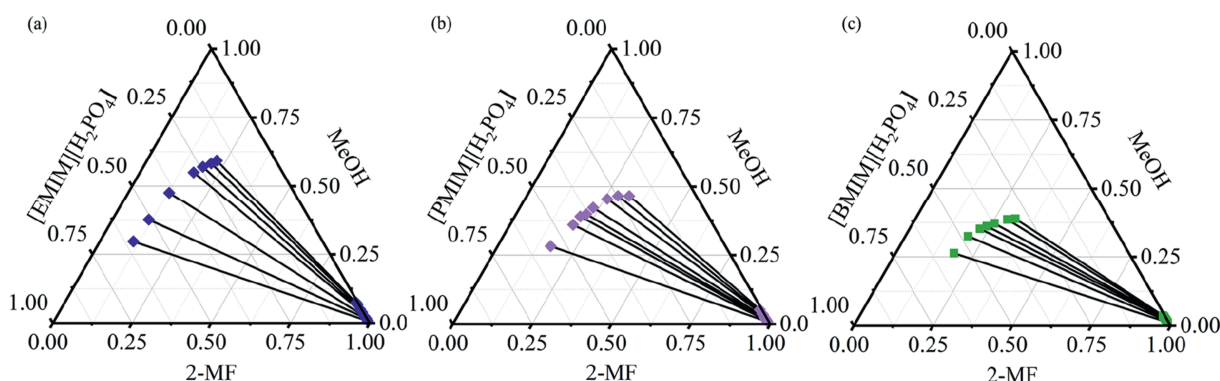


Fig. 2. σ -profiles of (a) MeOH and 2-MF, (b) anions and cations in ILs.

Table 1Experimental (liquid + liquid) equilibrium mole fractions x_i for different ternary systems at temperature $T = 30\text{ }^{\circ}\text{C}$ and pressure $p = 101.32\text{ kPa}^{\oplus}$.

Raffinate		Extractive		β	S
x_1^I	x_2^I	x_1^{II}	x_2^{II}		
2-MF(1) + MeOH(2) + [EMIM][H ₂ PO ₄](3)					
0.919977	0.074747	0.220813	0.593010	7.96	33.05
0.927649	0.067174	0.208367	0.582901	8.70	38.63
0.944876	0.050176	0.178108	0.570496	11.39	60.32
0.956135	0.039605	0.169295	0.550100	13.91	78.45
0.973195	0.023356	0.129316	0.475857	20.40	153.33
0.981083	0.016576	0.114804	0.376273	22.70	193.99
0.989987	0.008101	0.105559	0.297003	36.66	343.86
2-MF(1) + MeOH(2) + [PMIM][H ₂ PO ₄](3)					
0.940495	0.052642	0.322658	0.466113	8.85	25.81
0.955368	0.038428	0.287298	0.465726	12.12	40.30
0.961063	0.033356	0.259155	0.454640	13.63	50.55
0.971016	0.023667	0.230940	0.422425	17.85	75.05
0.975225	0.019654	0.221212	0.398468	20.27	89.38
0.979473	0.015595	0.206636	0.390325	25.03	118.64
0.982168	0.013106	0.199057	0.359903	27.46	135.50
0.986582	0.008757	0.166850	0.282568	32.27	190.80
2-MF(1) + MeOH(2) + [BMIM][H ₂ PO ₄](3)					
0.956415	0.037238	0.314787	0.389154	10.45	31.75
0.959626	0.034184	0.291721	0.386479	11.31	37.19
0.962670	0.031969	0.257410	0.382230	11.96	44.71
0.964319	0.030968	0.238364	0.382213	12.34	49.93
0.971553	0.024391	0.221836	0.352188	14.44	63.24
0.978025	0.018425	0.198118	0.325208	17.65	87.13
0.984374	0.012428	0.183972	0.263657	21.22	113.52

[⊕] Standard uncertainties u is $u(T) = 0.1\text{ }^{\circ}\text{C}$, $u(p) = 1\text{ kPa}$, $u(x_i) = 0.0015$, mean $\pm$ SD = 0.0005 ($n = 3$).**Fig. 4.** Ternary phase diagrams of experimental data for 2-MF(1) + MeOH(2) + ILs(3) system.

range of LLEs, especially [EMIM][H₂PO₄] which can be manipulated.

