

Effects of Deep Eutectic Solvents on H₂SO₄-catalyzed Alkylation: Combining Experiment and Molecular Dynamics Simulation

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Abstract

To enhance the catalytic performance of H₂SO₄-catalyzed alkylation, various catalytic additives have drawn considerable attention. Herein, the effects of deep eutectic solvents additives (DESs) on catalytic performance and interfacial properties of H₂SO₄ alkylation were systematically investigated using experimental methods and molecular dynamics (MD) simulation. Experimental results indicate that DESs additives with the optimal concentration about 1.0 wt% can efficiently improve C₈ selectivity and research octane number (RON) of alkylate. However, DESs additives contribute less to the quality of alkylate at low temperature and to the lifetime of H₂SO₄. MD results reveal that the phenyl molecules of DESs additives play a major role in enhancing interfacial properties of H₂SO₄ alkylation, including enlargement of interfacial thickness, promotion of isobutane relative solubility and diffusion to butene, which is probably the main reason for the better quality of alkylate. This work gives a good guideline for the design of novel DESs for H₂SO₄ alkylation.

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Abstract

To enhance the catalytic performance of H₂SO₄-catalyzed alkylation, various catalytic additives have drawn considerable attention. Herein, the effects of deep eutectic solvents additives (DESs) on catalytic performance and interfacial properties of H₂SO₄ alkylation were systematically investigated using experimental methods and molecular dynamics (MD) simulation. Experimental results indicate that DESs additives with the optimal concentration about 1.0 wt% can efficiently improve C₈ selectivity and research octane number (RON) of alkylate. However, DESs additives contribute less to the quality of alkylate at low temperature and to the lifetime of H₂SO₄. MD results reveal that the phenyl molecules of DESs additives play a major role in enhancing interfacial properties of H₂SO₄ alkylation, including enlargement of interfacial thickness, promotion of isobutane relative solubility and diffusion to butene, which is probably the main reason for the better quality of alkylate. This work gives a good guideline for the design of novel DESs for H₂SO₄ alkylation.

Keywords : H₂SO₄ alkylation, DESs, Liquid/liquid interface, MD simulation.

Introduction

The alkylate, produced by isobutane alkylation (C4 alkylation) with C3-C5 olefins using strong acid as catalyst, is an ideal blending component of the gasoline pool, owing to its numerous advantages, such as high RON, low Reid vapor pressure, free of sulfur, absence of aromatics and alkenes compounds¹⁻⁴. The commercial alkylation process usually uses liquid acid as catalyst, including concentrated sulfuric acid (H_2SO_4) and hydrofluoric acid (HF)^{5,6}. However, HF suffers from high toxicity and volatility once it releases or forms aerosol, which can result in large potential danger^{3,7}. The solid acid as an environmentally friendly alternative shows a good selectivity and catalytic activity⁸⁻¹¹. However, the disadvantages of easy deactivation by coking and difficult regeneration restrict its industrial application^{1,11-13}. Ionic liquids (ILs) are also the promising alternative to catalyze C4 alkylation, but the disposal of spent salt is too difficult. Currently, H_2SO_4 is still the dominant catalyst for the industrial alkylation process. However, the drawbacks of equipment corrosion and high acid consumption of H_2SO_4 alkylation process motivate researchers to develop various additives, such as aromatics, surfactants, and ILs, to improve the catalytic activity of H_2SO_4 ^{6,10,13,14}.

It is well-confirmed that surfactants as the additives of H_2SO_4 alkylation can efficiently enhance the quality of alkylate^{15,16}. Chen et al. reported several cationic, anionic, and amphoteric surfactants as additives in C4 alkylation in 2003¹⁷. Our recent work gave a detailed investigation about the effect of surfactants on the catalytic performance and interfacial features of H_2SO_4 alkylation using experiments and molecular dynamics (MD) simulation^{15,18}. In spite of the good performance of surfactants for C4 alkylation, the commercial surfactants, such as sodium dodecyl benzene sulfonate (SDBS) and hexadecyltrimethylammonium bromide (CTAB), contain the sodium and bromine elements, which can accelerate equipment corrosion¹⁵. ILs have been proved as potential catalysts or additives for C4 alkylation^{4,19-21}. The chloroaluminate-based ILs with Lewis acidity were the most frequently studied to enhance the C4 alkylation. Liu et al. reported that chloroaluminate-based ILs containing CuAlCl_4 complexes show better catalytic performance²². In addition, Brønsted acidic ILs (BILs) were also demonstrated to possess excellent catalytic activity for C4 alkylation. For example, 1-(3-sulfopropyl)-3-methyl-imidazolium hydrogen sulfate and 1-(3-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([MBSIm][HSO_4]) coupled with strong acid were investigated by Tang et al²³. However, despite the efficient improvement of ILs, the high cost of raw material and complicated preparation process inhibit its further development to some extent.

More recently, DESs have been attracting numerous attentions, which consist of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) via hydrogen-bonding interaction, and thus the melting point is obviously lower than either individual pure component^{24,25}. The DESs exhibit excellent physical and chemical properties, such as low vapor pressure, relatively wide liquid range, non-flammable, conductivity, non-toxicity, sharing similar properties as ILs²⁴⁻²⁶. Moreover, DESs can be prepared easier with lower cost of raw materials, resulting in that DESs has emerged as the promising alternatives to ILs. Yu et al used acidic DES, consisting of trifluoromethanesulfonic acid (TfOH) and taurine (TAU), as the catalyst for C4 alkylation. They found that [TfOH]₃[TAU]/PEG-200 catalytic system displays the encouraging increase in catalytic activity and selectivity with the C₈ selectivity up to 85.54%²⁷. However, the applications of DESs as additives in C4 alkylation still remain seldom. More importantly, there is no systematical report regarding to the effect of DESs additives on the catalytic and recycle performance of H_2SO_4 alkylation. In addition, the behaviors of DESs additives at the H_2SO_4 /C4 hydrocarbons interface are still insufficient. Fortunately, molecular dynamics (MD) simulation is a powerful tool to probe the microscale interfacial properties, which has been well proved to be able to efficiently reveal the interfacial behaviors of ILs and surfactants additives at the H_2SO_4 /C4 hydrocarbons interface in our previous papers^{7,15,18,28-32}.

