

# Screening of Double Solvents Based on Multi-Index Evaluation Method for the Selective Separation *m*-Cresol from Model Oil

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Cite This: *ACS Omega* 2022, 7, 25798–25810

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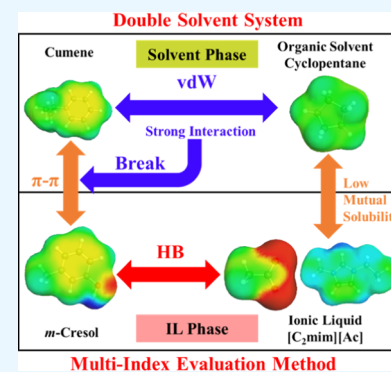
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**ABSTRACT:** Ionic liquid (IL) as an extractant is an effective method for separating oil–phenol mixtures. However, relatively high neutral oil entrainment can lead to oil loss and a remarkable reduction in phenol purity. To reduce the entrainment of neutral oil in the extraction process, a double-solvent extraction system composed of IL 1-ethyl-3-methyl imidazolium acetate ( $[\text{C}_2\text{mim}][\text{Ac}]$ ) and an organic solvent was investigated. The multi-index evaluation method was used to screen the conventional organic solvent. The double-solvent extraction experiments were employed to verify the accuracy of the COSMO-RS prediction. Eighteen organic solvents, the interaction energy with *m*-cresol and cumene (neutral oil), their extraction ability, and mutual solubility with  $[\text{C}_2\text{mim}][\text{Ac}]$ , were calculated by COSMO-RS. Alkane and cycloalkane were screened due to their strong interaction and low distribution coefficient with cumene, as well as the low mutual solubility with  $[\text{C}_2\text{mim}][\text{Ac}]$ . The experimental results were in good agreement with the COSMO-RS prediction, and cyclopentane as an organic solvent had the lowest distribution coefficient

and entrainment of cumene because of its strong nonpolarity and hydrogen-bond repulsive interaction, which was explained by the  $\sigma$ -profile and  $\sigma$ -potential analysis. When the cyclopentane-to- $[\text{C}_2\text{mim}][\text{Ac}]$  mass ratio increased from 0.0 to 3.0, the entrainment of cumene was evidently declined from 39.5 to 5.8% and the selectivity to *m*-cresol was improved from 378.0 to 1058.5.



## 1. INTRODUCTION

Low-temperature coal tar (LTCT) contains a large number of phenolic compounds and aromatic hydrocarbons.<sup>1–3</sup> Phenolic compounds are important chemical raw materials and the separation of phenolic compounds in LTCT has a beneficial effect on subsequent oil processing.<sup>4–6</sup> In recent years, ionic liquids (ILs) are widely reported to use phenol separation from LTCT and model oil mixtures.<sup>7,8</sup> For example, Hou et al. used 1-butyl-3-methyl imidazolium chloride ( $[\text{C}_4\text{mim}][\text{Cl}]$ ) to extract phenol from hexane and the extraction efficiency was up to 99.1%.<sup>9</sup> Then, some ILs with low viscosity and without corrosive halogen ions were designed to separate phenolic compounds, such as 1-ethyl-3-methyl imidazolium thiocyanate ( $[\text{C}_2\text{mim}][\text{SCN}]$ ),<sup>10</sup> 1-ethyl-3-methyl imidazolium lactate ( $[\text{C}_2\text{mim}][\text{LAC}]$ ),<sup>11</sup> and tetraethylammonium amino acid (TAA) ILs.<sup>12</sup>

Although the above-mentioned ILs have high separation efficiencies of phenolic compounds, there is a large amount of neutral oil entrainment (30%) along with the extraction process and it reduces the purity and selectivity of phenols.<sup>13</sup> To solve this problem, Ji et al. used *n*-hexane as an anti-extractant for the removal of neutral oil in the deep eutectic solvent (DES) formed by  $\text{ChCl}$  and phenol.<sup>14</sup> Yi et al. proposed to use the ready DES composed of  $\text{ChCl}$  and glycerol as an extractant to separate *m*-cresol from model oil.<sup>15</sup> The  $\text{ChCl}$ –glycerol (mole ratio 1:1) DES had equally high phenol extraction efficiency and much lower neutral oil entrainment than  $\text{ChCl}$ . However, these methods of screening

extractants mainly depend on the experiments, which are time-consuming and expensive.

Conductor-like screening model for real solvents (COSMO-RS) is a very useful method to screen extractants for mixture separation.<sup>16,17</sup> For IL screening, Lyu et al. investigated the extraction capacity and separation selectivity at infinite dilution of 264 ILs to separate benzene and cyclohexane.<sup>18</sup> Gao et al. studied the capacity of 1860 ILs for thiophene (TS) and dibenzothiophene (DBT).<sup>19</sup> Song et al. predicted the solubilities of 220 ILs in different fuel oils.<sup>20</sup> In the separation of oil–phenol mixtures, Liu et al. calculated the infinite-dilution activity coefficients of *m*-cresol, cumene, and *n*-heptane in 200 ILs by the COSMO-RS model, and 1-ethyl-3-methyl imidazolium acetate ( $[\text{C}_2\text{mim}][\text{Ac}]$ ) was screened as the best extractant to extract *m*-cresol from the mixture of cumene and *n*-heptane.<sup>21</sup> For DES screening, Salleh et al. screened 40 DESs by selectivity and capacity for the separation of cyclohexane–benzene mixtures.<sup>22</sup> Cheng et al. screened 49 DESs for the extractive desulfurization of fuel.<sup>23</sup>