In addition, the distribution coefficient and selectivity values decreased with the decrease of MeOH content in the extraction phase (Fig. 5). Among the three ILs, [EMIM][H₂PO₄] showed the highest distribution coefficient and lower azeotrope, which reached 36.75 and 343.86, respectively. The above study shows that all three ILs are suitable for the effective separation of 2-MF–MeOH azeotropes.

3.2.3. Thermodynamic validation

Validating the reliability of LLE data is essential because the accuracy of the data can affect industrial simulation calculations and process scale-up of the extraction process. The classical Othmer–Tobias [43] and Hand [44] equations were used to perform the thermodynamic consistency test. The expressions are listed in Eqs. (6) and (7). The higher the linear fit result, the more thermodynamically consistent the data. According to Table S6, R^2 is closer to 1, indicating that the LLE data conform to thermodynamic consistency and the experimental data is credible.

$$\ln\left(\frac{1-x_3^{II}}{x_3^{II}}\right) = a + b \ln\left(\frac{1-x_2^I}{x_2^I}\right) \quad (6)$$

$$\ln\left(\frac{x_1^{II}}{x_3^{II}}\right) = e + f \ln\left(\frac{x_1^I}{x_2^I}\right) \quad (7)$$

where, the subscripts I and II refer to raffinate and extracted phases, x stands for mole fraction, while 2-MF, MeOH and IL are represented by 1, 2 and 3, respectively.

3.2.4. LLE correlation

The NRTL model was used to regress the experimental data and lay the foundation for subsequent industrialization. Detailed regression procedures can be found in the supporting information. As shown in Fig. S2, the regressed data overlap well with the experimental data. The root mean square deviation (RMSD) < 2% and maximum deviation value < 0.05 in Table S7, indicating that the binary interaction parameters obtained by NRTL can accurately predict the ternary phase equilibrium rows in this paper.

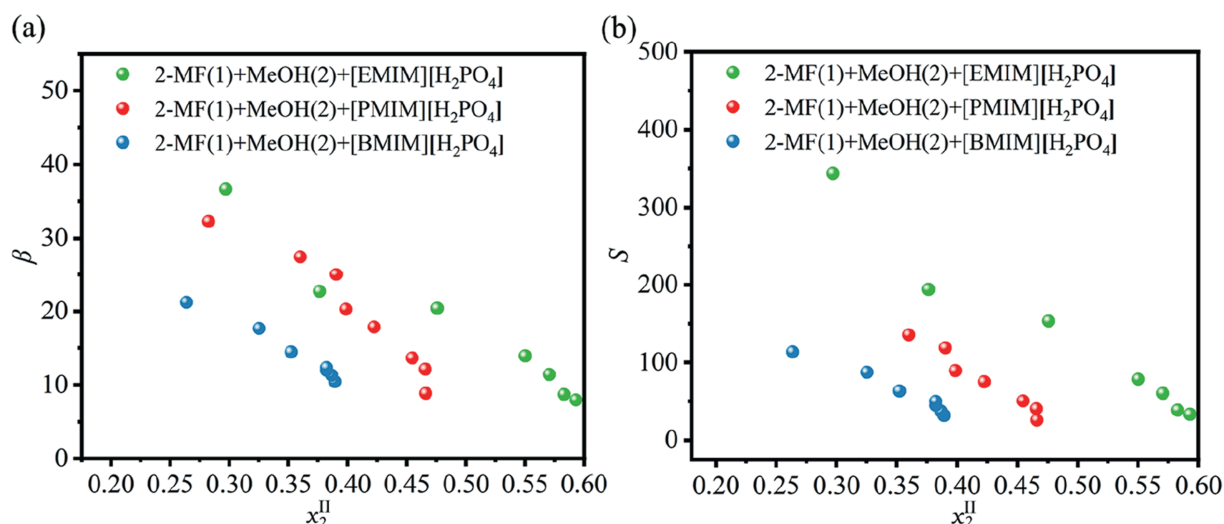


Fig. 5. (a) β and (b) S of 2-MF + MeOH + ILs.