Therefore, in this paper, the effects of DESs additives on the catalytic performance and interfacial properties of H_2SO_4 -catalyzed C4 alkylation were studied in details using experimental methods and MD simulation. The investigated DESs include choline chlorides-phenol (ChCl-Pho (1:2)), choline chlorides-p-toluenesulfonic acid (ChCl-TsOH (1:1)), choline chlorides-benzoic acid (ChCl-BOA (1:2)), and choline chlorides-hydroxylamine hydrochloride (ChCl-NH₂OH·HCl (1:2)). The effect of DESs concentration, reaction time, temperature and recycle times on the C4 alkylation were investigated systematically. Additionally, MD simulations were used to reveal the enhancement of (ChCl-Pho (1:2)), ChCl-TsOH (1:1), and ChCl-BOA (1:2) on the interfacial properties of H_2SO_4 alkylation.

2. METHODOLOGY

2.1 Materials

All chemicals (AR grade) were purchased commercially and used as received. H_2SO_4 (A.R, 98 wt%) was bought from Sinopharm Chemical Reagent Co., Ltd. Choline chlorides and carbon tetrachloride ([?]99.5%) were purchased from Shanghai Titan Scientific Co., Ltd. Phenol ([?]99.0%) and benzoic acid (99.5%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. P-toluenesulfonic acid (99.0%) and hydroxylamine hydrochloride (98.5%) were purchased from Shanghai MackLin Biochemical Technology Co., Ltd. Isobutane/2-butene mixture (86.9/13.1 wt%) was obtained from Shanghai Weichuang Standard Gas Analysis Technology Co., Ltd. Nitrogen (99.99%) gas was purchased from Air Liquide (Shanghai) Gas Co., Ltd.

2.2 Preparation of DESs

ChCl was chosen as the HBA, and phenol (Pho), p-toluenesulfonic acid (TsOH), benzoic acid (BOA) and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) were selected as HBD, respectively. The synthesis of DESs was carried out in a glass flask. The acceptor and donor of the hydrogen bond were mixed according to molar ratio of 1/2, 1/1, 1/2, 1/2 to prepare ChCl -Pho (1:2), ChCl -TsOH (1:1), ChCl -BOA (1:2), and ChCl - $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1:2), respectively, with the structures shown in Figure 1³³⁻³⁵. The mixtures were heated with stirring for 1 h after the appearance of homogeneous liquid phase in the oil bath.

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Figure 1. Structures of different DESs.

2.3 Experimental process

For the typical alkylation process, the reaction took place in a batch reactor with 1 L volume equipped with a cooling system. At first, the 180 ml DESs/ H_2SO_4 mixture was put into the reactor, in which the ratio of DESs to H_2SO_4 was set to be 0.5, 1.0, 3.0, 5.0 and 8.0 wt%, respectively. Subsequently, the N_2 gas was added to purge the reactor by three times to remove the air, after which the cooling system turned on to keep reaction temperature at the given temperature. The pressure in the reactor was controlled at 0.5 MPa to maintain the C4 reactants as liquid phase. Then, 120 mL of isobutane/2-butene mixture with a given ratio were quickly injected into the reactor and the agitation started to work at the stirring rate of 3000 rpm to achieve a well-distributed dispersion between C4 reactants phase and acid phase. After the reaction stopped, the products were collected and analyzed by GC after being extracted and separated from acid phase using carbon tetrachloride. The details of the analysis of the products displayed on our previous work¹⁸.

2.4 MD simulation details

The potential parameters and models of the concentrated H_2SO_4 and C4 reactants for MD simulations were from the same as our previous work.^{6,7} The C4 reactants model includes equivalent 2-butene and isobutane with size of $6.0 \times 6.0 \times 4.0 \text{ nm}^3$. The size of H_2SO_4 model is $6.0 \times 6.0 \times 8.0 \text{ nm}^3$, containing 2848 H_2SO_4 molecules, 84 hydronium ions, and 84 bisulphate ions. For the interfacial model, the sandwich-like models were constructed with pure H_2SO_4 model in the middle and pure C4 reactants model in the both sides. 2 nm gap between pure H_2SO_4 model and pure C4 reactants model was used to place DESs. The number of ChCl -Pho (1:2) in the gap are 6, 15, and 24, corresponding to the concentration of 1.0 wt%, 3.0 wt%, and 5.0 wt%, respectively. For ChCl -TsOH (1:1), the number is 6, 16, and 26, respectively. For ChCl -BOA (1:2), the number is 6, 12, and 21, respectively. Initially, the energy minimization of 5000 steps was carried out, followed by 8 ns canonical (NVT) simulations at 298.2 K with nose-hoover thermostat. The isothermal-isobaric (NPT) ensemble was further conducted for 10 ns to fully equilibrate configurations. During the simulation, the number density distribution of each moiety was calculated every 2 ns, and the

configures were fully equilibrated after there are no apparent deviations for the density. At last, 6 ns *NVT* was carried out for data collection of interest with the time steps of 2.0 fs. The semi-isotropic Parrinello Rahman barostat method on *z* axis was used with 2.0 ps relaxation time at 1 bar for all the *NPT* ensemble to keep the interface unchanged¹⁵.

For all the MD simulations, GROMACS software was employed with periodic boundary conditions (PBC) in three dimensions³⁶. The Lennard-Jones interaction and Coulombic interaction were cut off at 1.2 nm. All the covalent bonds related to hydrogen atoms were treated using the LINCS algorithm. Maxwell distribution was employed to obtain the initial atomic velocity. The particle grid Ewald method was used to treat long-range electrostatic interactions. The OPLS-AA was used to treat the interaction between the DESs, H₂SO₄ and C4 hydrocarbons^{6,7,29}. At the same time, the charges of the DESs were refitted based on the ChelpG method at the Basis set of 6-311++G(d,p) level with Gaussian 09 program³⁷.

3. Results and discussions

3.1 Effect of DESs on reaction time

The effects of ChCl-Pho (1:2), ChCl-TsOH (1:1), ChCl-BOA (1:2) and ChCl-NH₂OH·HCl (1:2) additives on the alkylate components as a function of time were initially investigated, as shown in Figure 2. At the initial time, the C₉+ components are relatively high with the low conversion of C₈ key components. With the extended reaction time, the RON and C₈ key components increase gradually, and the LEs (C₅-C₇) and C₉+ components present a decreasing trend. The RON and C₈ approach a plateau basically after 15 min, as same as the reaction time of H₂SO₄ system without any additive (see Figure S1). Among the reaction, the trimethylpentanes (TMPs) with higher RON (>100.0) grow in pace with the C₈ components, leading to the higher RON of alkylate. Hence, the addition of DESs have no effect of the reaction time of H₂SO₄ alkylation in contrast to the pure H₂SO₄ system. The reaction time of 15 min was taken for the following experiments.