Received: May 18, 2022

Accepted: June 27, 2022

Published: July 11, 2022



For the COSMO-RS model, the reliability of the screening results is closely related to the selected screening indicators. For instance, Liu et al. only used the distribution coefficient and selectivity of *m*-cresol at infinite dilution as the screening index. The screened  $[C_2mim][Ac]$  had high extraction efficiency of *m*-cresol, but the entrainment of cumene was also high.<sup>21</sup> Gao et al. investigated the mutual solubility between 1830 ILs with fuel oil and 1-methyl-2-pyrrolidone phosphate ( $[C_1pyr][H_2PO_4]$ ) was screened out for desulfurization, which reduced the fuel oil loss in the desulfurization process.<sup>24</sup> The sulfur content in fuel oil could be reduced to 9.79 ppm after six stages of extractive desulfurization. Cheng et al. designed a biphasic extraction system composed of organic salt and organic solvent to reduce the entrainment of oil for the separation of vitamin E from methyl linoleate.<sup>25</sup> The interactions between the organic solvent and methyl linoleate were calculated by COSMO-RS, which further screened the preferable organic solvent. This method solves the problem of neutral oil entrainment in the efficient screening of extractants by the COSMO-RS model. The selection of these screening methods and indexes in the COSMO-RS model provides good guidance for the separation of oil–phenol mixtures.

The formation of hydrogen-bond interaction between the anion of  $[C_2mim][Ac]$  and the phenolic hydroxyl group of *m*-cresol was reported in our previous research, which showed high extraction efficiency for *m*-cresol separation.<sup>21</sup> On the other hand, the relatively strong  $\pi$ – $\pi$  interaction between aromatic hydrocarbons and phenolic compounds could cause the entrainment of neutral oil.<sup>13</sup> To reduce neutral oil entrainment, a double-solvent extraction system containing IL and an organic solvent was studied in this work. IL was used to extract a phenolic compound via the hydrogen-bond interaction, while the organic solvent was designed to remove neutral oil by van der Waals interaction.  $[C_2mim][Ac]$  was selected as the suitable IL by the COSMO-RS model in our previous work,<sup>21</sup> and a suitable organic solvent was screened by multi-index evaluation method from the COSMO-RS calculation.

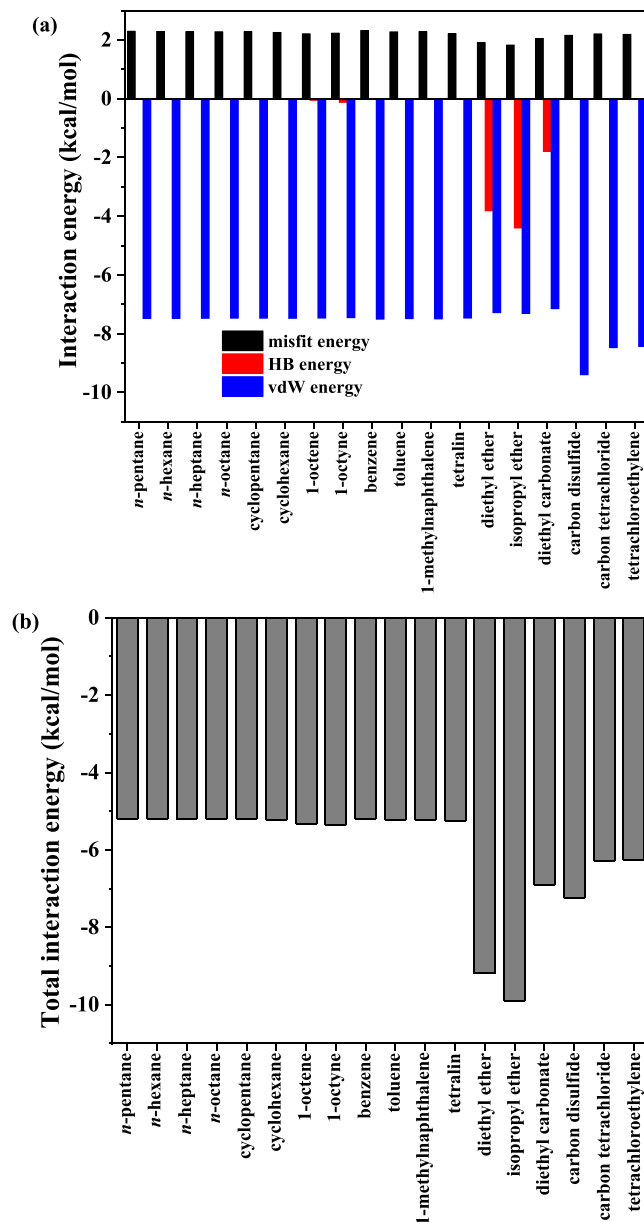
In this work, the screening indexes and principles of organic solvents by the COSMO-RS model were determined according to the characteristics of the oil–phenol mixture system. First, the interaction energies between organic solvents with *m*-cresol and cumene were calculated. Also, the mutual solubility of  $[C_2mim][Ac]$  and organic solvents was also considered. Then, the distribution coefficient for *m*-cresol and cumene, as well as selectivity to *m*-cresol were predicted. The double-solvent extraction experiment was adopted to prove COSMO-RS calculations. Finally, the influences of mass ratio of organic solvent to  $[C_2mim][Ac]$ , temperature, and the initial phenol content in model oil on the separation of *m*-cresol were investigated.

## 2. RESULTS AND DISCUSSION

**2.1. Screening of Organic Solvent for a Double-Solvent Extraction System.** To improve the purity and selectivity of phenolic compounds in the separation process, the suitable organic solvent for the double-solvent extraction system should have strong interaction with cumene and weak interaction with *m*-cresol meanwhile have low mutual solubility with  $[C_2mim][Ac]$ . To this end, 18 organic solvents were investigated. The distribution coefficient for *m*-cresol and cumene, as well as the selectivity to *m*-cresol, were also calculated. Then, the double-solvent extraction experiments

were studied to verify the prediction results of the COSMO-RS model.