3.3. Quantum chemical calculations

3.3.1. ESP analysis

As illustrated in Fig. 6(a), the minimum ESP value of MeOH ($-152.67 \text{ kJ}\cdot\text{mol}^{-1}$) is localized below the hydroxyl O atom,

corresponding to a negatively charged electron-rich region. Conversely, the maximum ESP value ($+183.55 \text{ kJ}\cdot\text{mol}^{-1}$) appears above the hydroxyl H atom. Notably, the absolute ESP value of H atom in MeOH significantly exceeds the absolute ESP value near O atom, confirming MeOH strong Lewis acid nature and is prone to

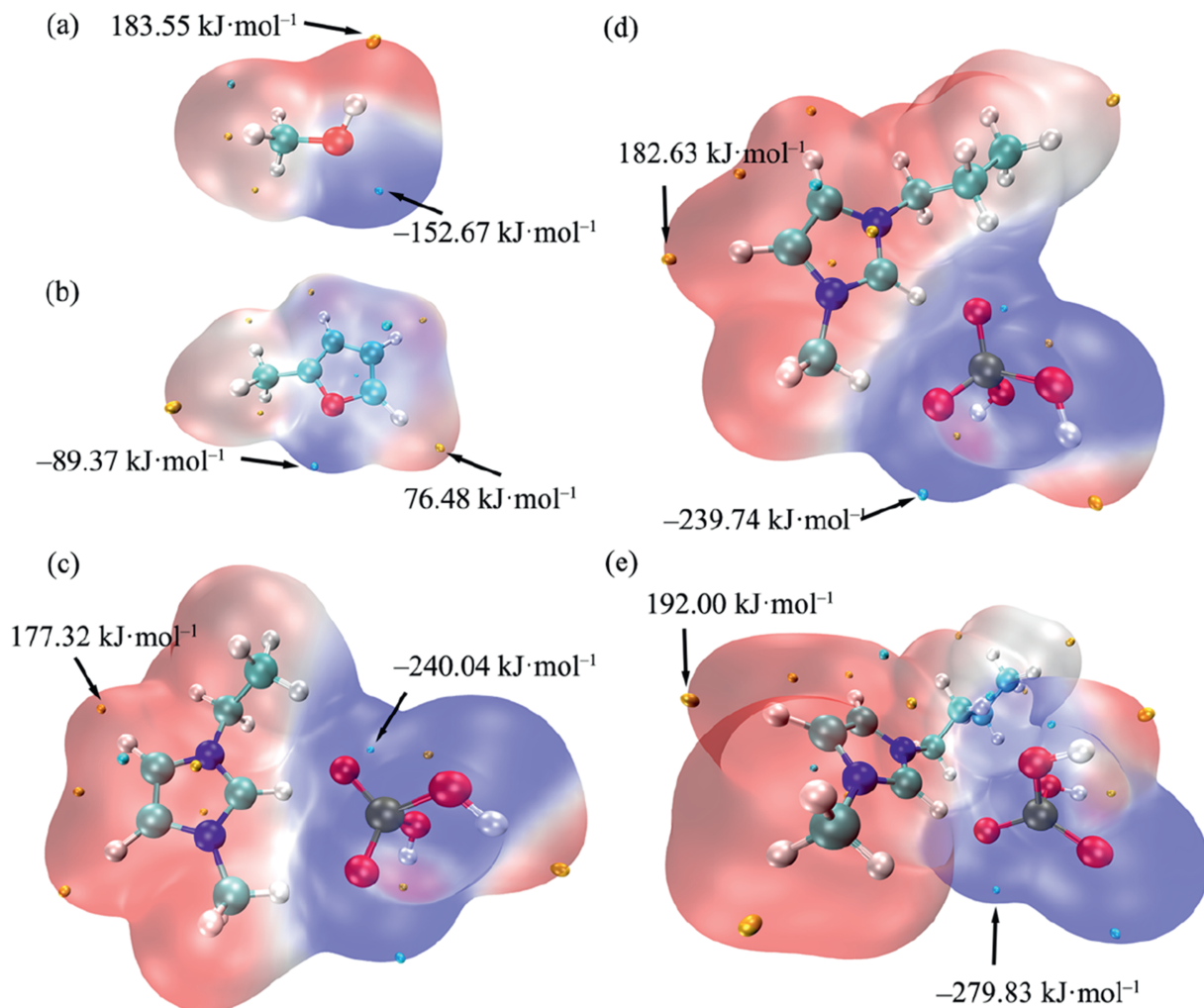


Fig. 6. ESP colored maps of (a) MeOH, (b) 2-MF, (c) [EMIM][H₂PO₄], (d) [PMIM][H₂PO₄], and (e) [BMIM][H₂PO₄].