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Figure 2. Alkylate as a function of time with ChCl-Pho (1:2) (a), ChCl-TsOH (1:1) (b), ChCl-BOA (1:2) (c) and ChCl-NH₂OH·HCl (1:2) (d). Reaction conditions: temperature 281.2 K, stirring rate 3000 r/min, mass ratio of DESs/H₂SO₄ 1.0 wt%, volume ratio of H₂SO₄/hydrocarbon 1.5:1, volume ratio of I/O 12:1.

3.2 Effect of DES concentrations

In order to explore the effect of the DES amounts on the alkylate components, ChCl-Pho (1:2) and ChCl-TsOH (1:1) additives were chosen. The alkylate components as a function of DESs concentrations are shown in Figure 3. From Figure 3a, the amount of ChCl-Pho (1:2) changes from 0 wt% to 5.0 wt% with the optimal mass ratio is about 1.0 wt%, in which the C₈ selectivity and TMPs components are 83.64% and 76.85%, respectively, at the temperature of 281.2 K. Meanwhile, with the amount of ChCl-Pho (1:2) increasing from 0 wt% to 0.5 wt%, the LEs and C₉+ components decrease slightly, and C₈ and TMPs increase obviously, which demonstrates that ChCl-Pho (1:2) has a promoting effect on the generation of C₈ components to a considerable extent. When the amount of ChCl-Pho (1:2) increase from 0.5 wt% to 3.0 wt%, the RON of alkylate reaches 97.30, which is ascribed to the conversion of LEs and C₉+ components to the TMPs with higher RON. However, when the amount of ChCl-Pho (1:2) reaches 5.0 wt%, the catalytic effect significantly decreases, owing to the fact that excessive additives lead to the decrease of H₂SO₄ acidity for C4 alkylation. As we all know, the oligomerization of butene and the growth of red oil take place with the lower acidity of catalyst, which results in the increase of C₉+ components and the decrease of key components dramatically³⁸.

When ChCl-TsOH (1:1) is used as additives, the change of LEs, C₈ and C₉+ components follow the similar trend as that of ChCl-Pho (1:2). The difference is that the promoted catalytic performance of ChCl-TsOH

(1:1) is slightly weaker compared to ChCl-Pho (1:2). From Figure 3b, the optimal mass ratio is 1.0 wt%, in which the RON is 96.93 and the C₈ selectivity and TMPs components are 80.71% and 74.00%, respectively, at the temperature of 281.2 K. According to the previous work, Liu et al found that the addition of little amount of benzene for the C4 alkylation catalyzed by ILs could buffer the strong acidity of chloroaluminate anions to adjust acidity of catalysts and enrich the isobutane at the interface, which confirms that the addition of aromatics has a positive effect in C4 alkylation³⁹. Thus, it is inferred that the intensified catalytic performance of ChCl-Pho (1:2) and ChCl-TsOH (1:1) additives probably comes from the phenol and TsOH, the subclass of aromatics, respectively.

Figure 3c and 3d plot the effect of the ChCl-Pho (1:2) and ChCl-TsOH (1:1) on the C₈ components. Clearly, there is a dramatic influence on TMP components, which are 2,2,4-TMPs, 2,3,3-TMPs, and 2,2,3-TMPs. Particularly, at the optimal ratio, the 2,2,4-TMPs, 2,3,3-TMPs, and 2,2,3-TMPs have an increasing trend, which is consistent with the improvement of alkylate quality. In addition, ChCl-Pho (1:2) and ChCl-TsOH (1:1) have a little influence on 2,3,4-TMPs and DMHs, including 2,5-DMH, 2,4-DMH, and 2,3-DMH with lower RON. Therefore, the above results illustrate that the ChCl-Pho (1:2) and ChCl-TsOH (1:1) have a great effect on the conversion of LEs and HEs to TMPs with the higher selectivity of 2,2,4-TMPs, 2,3,3-TMPs and 2,2,3-TMPs. The enhancement of ChCl-Pho (1:2) and ChCl-TsOH (1:1) additives on the quality of alkylate is inferred to be ascribed to improvement of interfacial properties, which will be explained systematically at the molecular level via MD simulation in the following sections.

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Figure 3. Alkylate components as a function of DESs concentrations. (a) and (c) for ChCl-Pho (1:2). (b) and (d) for ChCl-TsOH (1:1). Reaction conditions: temperature 281.2 K, stirring rate 3000 r/min, reaction time 15 min, volume ratio of H₂SO₄/hydrocarbon 1.5:1, volume ratio of I/O 12:1.

3.3 Effect of temperature

C4 alkylation is an exothermic reaction. The low temperature is beneficial to the formation of C₈ key components with higher RON^{40,41}. Thus, the effect of reaction temperature on C4 alkylation from 281.2 K to 269.2 K with ChCl-Pho (1:2) additive was listed in Table 1. The difference of alkylate components between DESs-aiding systems and pure H₂SO₄ system as a function of temperature are shown in Figure 4. For the system with 1.0 wt% ChCl-Pho (1:2), it is clear that the targeted C₈ components and the RON increase obviously from 83.77% at 281.2 K to 86.07% at 274.2 K, 97.39 at 281.2 K to 98.27 at 274.2 K, respectively, which is mainly attributed to lower reaction temperature. This tendency is in good agreement with our previous work, in which, lower temperature leads to a great increase in C₈ contents and significant decrease in LEs, HEs and DMHs components¹⁵. However, in ChCl-Pho (1:2)-aiding system, when the temperature is below 274.2 K, the quality of alkylate is not improved as expected. The C₈ contents dramatically decrease and HEs sharply increase at the 269.2 K. The C₈ key components and the RON decrease obviously, and the content of C₉+ components dramatically increase.

Table 1. Temperature-dependent alkylate components for H₂SO₄ alkylation with ChCl-Pho (1:2) as additive.

Additive	Additive	Alkylate composition (wt%)					
	Temp /K	C5~C7	C8	TMP	C9+	DMH	RON
Pure H ₂ SO ₄	281.2	11.05	74.50	67.56	14.45	6.94	95.80

ChCl-Pho (1:2)	281.2	6.46	83.77	76.98	9.77	6.79	97.39
	277.2	6.07	85.65	79.45	8.28	6.20	98.05
	274.2	5.62	86.07	80.15	8.30	5.92	98.27
	273.2	4.65	84.21	78.67	11.14	5.54	97.86
	269.2	6.67	71.20	67.31	22.12	3.89	95.74

^a Reaction conditions: ChCl-Pho (1:2) concentration 1.0 wt%, stirring rate 3000 r/min, reaction time 20 min, volume ratio of H₂SO₄/hydrocarbon 1.5:1, volume ratio of I/O 12:1.