**2.1.1. Interaction of Organic Solvent with *m*-Cresol and Cumene.** The interaction of organic solvent with *m*-cresol and cumene can affect the distribution of *m*-cresol and cumene in the double-solvent extraction system. As shown in Figure 1a,



**Figure 1.** COSMO-RS calculation of interaction energies between organic solvent and *m*-cresol. (a) Misfit, HB, and vdW interaction energies. (b) Total interaction energy.

the interaction energies between *m*-cresol and different organic solvents are calculated by the COSMO-RS model, including misfit interaction energy, HB interaction energy, and vdW interaction energy. Diethyl ether, isopropyl ether, and diethyl carbonate have strong HB interaction with *m*-cresol. For 1-octene and 1-octyne, their HB interaction with *m*-cresol is weak but still stronger than other organic solvents. For the remaining thirteen organic solvents, the vdW interaction between *m*-cresol and organic solvent plays a leading role, where carbon disulfide, carbon tetrachloride, and tetrachloro-

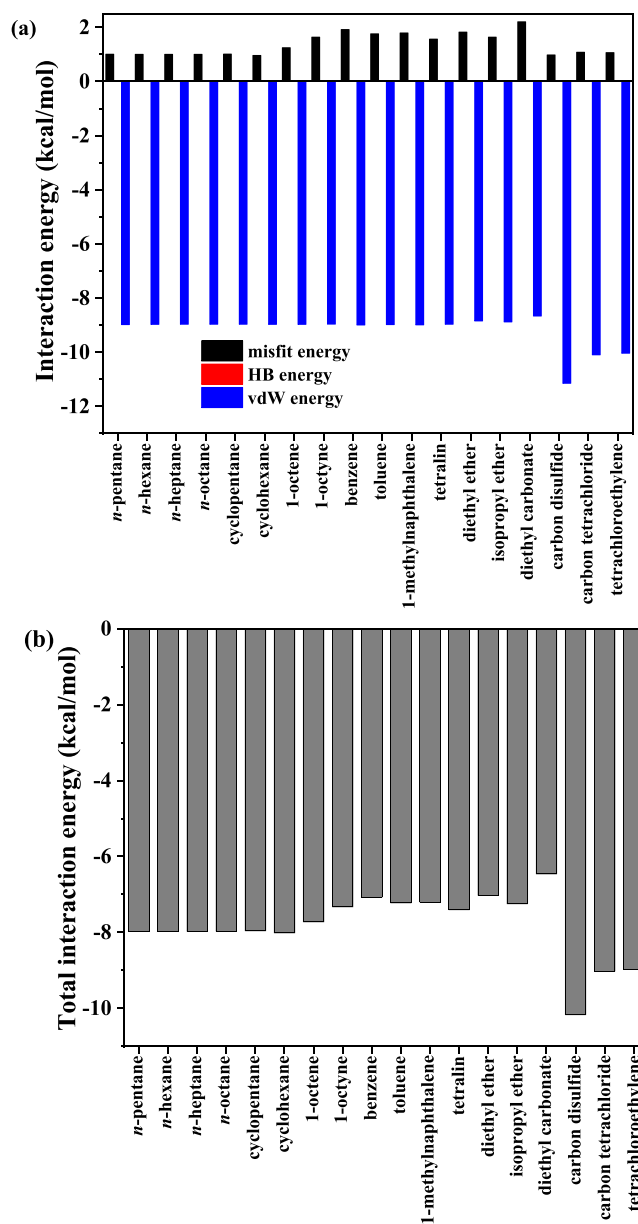
ethylene demonstrate slightly stronger vdW interaction than alkane (*n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane), cycloalkane (cyclopentane and cyclohexane), and arene (benzene, toluene, 1-methylnaphthalene, and tetralin). In addition, thirteen organic solvents have similar misfit interaction with *m*-cresol.

Among the three interaction energies, the misfit energy is positive energy, which represents a repulsive interaction. HB energy and vdW energy are negative energies, both of which suggest attractive interactions. Also, HB energy plays a more important role among the three interaction energies.<sup>21,25</sup> Thus, these five organic solvents (diethyl ether, isopropyl ether, diethyl carbonate, 1-octene, and 1-octyne) can convert *m*-cresol from the IL phase into an organic solvent phase, which is not conducive to the separation of *m*-cresol.

The sum of the three interaction energies is shown in Figure 1b. The weak interaction between organic solvent and *m*-cresol can ensure the existence of *m*-cresol in the IL phase, which could maintain a high extraction rate of *m*-cresol. Consequently, the weaker total interaction energy between organic solvent (such as alkane, cycloalkane, and arene) and *m*-cresol indicates that *m*-cresol is more easily distributed in the IL phase.

The three interaction energies between organic solvent and cumene are shown in Figure 2a. For all of the involved organic solvents, the HB interaction with cumene is negligible, and the misfit interaction with cumene suggests a repulsive electrostatic interaction. The strong misfit interaction energy indicates that there is a strong repulsion between cumene and organic solvents, such as 1-octene, 1-octyne, diethyl ether, isopropyl ether, diethyl carbonate, and arene. The carbon disulfide, carbon tetrachloride, and tetrachloroethylene with cumene have stronger vdW interaction energy than alkane and cycloalkane. The strong vdW interaction energy between organic solvent and cumene is beneficial for extracting cumene from the IL phase to the organic solvent phase and further improving the purity of *m*-cresol. However, the vdW interaction energy between carbon disulfide, carbon tetrachloride, and tetrachloroethylene with *m*-cresol is also strong, which could reduce the separation efficiency of *m*-cresol. Together with the total interaction energy between organic solvent and cumene in Figure 2b, alkane and cycloalkane are more suitable as an organic solvent phase in the double-solvent extraction.