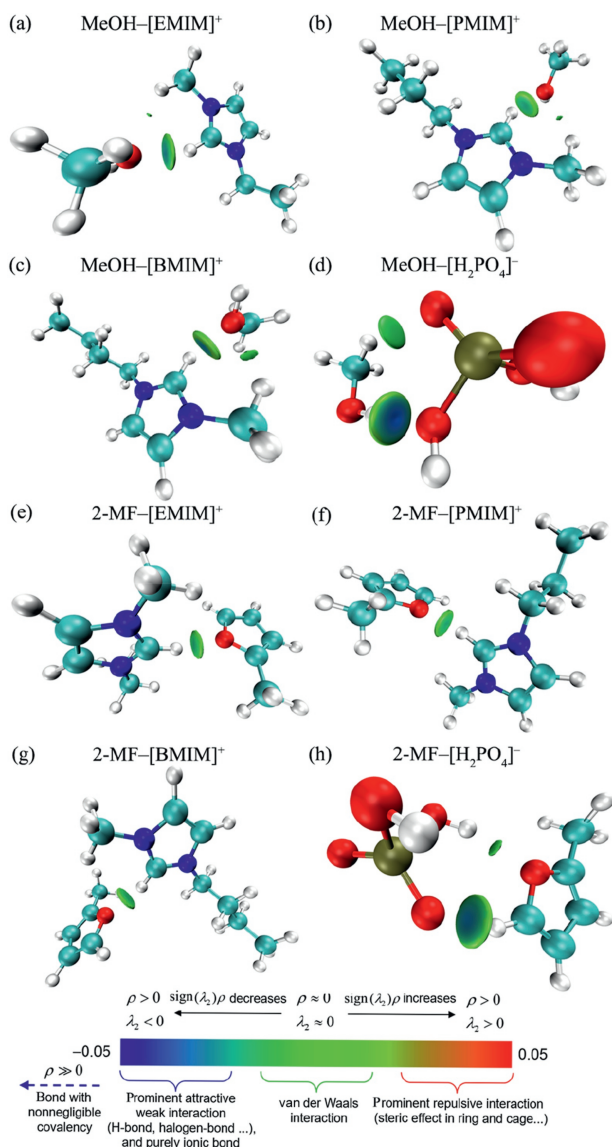


Fig. 7. IGMH analysis between MeOH/2-MF and ILs.

electrostatic attraction with Lewis bases. Besides, the H atom of MeOH may be more suitable for electrostatic interaction sites than O atom. Fig. 6(b) reveals that 2-MF exhibits substantially reduced ESP extrema compared to MeOH, with its minimum ($-89.37 \text{ kJ} \cdot \text{mol}^{-1}$) and maximum ($+76.48 \text{ kJ} \cdot \text{mol}^{-1}$) values distributed near the O atom in the pentacyclic structure and α -H position, respectively. The ESP of [EMIM][H₂PO₄], [PMIM][H₂PO₄] and [BMIM][H₂PO₄] are systematically presented in Fig. 6(c)–(e). All three ILs display characteristic ESP minima (-240.04 , -239.74 and $-279.83 \text{ kJ} \cdot \text{mol}^{-1}$, respectively) concentrated around the O atoms of the [H₂PO₄][−] anions. These values markedly exceed the van der Waals surface potentials, confirming their strong Lewis basic nature. Thus, the observed electron-rich region of ILs and the MeOH proton donor site (ESP maximum), *i.e.* the O([H₂PO₄][−])–H (MeOH) electrostatic interaction *via* acid-base pairing.

3.3.2. IGMH analysis

The IGMH analysis is used to study binary interactions between components, allowing the visualization of intermolecular interaction patterns and comparison of inter-component interaction

patterns. In Fig. 7, the blue color indicates the strong western medical interaction, the green color indicates the van der Waals and the red color indicates the repulsive interaction. The presence of green and blue equipotential surfaces for anions and cations in MeOH and ILs suggests strong hydrogen bonding and van der Waals interactions between MeOH and ILs. Among them, the strongest interaction force is between [H₂PO₄][−] and MeOH. And for the interaction between 2-MF and cations, only van der Waals interactions exist. Between the 2-MF and anion, there is a weak blue equipotential surface, much smaller than that between MeOH–[H₂PO₄][−]. This IGMH analysis indicates that the selected three ILs can separate the azeotrope MeOH from 2-MF through hydrogen bonding interactions, which is consistent with the ESP analysis.