Furthermore, the difference of alkylate components and C₈ components of H₂SO₄ alkylation with ChCl-Pho (1:2) additive as a function of temperature. From Figure 4a, compared with the pure H₂SO₄ system at 281.2 K, the C₈ contents and TMPs increase 9.27%, 11.15%, 11.57% and 9.71%, 9.42%, 11.89%, 12.59% and 11.11% at 281.2 K, 277.2 K, 274.2 K, and 273.2 K, respectively. In Figure 4b, 2,2,4-TMPs, 2,3,3-TMPs and 2,2,3-TMPs follow the similar trend as the C₈ components, which suggests the change of the reaction temperature mostly impacts on the TMP components with higher RON.

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Figure 4. The difference of alkylate components between H₂SO₄ alkylation with ChCl-Pho (1:2) as a function of temperature (a). Temperature-dependent C₈ components for H₂SO₄-catalyzed alkylation with ChCl-Pho (1:2) additive (b). Reaction conditions: ChCl-Pho (1:2) concentration 1.0 wt%, stirring rate 3000 r/min, reaction time 20 min, volume ratio of H₂SO₄/hydrocarbon 1.5:1, volume ratio of I/O 12:1.

3.4 Lifetime of H₂SO₄ with DESs

Based on the optimal reaction results at 281.2 K, ChCl-Pho (1:2) and ChCl-TsOH (1:1) were chosen to probe the effect of DESs on the recycling capability for the H₂SO₄. The recycling run of H₂SO₄/ChCl-Pho (1:2), H₂SO₄/ChCl-TsOH (1:1) and pure H₂SO₄ are shown in Figure 5(a), Figure 5(b) and Figure S2, respectively. From Figure 5(a), the RON and C₈ components slightly increase initially and then decrease slowly. The C₉⁺ components increase with the increased recycle times. The first 3 runs can be defined as catalytic activity strengthening stage. The RON and the C₈ contents increase from 93.62 and 63.83% to 94.50 and 68.07%, respectively. In the initial strengthening stage, the acidity of catalyst is still high to promote the main reactions. The trace amount of side reactions products of H₂O, esters and acid soluble oil (ASO) has a positive effect on C4 alkylation, which is the reason why the quality of alkylate is improved in first 3 times⁴². Nevertheless, the 4th-11th recycles step into the gradual deactivation stage. The C₈ contents and RON decrease from 66.00% and 93.78 to 51.23% and 90.90, respectively. In this stage, the notorious side reactions products of H₂O, esters and ASO gradually accumulate with the increase of recycle times and leads to the gradual decrease in the acid strength and the quality of the alkylate. After 11th runs, the catalyst tends to be inactive and the C₉⁺ components dramatically increase from 36.77% to 53.55%.

The lifetime performance of H₂SO₄ catalyst with ChCl-TsOH (1:1) additives is similar as that with ChCl-Pho (1:2) as additives. The first 2 recycle times is the stage of catalytic activity strengthening. After the 10 runs, the activity of catalyst dramatically decreases with RON down to 84.90 at 16 runs. The difference is the lifetime test with ChCl-TsOH (1:1) additives has a relatively stable high catalytic activity stage from 3th to 10th. In high catalytic activity stage, the performance of the catalyst remains stable, the RON and the C₈ contents is still above 93.0 and 63.00%, respectively. In comparison to lifetime test of the pure H₂SO₄, however, the addition of ChCl-Pho (1:2) and ChCl-TsOH (1:1) do not improve the catalytic lifetime of H₂SO₄, although they show the effective catalytic performance,

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Figure 5. Alkylate components as a function of recycle times. (a) ChCl-Pho (1:2) at 1.0 wt%. (b) ChCl-TsOH (1:1) at 1.0 wt%. Reaction conditions: temperature 281.2 K, stirring rate 3000 r/min, reaction time 15 min, volume ratio of H₂SO₄/hydrocarbon 1.5:1, volume ratio of I/O 8:1.

3.5 Distributions of DESs at the interface

From the above experimental results, it is clear that the introduction of DESs can effectively increase the RON of alkylate, but the lifetime of H₂SO₄ catalyst was almost not promoted. It can be inferred that the better performance of alkylate is probably due to the intensification of acid/hydrocarbons interface, rather than the tunability of H₂SO₄ microenvironment. However, the effect of DESs on the acid/hydrocarbons interface remains unclear to a great extent. Thus, the acid/hydrocarbons interfacial behaviors with the addition of ChCl-Pho (1:2), ChCl-TsOH (1:1), and ChCl-BOA (1:2), respectively, were further investigated using MD simulations in details.

Initially, the equilibrated snapshots of DES distributions at different concentrations were presented in Figure 6. For all the systems, ChCl molecules were clearly observed with a better dispersion in H₂SO₄ phase, while the phenyl molecules, such as Pho, TsOH, and BOA molecules, tend to aggregate in the interfacial regions. Quantitatively, the mass density profiles along *z* axis with DESs at different concentrations were displayed in Figure 7 and Figure S3. For the density profiles of different moieties of DESs, the distinct difference is that the phenyl molecules present an obvious peak in the interfacial regions, and the intensity of the peak becomes much larger with the increased DES concentrations. Conversely, ChCl molecules show a uniform distribution in the H₂SO₄ phase along *z* axis. One can conclude that the phenyl molecules play the essentially important role in the tunability of acid/hydrocarbons interface. In addition, there is a larger peak intensity of TsOH molecules in the interfacial regions compared to Pho and BOA molecules at the same concentrations, suggesting the stronger aggregation of TsOH molecules at the interface. Moreover, the TsOH molecules stay closer to the H₂SO₄ phase than Pho and BOA molecules, probably due to the strong interaction between SO₃H groups and H₂SO₄.

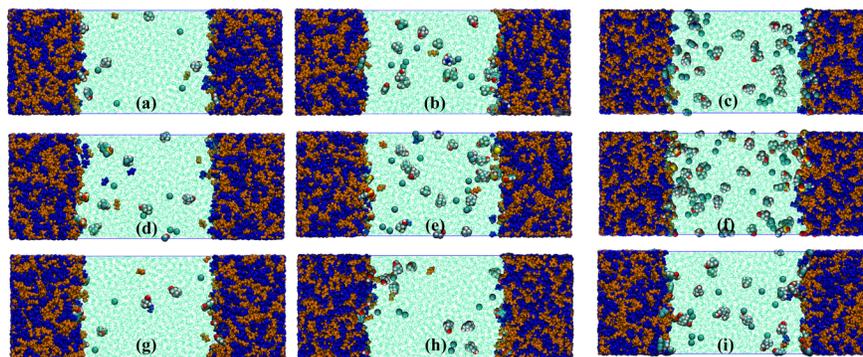


Figure 6. Equilibrated snapshots of DESs distributions with different concentrations at acid/hydrocarbons interface. (a), (b), and (c) ChCl-Pho (1:2) at 1.0 wt%, 3.0 wt%, and 5.0 wt%, respectively. (d), (e), and (f) ChCl-TsOH (1:1) at 1.0 wt%, 3.0 wt%, and 5.0 wt%, respectively. (g), (h), and (i) ChCl-BOA (1:2) at 1.0 wt%, 3.0 wt%, and 5.0 wt%, respectively.