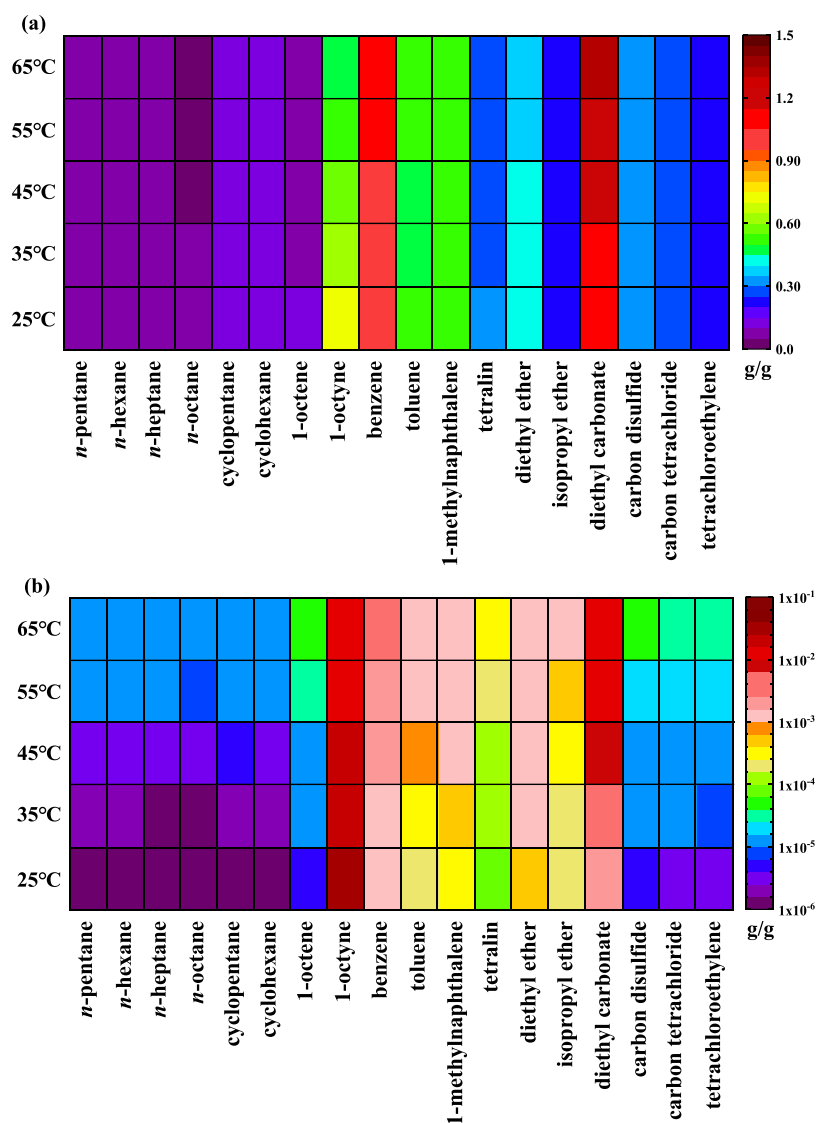
**2.1.2. Mutual Solubility of [C<sub>2</sub>mim][Ac] and Organic Solvent.** The mutual solubility of [C<sub>2</sub>mim][Ac] and organic solvent can cause the wastage of [C<sub>2</sub>mim][Ac] in the solvent phase and organic solvent in the IL phase, respectively. The lower mutual solubility implies less wastage of [C<sub>2</sub>mim][Ac] and organic solvent. Consequently, both the organic solvent in [C<sub>2</sub>mim][Ac] solubility and [C<sub>2</sub>mim][Ac] in organic solvent solubility are obtained through the COSMO-RS model. As demonstrated in Figure 3a, a lower value represents a smaller solubility of organic solvent in [C<sub>2</sub>mim][Ac]. The solubility of alkane and cycloalkane in [C<sub>2</sub>mim][Ac] is significantly lower than those of other organic solvents. All organic solvents in [C<sub>2</sub>mim][Ac] solubility have no obvious change with different temperatures. As shown in Figure 3b, the solubilities of [C<sub>2</sub>mim][Ac] in *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, and cyclohexane at 25 °C are  $1.670 \times 10^{-6}$ ,  $1.476 \times 10^{-6}$ ,  $1.331 \times 10^{-6}$ ,  $1.230 \times 10^{-6}$ ,  $2.063 \times 10^{-6}$ , and  $1.514 \times 10^{-6}$  g/g, respectively, much lower than that in 1-octyne (0.0599 g/g) and diethyl carbonate (0.0047 g/g).



**Figure 2.** COSMO-RS calculation of interaction energies between organic solvent and cumene. (a) Misfit, HB, and vdW interaction energies. (b) Total interaction energy.

Overall, the variation of [C<sub>2</sub>mim][Ac] in different organic solvents solubility is similar to that of organic solvents in [C<sub>2</sub>mim][Ac] solubility. Moreover, it is noted that [C<sub>2</sub>mim][Ac] in organic solvent solubility increases along with the increasing temperature. Therefore, alkane and cycloalkane can be selected as organic solvents in the double-solvent system from mutual solubility with [C<sub>2</sub>mim][Ac].

**2.1.3. Experimental Verification of Mutual Solubility.** The mutual solubilities of six organic solvents and the IL [C<sub>2</sub>mim][Ac] were measured and verified by experiments. The COSMO-RS prediction and experimental results are shown in Table 1. Both the experimental and COSMO-RS predicted organic solvent in [C<sub>2</sub>mim][Ac] solubility follow the order of *n*-heptane < *n*-hexane < cyclohexane < cyclopentane < isopropyl ether < tetralin, while [C<sub>2</sub>mim][Ac] in organic solvent solubility follow the order of *n*-heptane < *n*-hexane < cyclohexane < cyclopentane < tetralin < isopropyl ether.