3.3.3. Interaction energy calculation

Interaction energy calculations can quantitatively express the strength of the interaction between IL and 2-MF/MeOH. As shown in Table 2, the interaction energies of MeOH–ILs are all greater than 2-MF–ILs, indicating that ILs are more likely to bind with MeOH, thereby extracting MeOH from the 2-MF and MeOH azeotropic mixture. Additionally, the interaction energies between MeOH and [EMIM][H₂PO₄], [PMIM][H₂PO₄] and [BMIM][H₂PO₄] are -24.2856 , -22.1001 , and $-19.7667 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, indicating that MeOH is more easily dissolved in [EMIM][H₂PO₄]. The order of interaction energy magnitudes is consistent with the distribution coefficients and selectivity observed in the LLE experiments.

3.4. Molecular dynamics simulation

3.4.1. State distribution before and after simulation

In order to observe and analyze the reaction processes and mechanisms during the LLE at the macroscopic level, the kinetic behavior and macroscopic properties of the system were investigated using MD. As illustrated in Fig. 8(a)–(c), [EMIM][H₂PO₄], [PMIM][H₂PO₄] and [BMIM][H₂PO₄] (extractive phases) are depicted on both sides of the simulation box, while a mixture of MeOH and 2-MF (raffinate phase) is displayed in the central region of the box. To enhance visibility, MeOH is represented in fill form. After 50 ns of process simulation, it is evident that MeOH is attracted by the ILs from 2-MF to both sides of the box (Fig. 8(d)–(f)). This simulation phenomenon indicates that all three ILs can effectively separate MeOH from the azeotrope.

3.4.2. Mean square displacement

The extraction actions of different ILs on the LLE process were analyzed using the self-diffusion coefficient (D). The D values of the molecules in the mix systems were used Einstein Eq. (8) to calculate:

Table 2
BSSE-corrected interaction energies between 2-MF/MeOH and ILs.

System	$\Delta E/\text{Hartree}^{\text{①}}$	$E_{\text{BSSE}}/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta E_{\text{int}}/\text{kJ} \cdot \text{mol}^{-1}$
2-MF	−269.3346	—	—
MeOH	−115.7349	—	—
[EMIM][H ₂ PO ₄]	−988.3559	—	—
[PMIM][H ₂ PO ₄]	−1027.2925	—	—
[BMIM][H ₂ PO ₄]	−1066.5953	—	—
2-MF–[EMIM][H ₂ PO ₄]	−1257.6980	0.004888	−6.8585
MeOH–[EMIM][H ₂ PO ₄]	−1104.1036	0.003551	−24.2856
2-MF–[PMIM][H ₂ PO ₄]	−1296.6373	0.007916	−5.9972
MeOH–[PMIM][H ₂ PO ₄]	−1143.0447	0.008883	−22.1001
2-MF–[BMIM][H ₂ PO ₄]	−1335.9378	0.006340	−4.0962
MeOH–[BMIM][H ₂ PO ₄]	−1182.3465	0.008772	−19.7667

^① 1 Hartree = 2625.753 kJ·mol^{−1}.