Green color represents the H₂SO₄ molecules in line style. Blue color represents isobutane molecules in VDW style. Brown color means 2-butene molecules in VDW style.

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Figure 7. Mass density profiles along z axis of the simulated box with different DESs at different concentrations. (a), (b), and (c) ChCl-Pho (1:2) at 1.0 wt%, 3.0 wt%, and 5.0 wt%, respectively. (d), (e), and (f) ChCl-TsOH (1:1) at 1.0 wt%, 3.0 wt%, and 5.0 wt%, respectively.

3.6 Interfacial thickness

The capillary-wave theory can well describe the density of component A and B in the interfacial system⁴³,

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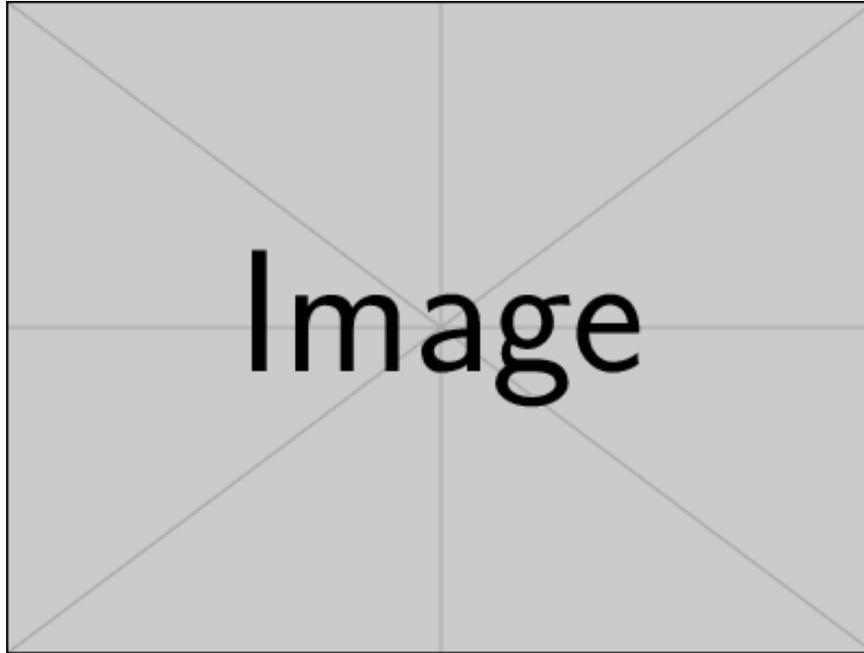
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and mean the position of the Gibbs dividing surface of component A and B , respectively, and represent component A and B bulk density, respectively.

is the contribution of thermal fluctuations to interfacial thickness. Using equation (1) and (2), the parameters, and can be calculated. Thus, the interfacial intrinsic thickness (δ) is obtained,

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(3)

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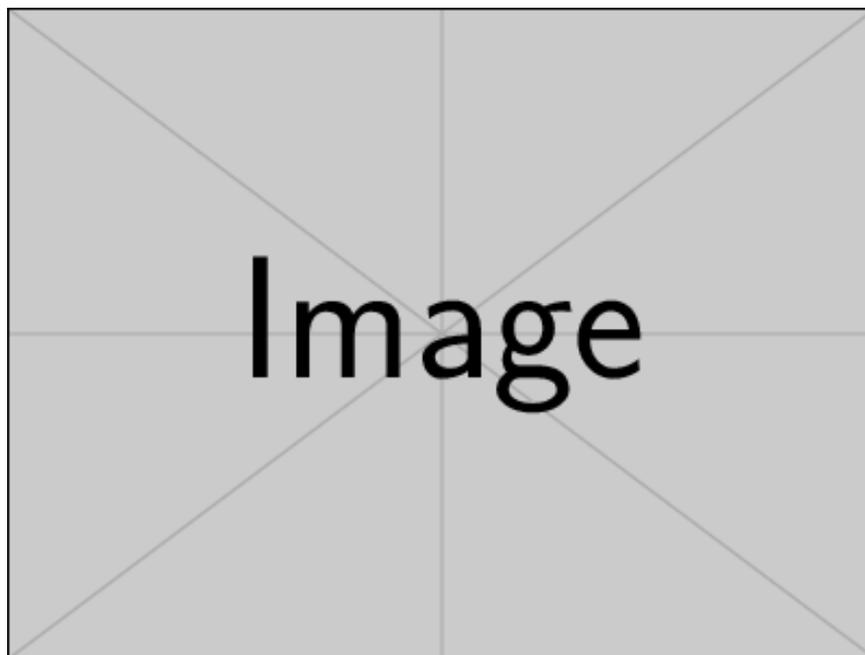
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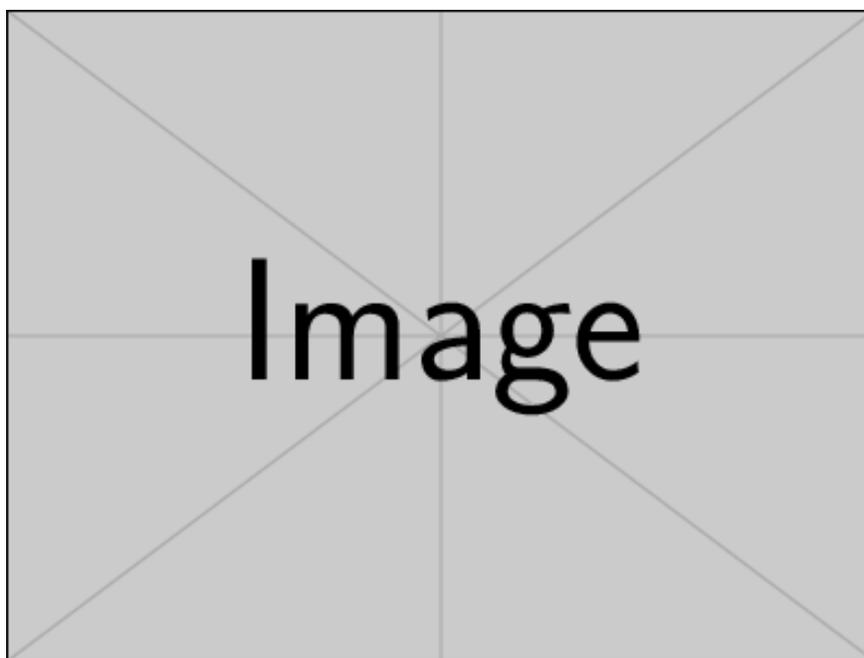
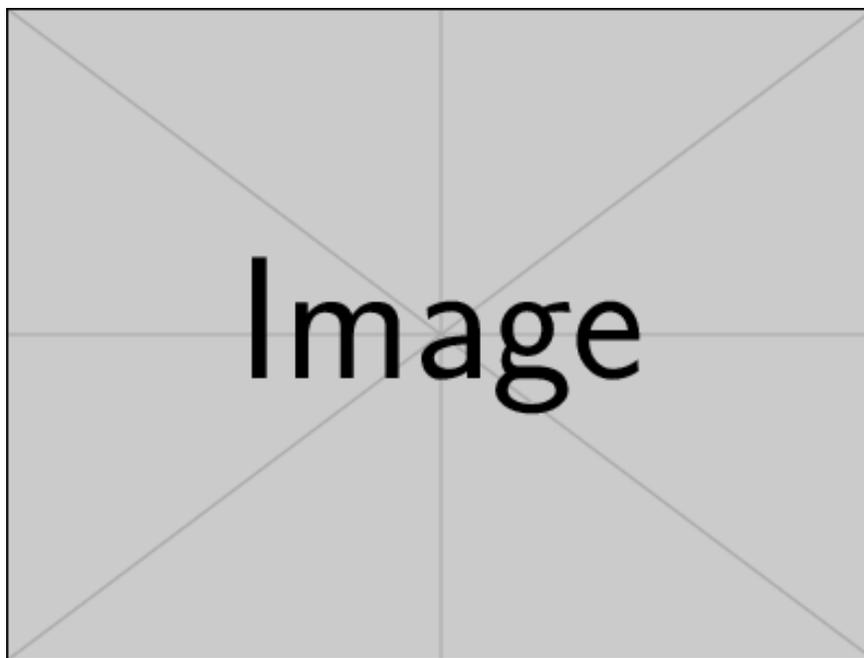
The total interfacial thickness (δ) consists of the intrinsic width and thermal fluctuations using equation (4),