**Figure 3.** COSMO-RS predicted the mutual solubility of  $[\text{C}_2\text{mim}][\text{Ac}]$  and organic solvents at different temperatures. (a) Organic solvent in  $[\text{C}_2\text{mim}][\text{Ac}]$  solubility. (b)  $[\text{C}_2\text{mim}][\text{Ac}]$  in organic solvent solubility.

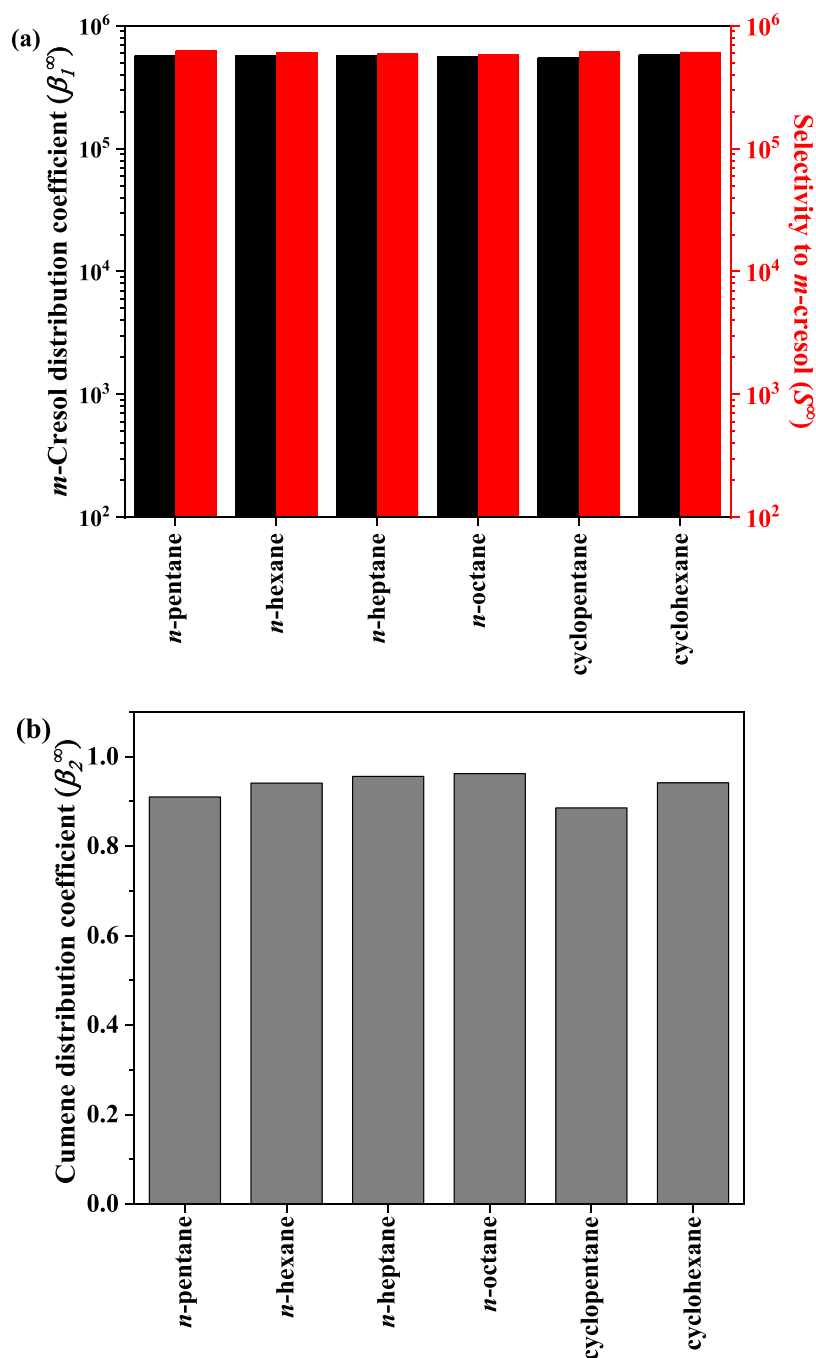
**Table 1. Mutual Solubilities of Organic Solvents with  $[\text{C}_2\text{mim}][\text{Ac}]$  at 25 °C from COSMO-RS Predicted and Experimental Results**

organic solvents	organic solvent in $[\text{C}_2\text{mim}][\text{Ac}]$ solubility (g/g)		$[\text{C}_2\text{mim}][\text{Ac}]$ in organic solvent solubility (g/g)	
	COSMO-RS	experiment	COSMO-RS	experiment
<i>n</i> -hexane	0.0736	0.0458	$1.476 \times 10^{-6}$	$9.623 \times 10^{-6}$
<i>n</i> -heptane	0.0621	0.0347	$1.331 \times 10^{-6}$	$8.193 \times 10^{-6}$
cyclopentane	0.1276	0.0962	$2.063 \times 10^{-6}$	$7.375 \times 10^{-5}$
cyclohexane	0.1159	0.0879	$1.514 \times 10^{-6}$	$4.899 \times 10^{-5}$
tetralin	0.3043	0.3023	$9.326 \times 10^{-5}$	$2.088 \times 10^{-4}$
isopropyl ether	0.2426	0.2245	$3.501 \times 10^{-4}$	$8.594 \times 10^{-4}$

Therefore, the experimentally measured mutual solubility is in agreement with the COSMO-RS prediction. Alkane and cycloalkane present lower mutual solubility with  $[\text{C}_2\text{mim}][\text{Ac}]$  than other organic solvents.