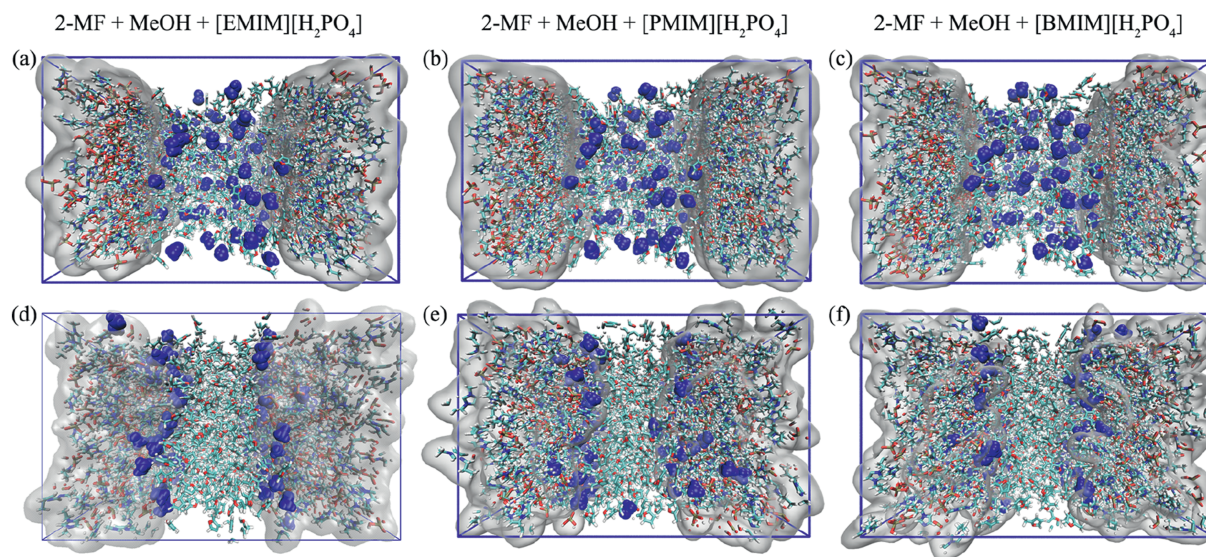


Fig. 8. Box material and change in azeotrope distribution state simulated in the environments (a–c) before and (d–f) after the LLE experiment.

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N |r_i(t) - r_i(0)|^2 \quad (8)$$

where $r_i(t)$ and $r_i(0)$ are the positions of the i -th atom at time t and 0, respectively, $|r_i(t) - r_i(0)|$ represents the MSD displacement.

The D data versus MSD in Fig. 9 reveal the differences in the migration properties of MeOH and 2-MF in three different ILs. The systematic analysis showed that the slopes of the MSD curves of the substances in the same time period were positively correlated with their migratory abilities, and the larger slopes implied that the molecules were more mobile, which corresponded to the higher difficulty of extraction and separation [45]. It is noteworthy that 2-MF in ILs showed the largest D value and the highest slope, indicating that its molecular mobility is the most significant, which is consistent with its difficult extraction by ILs (Fig. 9(a)). In contrast, the D value of MeOH in the three ILs is close to 0, and the slope of the MSD curve of MeOH in the three ILs are $[\text{EMIM}][\text{H}_2\text{PO}_4] > [\text{PMIM}][\text{H}_2\text{PO}_4] > [\text{BMIM}][\text{H}_2\text{PO}_4]$ (Fig. 9(b)), indicating that $[\text{EMIM}][\text{H}_2\text{PO}_4]$ has the best affinity for MeOH, which is consistent with the distribution coefficient and selectivity. Further

time evolution analysis showed that, as the system reached dynamic equilibrium, the slope of the MSD curve of MeOH showed a gradual decay, corresponding to a continuous decrease in the value of the diffusion coefficient D . This phenomenon signified that the MeOH molecules had entered the IL-enriched phase, and its diffusion rate was significantly limited, which finally realized the selective retention of solute molecules in the IL phase.

3.4.3. Radial distribution functions

The RDF quantitatively describes the proportion of the local density to the average density at r of the central molecular system. In this study, the ILs and mixed solutes are investigated from the RDF thus analyzing the characteristic intermolecular interactions and strengths. The N and H atoms of $[\text{EMIM}]^+$, the H and O atoms of $[\text{H}_2\text{PO}_4]^-$ (divided into O2 and O6), the H1, H4 and O atoms of MeOH, and the H and O atoms of 2-MF (atomic labels are in Fig. S3) in the ions were selected and the RDF plots between them were plotted. The results in Fig. 10 show that the $g(r)$ of 2-MF with $[\text{EMIM}]^+ / [\text{PMIM}]^+ / [\text{BMIM}]^+ / [\text{H}_2\text{PO}_4]^-$ increases at 0–2.8 nm, and finally tends to 1. This phenomenon suggests weak interaction