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(4)





For the DESs-aiding systems, the density profiles of H_2SO_4 and MixC4 (isobutane + butene) are shown in Figure 8 and Figure S4, respectively. It is clearly seen that there is a good fitting for all the systems. The obtained

for different DESs as a function of concentrations as shown in Figure 8d. The of pure H_2SO_4 system is taken from our recent work as a benchmark¹⁵. The results indicate that the addition of DESs can significantly increase

in comparison to the pure H_2SO_4 systems. Furthermore, the interfacial thickness rises along with the concentration of DESs. From experimental point of view, the enlargement of the interfacial thickness provides the larger interfacial reaction zones, which is better for higher-quality alkylate. At the same conditions, the ChCl-TsOH (1:1) additive can contribute more to the interfacial thickness compared to ChCl-Pho (1:2) and ChCl-BOA (1:2) additives.

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Figure 8. The fitting results of H_2SO_4 and MixC4 mass density for the calculation of interfacial thickness in the DES-aiding systems with different concentrations. (a), (b), and (c) ChCl-Pho (1:2) at 1.0 wt%, 3.0 wt%, and 5.0 wt%, respectively. The obtained interfacial thickness for different DESs as a function of concentrations (d).

3.7 Interfacial compositions and diffusion

To further study the effect of DESs on the interfacial behaviors of the MixC4 reactants, the interfacial compositions and diffusion coefficients of MixC4 reactants for different DES systems at different concentrations were calculated, as listed in Table 2. In the interfacial regions, there are almost no ChCl molecules, while the ratio of phenyl molecules increases as the concentrations of DESs. This observation is in good agreement with the finding from density profiles. Due to the higher ratio of phenyl molecules at higher concentration of DESs, the ratio of both isobutane and butene gradually declines as a function of concentration. However, the key point factor for alkylation is the ratio of isobutane to butene (I/O ratio) in the interfacial reaction zone. Meaningfully, the I/O ratio of all the systems with DESs additives are quite higher than that of pure H_2SO_4 system (0.850)¹⁵. This strongly indicates that the DESs additives can significantly improve the I/O ratio, which can restrain the oligomerization of butene, promote the hydride transfer, and thus lead to higher-quality of alkylate. For ChCl-Pho (1:2)-containing systems, the I/O ratio rises with the concentrations, while the opposite trend is found for ChCl-TsOH (1:1)- and ChCl-BOA (1:2)-containing systems. For the dynamics, the diffusion coefficients ratio of isobutane to butene is also generally larger than that in pure H_2SO_4 system (0.858)¹⁵. Thus, the introduction of DESs can promote the diffusion of isobutane with respect to butene, which is also helpful to restrain the oligomerization of butene, and promote the hydride transfer, resulting in higher-quality of alkylate. For different DESs, the diffusion coefficient ratio of isobutane to butene follows similar trend as the I/O ratio as a function of concentrations. To sum up, one can safely say that the DES additives can efficiently promote the solubility and diffusion of isobutane with respect to butene, and thus make positively contributions to the quality of alkylate.

Table 2. The interfacial compositions and interfacial diffusion coefficients of isobutane and butene, and the ratio of isobutane to butene for different DES systems at different concentrations.