**2.1.4. Calculation of Thermodynamic Index for *m*-Cresol and Cumene in the Double-Solvent Extraction System.** A good extractant should have high selectivity and a reasonable distribution coefficient. Therefore, the selectivity and distribution coefficient of a double-solvent system composed of  $[\text{C}_2\text{mim}][\text{Ac}]$  and alkane or cycloalkane are further investigated. The distribution coefficient and selectivity to *m*-cresol are calculated at infinite dilution, and the results are shown in Figure 4a. All alkanes and cycloalkanes have similar distribution coefficient and selectivity for *m*-cresol, which means they have similar separation performance for *m*-cresol. The result is consistent with the analysis of interaction energy between organic solvent and *m*-cresol.

Although the interaction energy is similar between  $[\text{C}_2\text{mim}][\text{Ac}]$  with different alkane or cycloalkane, a certain difference in cumene distribution coefficient can further distinguish the entrainment of cumene in different double solvents. The distribution coefficient of the double-solvent system composed of  $[\text{C}_2\text{mim}][\text{Ac}]$  and alkane or cycloalkane to cumene is demonstrated in Figure 4b. For alkane and cycloalkane, cyclopentane presents the lowest distribution



**Figure 4.** COSMO-RS calculation of thermodynamic index at infinite dilution in a double-solvent system with different alkanes and cycloalkanes. (a) Distribution coefficient and selectivity for *m*-cresol. (b) Distribution coefficient for cumene.

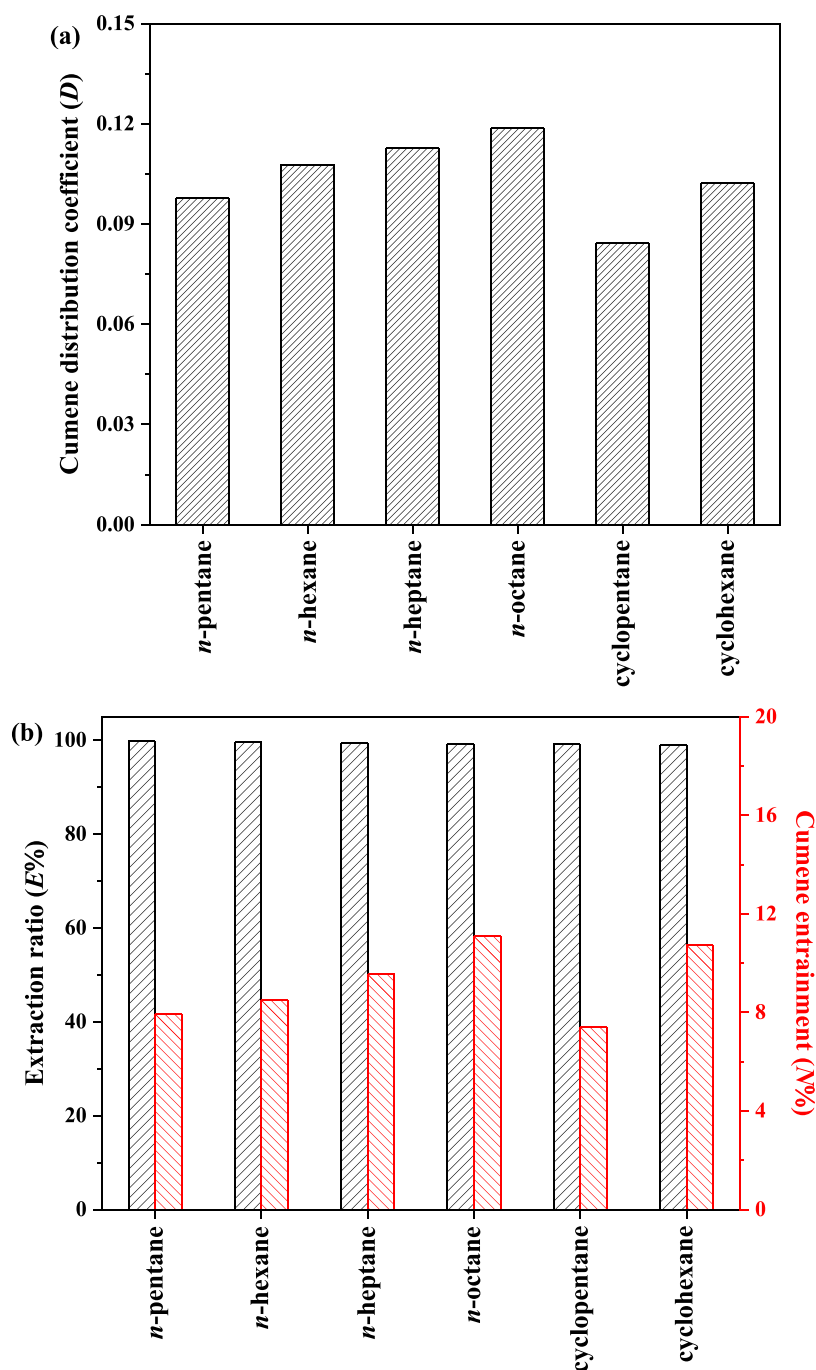
coefficient for cumene. A smaller value of  $\beta_2^\infty$  represents that cumene is preferably distributed in the solvent phase, which is beneficial to the separation process. In summary, cyclopentane as an organic solvent phase may have a good performance for *m*-cresol separation and purification in the double-solvent extraction system.

**2.1.5. Experimental Verification of the Double-Solvent Extraction System.** To verify the accuracy of COSMO-RS prediction, six organic solvents, including *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, and cyclohexane, are selected as the representative solvents to validate the prediction results by double-solvent extraction experiments. As shown in Figure 5a, cyclopentane reveals the lowest cumene

distribution coefficient among six organic solvents. Combined with Figure 5b, the entrainment of cumene in the IL phase is the lowest when cyclopentane is used as the organic solvent phase in the double-solvent extraction. For six organic solvents, the extraction ratios of *m*-cresol are more than 99%, which is a satisfactory phenol separation performance. Hence, the experimental results are coincident with COSMO-RS predictions. In summary, the COSMO-RS model can quickly screen out the organic solvents in the double-solvent extraction system for the separation of phenolic compounds from model oil and avoid a large number of experiments.