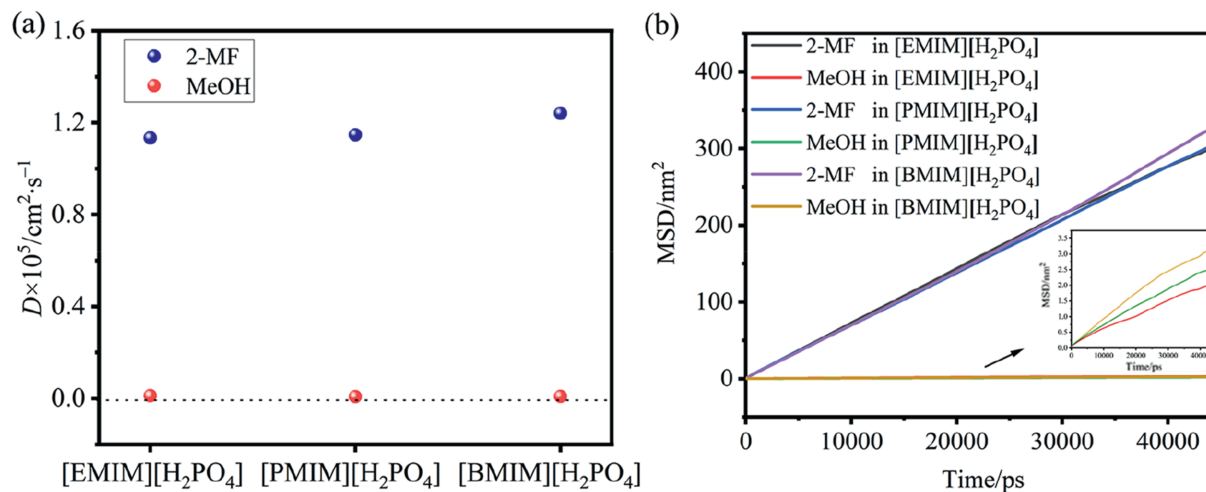


Fig. 9. MSD analysis.