Systems	Mass fraction (wt%)	Interfacial compositions	Interfacial compositions	Interfacial compositions	Interfacial compositions	Diffusion coefficients	Diffusion coefficients	Diffusion coefficients
		Phenyl molecules	Butene	Isobutane	Isobutane /butene	Butene	Isobutane	Isobutane /butene
ChCl-Pho (1:2)	1.0	0.0179	0.2452	0.2451	0.9999	0.2505	0.2150	0.8583
	3.0	0.0380	0.2313	0.2412	1.0426	0.2490	0.2156	0.8657
	5.0	0.0640	0.2149	0.2328	1.0833	0.2423	0.2137	0.8818
ChCl-TsOH (1:1)	1.0	0.0166	0.2400	0.2563	1.0679	0.2552	0.2295	0.8991

ChCl- BOA (1:2)	3.0	0.0490	0.2305	0.2460	1.0674	0.2447	0.2102	0.8590
	5.0	0.0808	0.2098	0.2238	1.0670	0.2418	0.2041	0.8441
	1.0	0.0230	0.2259	0.2601	1.1514	0.2520	0.2183	0.8663
	3.0	0.0428	0.2215	0.2428	1.0961	0.2436	0.2080	0.8538
	5.0	0.0707	0.2178	0.2289	1.0507	0.2422	0.2066	0.8530

4. Conclusions

The effect of several DESs on the quality of alkylate and the acid/hydrocarbons interfacial properties were investigated via experiments and MD simulations. It is found that the introduction of DESs almost has no impact on the reaction time. ChCl-Pho (1:2) displays the most outstanding catalytic performance with RON up to 97.37 and the C₈ selectivity up to 83.64%. The most suitable addition ratio for ChCl-Pho (1:2) and ChCl-TsOH (1:1) to H₂SO₄ is about 1.0 wt% with the improvement of C₈ contents from 74.50 wt% in pure H₂SO₄ system at 281.2 K to 83.64 wt% and 80.71 wt% as well as the increase in RON from 95.80 to 97.37 and 96.93, respectively. However, the excessive addition of DESs leads to the decrease in reaction enhancement, which is attributed to reduction of the H₂SO₄ acidity. ChCl-Pho (1:2) and ChCl-TsOH (1:1) have a little influence on 2,3,4-TMPs and DMHs, including 2,5-DMH, 2,4-DMH, and 2,3-DMH with lower RON. However, both of them have a great effect on the conversion of LEs and HEs to TMPs. With the addition of ChCl-Pho (1:2), the targeted C₈ components and the RON increase obviously from 83.77% at 281.2 K to 86.07% at 274.2 K, 97.39 at 281.2 K to 98.27 at 274.2 K, respectively, which is mainly contributed to low reaction temperature. The addition of ChCl-Pho (1:2) and ChCl-TsOH (1:1) show the effective catalytic performance, but both of them can not improve the catalytic lifetime of H₂SO₄ catalyst.

From MD simulations, the phenyl molecules, such as Pho, TsOH, and BOA molecules, is found to aggregate close to the interface with a higher density peak in the interfacial regions, which plays the essentially important role in the tunability of acid/hydrocarbons interface. The addition of DESs can significantly increase the interfacial thickness, promote the solubility and diffusion of isobutane with respect to butene in comparison to the pure H₂SO₄ system, thus making positively contributions to the quality of alkylate.

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Conflict of interest

The authors declare no competing interests.

References

1. Velazquez HD, Likhanova N, Aljammal N, Verpoort F, Martinez-Palou R. New Insights into the Progress on the Isobutane/Butene Alkylation Reaction and Related Processes for High-Quality Fuel Production. A Critical Review. *Energ. Fuel.* Dec 2020;34(12):15525-15556.
2. Kore R, Scurto AM, Shiflett MB. Review of Isobutane Alkylation Technology Using Ionic Liquid-Based Catalysts-Where Do We Stand? *Ind. Eng. Chem. Res.* Sep 2020;59(36):15811-15838.
3. Wang H, Meng XZ, Zhao GY, Zhang SJ. Isobutane/butene alkylation catalyzed by ionic liquids: a more sustainable process for clean oil production. *Green Chem.* Mar 2017;19(6):1462-1489.
4. Gan PX, Tang SW. Research progress in ionic liquids catalyzed isobutane/butene alkylation. *Chin. J. Chem. Eng.* Nov 2016;24(11):1497-1504.

5. Minnick DL, Kore RR, Lyon CJ, Subramaniam B, Shiflett MB, Scurto AM. Understanding Sulfur Content in Alkylate from Sulfuric Acid-Catalyzed C3/C4 Alkylations. *Energ. Fuel.* Apr 2019;33(5):4659-4670.
6. Sun WZ, Zheng WZ, Cao P, Zhao L. Probing interfacial behaviors of Bronsted acidic ionic liquids improved isobutane alkylation with C4 olefin catalyzed by sulfuric acid. *Chem. Eng. J.* Dec 2019;377:119744.
7. Zheng WZ, Cao P, Yuan Y, et al. Experimental and modeling study of isobutane alkylation with C4 olefin catalyzed by Bronsted acidic ionic liquid/sulfuric acid. *Chem. Eng. J.* Dec 2019;377:119578.
8. Costa BOD, Querini CA. Isobutane alkylation with butenes in gas phase. *Chem. Eng. J.* Aug 2010;162(2):829-835.
9. Dalla Costa BO, Querini CA. Isobutane alkylation with solid catalysts based on beta zeolite. *Appl. Catal. A-Gen.* Sep 2010;385(1-2):144-152.
10. Sievers C, Liebert JS, Stratmann MA, Olindo R, Lercher JA. Comparison of zeolites LaX and LaY as catalysts for isobutane/2-butene alkylation. *Appl. Catal. A-Gen.* Mar 2008;336(1-2):89-100.
11. Guzman A, Zuazo I, Feller A, Olindo R, Sievers C, Lercher JA. Influence of the activation temperature on the physicochemical properties and catalytic activity of La-X zeolites for isobutane/cis-2-butene alkylation. *Microporous Mesoporous Mat.* Dec 2006;97(1-3):49-57.
12. Sheng XL, Wang BB, Mao CF, Sha X, Zhou YM. Influence of FeCl₃-modified chloroaluminate ionic liquids on long-chain alkenes alkylation. *Appl. Organomet. Chem.* Jan 2021;35(1):11.
13. Li LT, Zhang JS, Wang K, Luo GS. Caprolactam as a New Additive To Enhance Alkylation of Isobutane and Butene in H₂SO₄. *Ind. Eng. Chem. Res.* Dec 2016;55(50):12818-12824.
14. Ren H, Zhao G, Zhang S, Cui P, Huang J. Triflic acid catalyzed isobutane alkylation with trifluoroethanol as a promoter. *Catal Commun.* Feb 10 2012;18:85-88.
15. Zheng WZ, Wang Z, Sun WZ, Zhao L, Qian F. H₂SO₄-catalyzed isobutane alkylation under low temperatures promoted by long-alkyl-chain surfactant additives. *AIChE J* . DOI:10.1002/aic.17349.
16. Li XF, Kunieda H. Catanionic surfactants: microemulsion formation and solubilization. *Curr. Opin. Colloid Interface Sci.* Nov 2003;8(4-5):327-336.
17. Chen WS. Solubility measurements of isobutane/alkenes in sulfuric acid: applications to alkylation. *Appl. Catal. A-Gen.* Dec 2003;255(2):231-237.
18. Zheng WZ, Li D, Sun WZ, Zhao L. Multi-scale modeling of isobutane alkylation with 2-butene using composite ionic liquids as catalyst. *Chem. Eng. Sci.* Aug 2018;186:209-218.
19. Liu RX, Zhang P, Zhang SJ, Yan T, Xin JY, Zhang XP. Ionic liquids and supercritical carbon dioxide: green and alternative reaction media for chemical processes. *Rev. Chem. Eng.* Dec 2016;32(6):587-609.
20. Kumar P, Vermeiren W, Dath JP, Hoelderich WF. Production of alkylated gasoline using ionic liquids and immobilized ionic liquids. *Appl. Catal. A-Gen.* May 2006;304(1):131-141.
21. Wang AY, Zhao GY, Liu FF, Ullah L, Zhang SJ, Zheng AM. Anionic clusters enhanced catalytic performance of protic acid ionic liquids for isobutane alkylation. *Ind. Eng. Chem. Res.* Aug 2016;55(30):8271-8280.
22. Liu Y, Li R, Sun HJ, Hu RS. Effects of catalyst composition on the ionic liquid catalyzed isobutane/2-butene alkylation. *J. Mol. Catal. A-Chem.* Mar 2015;398:133-139.
23. Tang SW, Scurto AM, Subramaniam B. Improved 1-butene/isobutane alkylation with acidic ionic liquids and tunable acid/ionic liquid mixtures. *J. Catal.* Dec 2009;268(2):243-250.
24. Zhang QH, Vigier KD, Royer S, Jerome F. Deep eutectic solvents: syntheses, properties and applications. *Chem. Soc. Rev.* 2012;41(21):7108-7146.