Furthermore, recovery of organic solvent needs to be considered. The lower boiling point of organic solvent is





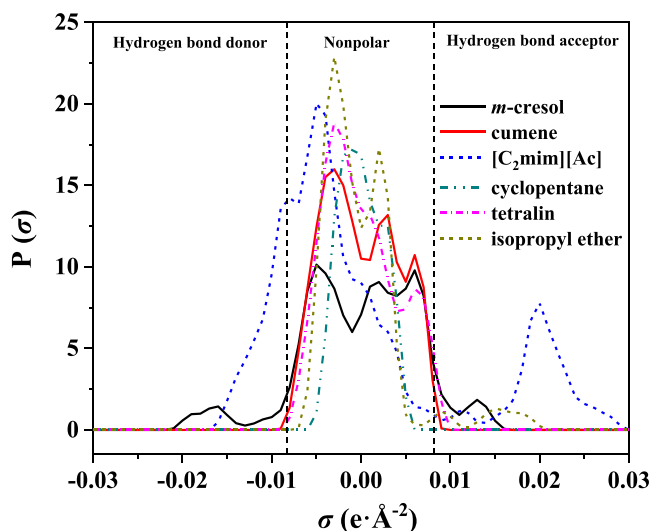
**Figure 5.** Effect of six organic solvents on the separation performances in the double-solvent system. (a) Distribution coefficient of cumene. (b) Extraction ratio of *m*-cresol and entrainment of cumene.

beneficial to energy conservation. The boiling points of *n*-pentane (36.1 °C), *n*-hexane (69 °C), *n*-heptane (98.5 °C), *n*-octane (125 °C), cyclopentane (49.3 °C), and cyclohexane (80.7 °C) are obtained from Table S1 (Supporting Information). Generally, the operating temperature of extraction of the phenolic compound is from 25 to 35 °C,<sup>26–29</sup> and *n*-pentane is very volatile in this condition. Cyclopentane has a more suitable boiling point and good separation performance for *m*-cresol in the double-solvent extraction, which was further studied as an organic solvent for *m*-cresol purification.

**2.2. COSMO-RS-Based Analysis of Molecular Interactions.** The extraction performance of organic solvents can

be understood by their  $\sigma$ -profile and  $\sigma$ -potential, and this method has been applied to the analysis of the interaction in the mixed-solution system.<sup>30,31</sup>

**2.2.1.  $\sigma$ -Profile Analysis.** The  $\sigma$ -profile analysis can explain the hydrogen bond donor ability ( $\sigma < -0.0084 \text{ e}/\text{\AA}^2$ ) and hydrogen bond acceptor ability ( $\sigma > 0.0084 \text{ e}/\text{\AA}^2$ ) of a molecule.<sup>32</sup> The  $\sigma$ -profile for *m*-cresol, cumene, [C<sub>2</sub>mim][Ac], cyclopentane, tetralin, and isopropyl ether is plotted in Figure 6. For *m*-cresol, the large peaks appear at around  $-0.016$  and  $0.013 \text{ e}/\text{\AA}^2$ , which are attributed to the H and O atoms in the hydroxyl group, respectively. This indicates that *m*-cresol has both strong hydrogen bond donor and acceptor abilities. The  $\sigma$ -profile of cumene is distributed within  $-0.009 \text{ e}/\text{\AA}^2 < \sigma <$



**Figure 6.**  $\sigma$ -Profile of *m*-cresol, cumene, [C<sub>2</sub>mim][Ac], cyclopentane, tetralin, and isopropyl ether.

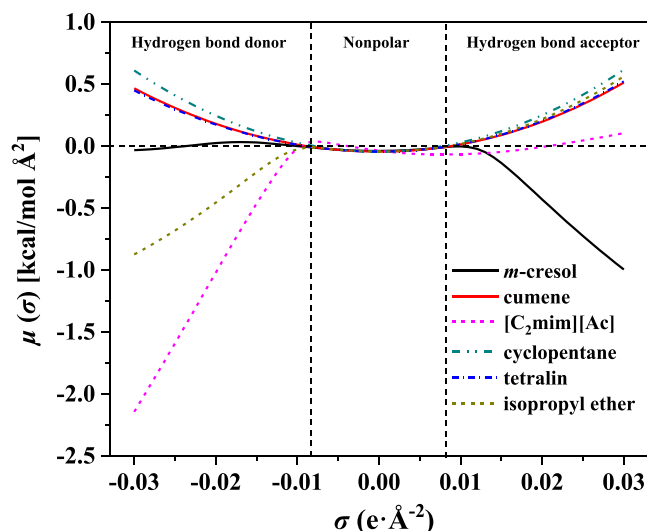
0.009 e/Å<sup>2</sup>, suggesting a nonpolar molecule. For [C<sub>2</sub>mim]-[Ac], the O atom in acetate and the H atom in the imidazole ring cause the existence of a large peak at around 0.020 e/Å<sup>2</sup> and small distribution within  $-0.017 \text{ e/Å}^2 < \sigma < -0.0084 \text{ e/Å}^2$ , indicating its strong hydrogen bond acceptor ability and weak hydrogen bond donor ability. Hence, IL [C<sub>2</sub>mim][Ac] has satisfactory extraction performance for *m*-cresol. However, the  $\sigma$ -profile of [C<sub>2</sub>mim][Ac] is widely distributed in the negative and positive nonpolar regions, which implies that cumene can be also dissolved in [C<sub>2</sub>mim][Ac].