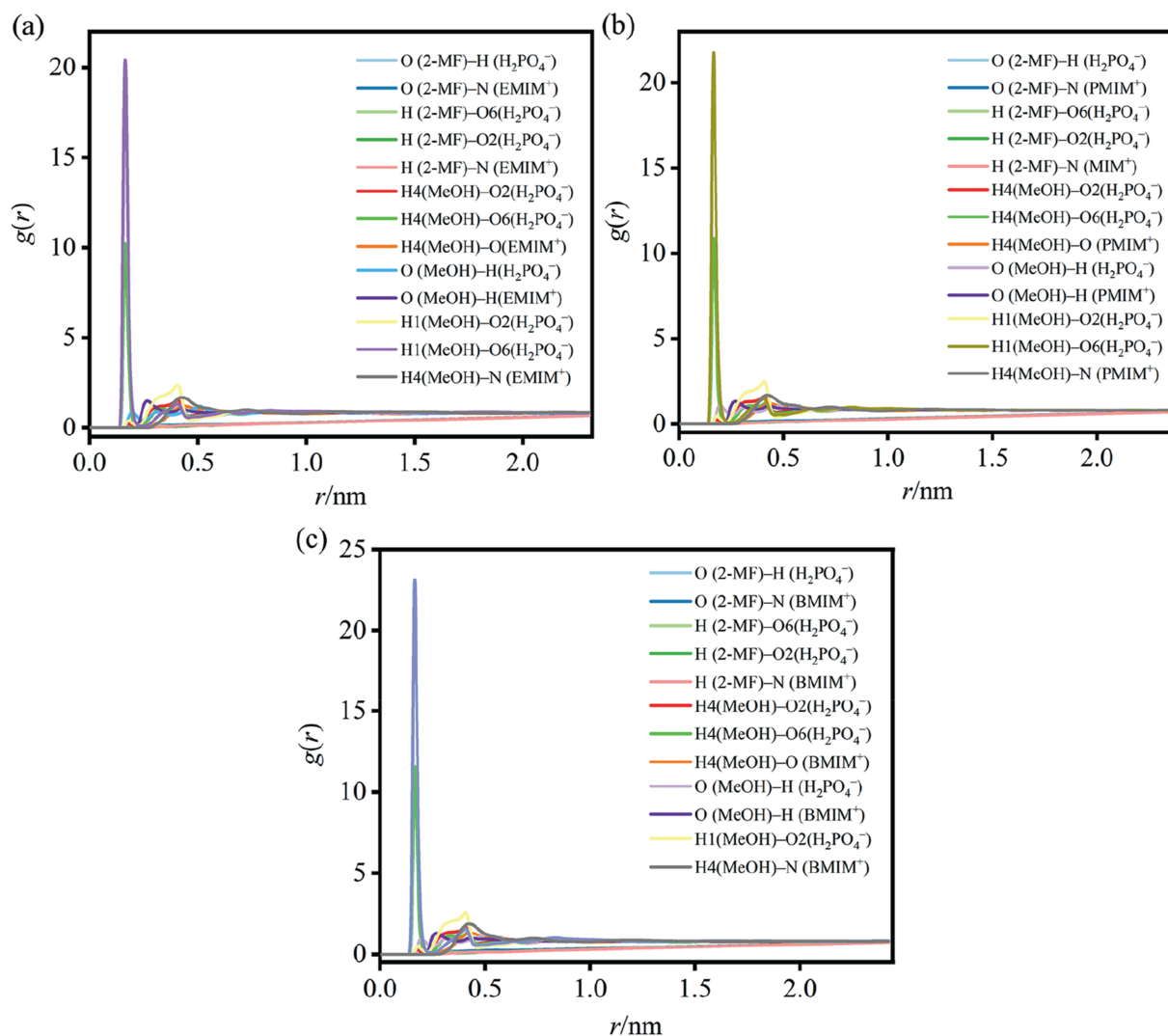


Fig. 10. RDF of atoms between various molecules in (a) [EMIM][H₂PO₄], (b) [PMIM][H₂PO₄] and (c) [BMIM][H₂PO₄].

between 2-MF and ILs and almost no attraction exists. However, two distinct sharp peaks at $r = 0.25$ nm can be clearly seen for MeOH, corresponding to strong hydrogen bonding interactions between the H1/H4 of the MeOH and the O6 in the [H₂PO₄][−] anion of the ILs ($g(r) > 5$), which are much stronger than the weak van der Waals interactions of the other atom pairs. Besides, a weak peak around $r = 0.4$ nm exists between H1 of MeOH and O2 in [H₂PO₄][−], H4 and N atoms in [EMIM]⁺, suggesting that MeOH has weak van der Waals interactions with [H₂PO₄][−] and cations. Therefore, by comparing the $g(r)$ values, the [H₂PO₄][−] anion in IL plays a dominant role in the separation process between 2-MF and MeOH, while the H atom on the hydroxyl group of MeOH occupies an important position in hydrogen bonding interactions. This is because the O6 in the [H₂PO₄][−] anion has a higher negative charge (−0.937), while the H on the hydroxyl group of MeOH has a higher positive charge (0.340) in Fig. S3, thereby strengthening the hydrogen bond. This finding elucidates the mechanism of selective MeOH extraction by IL on a molecular scale: anions preferentially capture MeOH molecules through specific hydrogen-bonding interactions, while 2-MF is difficult to be enriched by the IL phase due to the lack of strong interaction sites. This matches the structure analyzed in previous ESP.

4. Conclusions

In conclusion, this article presents the first systematic study of ILs as extractants applied to the azeotropes 2-MF and MeOH. Three ILs [EMIM][H₂PO₄], [PMIM][H₂PO₄] and [BMIM][H₂PO₄] were selected from 459 solvents using COSMO-RS model and σ -profiles. The LLE experimental results show that the distribution coefficients and selectivity of the three ILs are [EMIM][H₂PO₄] (36.66, 343.86) > [PMIM][H₂PO₄] (32.27, 190.80) > [BMIM][H₂PO₄] (21.22, 113.52), respectively. Othmer–Tobias and Hand equations ($R^2 > 0.90$) confirmed the thermodynamic consistency of phase equilibrium data. By correlating the experimental data with the NRTL model, the RMSD is less than 2% and the maximum deviation value < 0.05. This indicates that the NRTL model can predict the phase behavior of this system. Subsequently, ESP and IGMH analyses indicated that the hydrogen bonding interactions formed between IL and MeOH are the key driving forces for the separation of the 2-MF–MeOH mixture. RDF analysis showed that the anions in IL play a primary role during the extraction process. MSD results showed that the diffusion rate of MeOH in ILs is significantly lower than that of 2-MF, making it easier for ILs to extract MeOH from 2-MF. Energy calculations indicated that

the intermolecular interactions between ILs and MeOH are stronger than those between ILs and 2-MF. The interaction energies between MeOH and [EMIM][H₂PO₄], [PMIM][H₂PO₄], and [BMIM][H₂PO₄] are −24.2856, −22.1001, and −19.7667 kJ·mol^{−1}, respectively, which is consistent with the order of LLE data results.

Although the proposed ILs showed significant results for the azeotropes 2-MF and MeOH, the difficulty of synthesizing the selected ILs and their economic feasibility were also key factors of concern in the future.

CRedit Authorship Contribution Statement

Yue Wang: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Wenxiu Li: Writing – review & editing, Validation, Resources, Project administration, Conceptualization. Pengfei Wang: Data curation. Jiayi Liu: Software. Tao Zhang: Writing – review & editing, Validation, Supervision, Resources, Methodology, Conceptualization.

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.2025.09.002>.

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