25. Abbott AP, Boothby D, Capper G, Davies DL, Rasheed RK. Deep eutectic solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids. *J. Am. Chem. Soc.* Jul 2004;126(29):9142-9147.
26. Smith EL, Abbott AP, Ryder KS. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* Nov 2014;114(21):11060-11082.
27. Yu F-L, Gu Y-L, Gao X, Liu Q-C, Xie C-X, Yu S-T. Alkylation of isobutane and isobutene catalyzed by trifluoromethanesulfonic acid-taurine deep eutectic solvents in polyethylene glycol. *Chem. Comm.* Apr 2019;55(33):4833-4836.
28. Zheng WZ, Wang HY, Xie WX, Zhao L, Sun WZ. Understanding interfacial behaviors of isobutane alkylation with C4 olefin catalyzed by Sulfuric Acid or Ionic Liquids. *AIChE J.* Mar 2018;64(3):950-960.
29. Zheng WZ, Huang CZ, Sun WZ, Zhao L. Microstructures of the Sulfonic Acid-Functionalized Ionic Liquid/Sulfuric Acid and Their Interactions: A Perspective from the Isobutane Alkylation. *J. Phys. Chem. B.* Feb 2018;122(4):1460-1470.
30. Zheng WZ, Cao P, Sun WZ, Zhao L. Towards an understanding of the microstructure and interfacial properties of the ionic liquid/sulfuric acid catalyst in liquid-liquid reactions. *Chem. Eng. Sci.* Sep 2019;205:287-298.
31. Zheng WZ, Xie WX, Sun WZ, Zhao L. Modeling of the interfacial behaviors for the isobutane alkylation with C4 olefin using ionic liquid as catalyst. *Chem. Eng. Sci.* Jul 2017;166:42-52.
32. Sun WZ, Zheng WZ, Xie WX, Zhao L. Understanding Structure-Property Relationship of SO₃H-Functionalized Ionic Liquids together with Sulfuric Acid in Catalyzing Isobutane Alkylation with C4 Olefin. *Ind. Eng. Chem. Res.* Nov 2018;57(45):15310-15318.
33. Zhou XL, Huang TJ, Liu J, et al. Recyclable deep eutectic solvent coupling sodium hydroxide post-treatment for boosting woody/herbaceous biomass conversion at mild condition. *Bioresour. Technol.* Jan 2021;320:12437.
34. Khezeli T, Daneshfar A. Synthesis and application of magnetic deep eutectic solvents: Novel solvents for ultrasound assisted liquid-liquid microextraction of thiophene. *Ultrason. Sonochem.* Sep 2017;38:590-597.
35. Aroso IM, Silva JC, Mano F, et al. Dissolution enhancement of active pharmaceutical ingredients by therapeutic deep eutectic systems. *Eur. J. Pharm. Biopharm.* Jan 2016;98:57-66.
36. Van der Spoel D, Lindahl E, Hess B, Groenhof G, Mark AE, Berendsen HJC. GROMACS: Fast, flexible, and free. *J. Comput. Chem.* Dec 2005;26(16):1701-1718.
37. Frisch M, Trucks G, Schlegel HB, et al. gaussian 09, Revision d. 01, Gaussian. *Inc., Wallingford CT.* 2009;201.
38. Huang Q, Zhao G, Zhang S, Yang F. Improved Catalytic Lifetime of H₂SO₄ for Isobutane Alkylation with Trace Amount of Ionic Liquids Buffer. *Ind. Eng. Chem. Res.* 2015;54(5):1464-1469.
39. Liu Y, Wu GQ, Hu RS, Gao GJ. Effects of aromatics on ionic liquids for C-4 alkylation reaction: Insights from scale-up experiment and molecular dynamics simulation. *Chem. Eng. J.* Dec 2020;402:126252.
40. Wang HY, Ma S, Zhou ZM, Li MJ, Wang H. Alkylation of isobutane with butene catalyzed by deep eutectic ionic liquids. *Fuel.* Jun 2020;269:117419.
41. Liu ZC, Meng XH, Zhang R, Xu CM, Dong H, Hu YF. Reaction performance of isobutane alkylation catalyzed by a composite ionic liquid at a short contact time. *AIChE J.* Jun 2014;60(6):2244-2253.
42. Xin Y, Hu Y, Li M, et al. Isobutane Alkylation Catalyzed by H₂SO₄: Effect of H₂SO₄ Acid Impurities on Alkylate Distribution. *Energy & Fuels.* Dec 2021;35(2):1664-1676.

43. Riedleder AJ, Kentish SE, Perera JM, Stevens GW. Structural investigation of a water/n-heptane interface: A molecular dynamics study. *Solvent Extr. Ion Exch.* Feb 2007;25(1):41-52.