For isopropyl ether, the  $\sigma$ -profile is distributed a peak in the negative and positive nonpolar region, respectively, which as organic solvent phase can reduce the entrainment of cumene in IL phase. But more importantly, the O atom in isopropyl ether shows a small peak at 0.015 e/Å<sup>2</sup> in the hydrogen bond acceptor region, which can form hydrogen bonds with *m*-cresol and [C<sub>2</sub>mim][Ac]. The HB interaction leads to a low extraction ratio for *m*-cresol as well as a high mutual solubility with [C<sub>2</sub>mim][Ac]. Moreover, the screening charge density of cyclopentane is definitely distributed around 0 e/Å<sup>2</sup> within the nonpolar region, indicating a stronger nonpolar molecule and a lower mutual solubility with [C<sub>2</sub>mim][Ac] than tetralin.

**2.2.2.  $\sigma$ -Potential Analysis.** The  $\sigma$ -potential is obtained on the basis of the  $\sigma$ -profile, which can reflect the attraction and repulsion ability between one solvent and another in the mixture. In the three regions of  $\sigma$ -potential, a higher negative value for a solvent indicates a stronger attraction ability with other components. On the contrary, a higher positive value indicates repulsive interaction.<sup>33</sup>

As shown in Figure 7, the  $\sigma$ -potential of *m*-cresol only presents a high negative value in the hydrogen bond acceptor region, suggesting a strong attraction ability with other solvents, which has strong hydrogen bond acceptor ability. In other words, *m*-cresol prefers to be a hydrogen bond donor rather than an acceptor. The  $\sigma$ -potential of isopropyl ether shows a negative value in the hydrogen bond donor region, which indicates a strong attractive interaction between isopropyl ether and *m*-cresol.

Compared with tetralin and isopropyl ether, cyclopentane exhibits a higher positive value in hydrogen bond donor and acceptor regions, suggesting a more repulsive interaction and



**Figure 7.**  $\sigma$ -Potential of *m*-cresol, cumene, [C<sub>2</sub>mim][Ac], cyclopentane, tetralin, and isopropyl ether.

resulting in a lower mutual solubility in [C<sub>2</sub>mim][Ac]. Furthermore, all of the six studied components have a negative value in the nonpolar region, which leads to the distribution of cumene in the IL phase and organic solvent phase. Due to the stronger nonpolarity of cyclopentane, it has a lower distribution coefficient for cumene in the extraction process.

### 2.3. Removal of Neutral Oil and Improving Selectivity to Phenolic Compound by Double-Solvent Extraction.

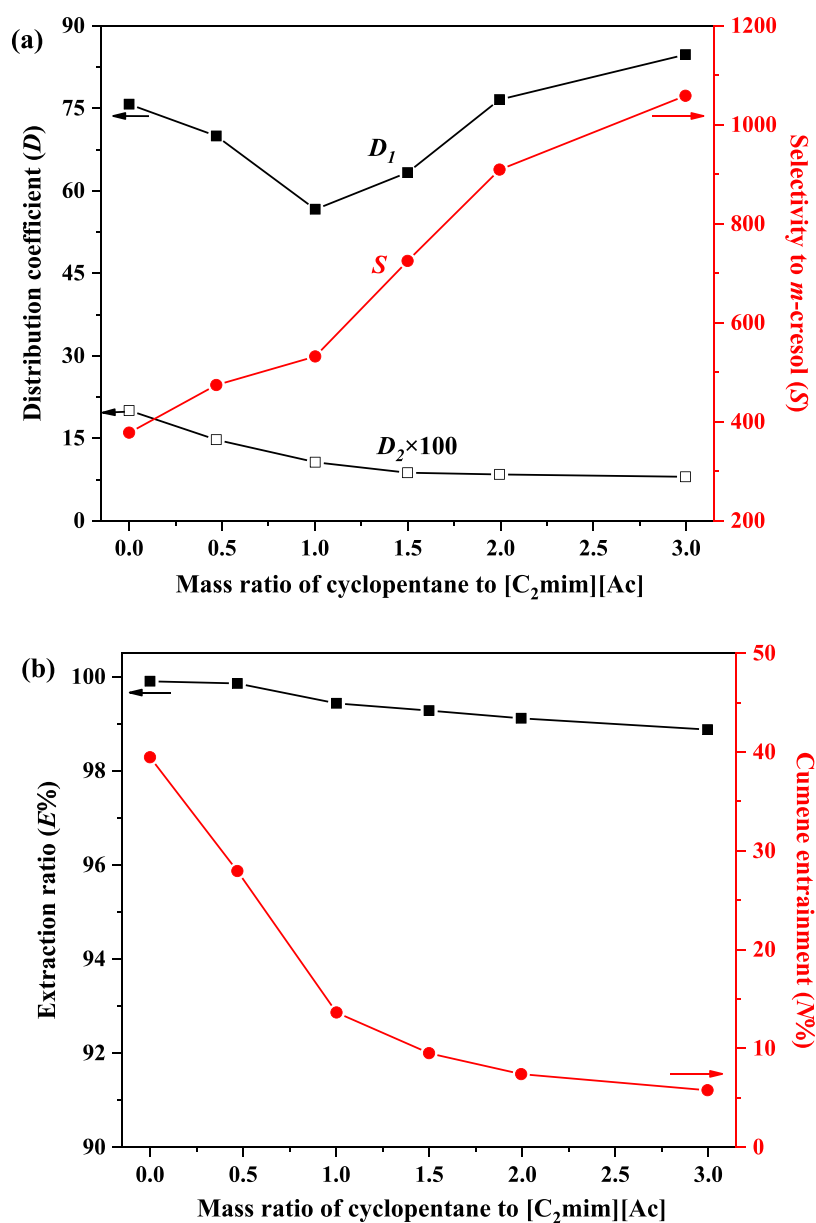
To further reduce neutral oil entrainment and improve the selectivity of the [C<sub>2</sub>mim][Ac]–cyclopentane solvent system to phenolic compound, the model oil composed of *m*-cresol and cumene was studied. The influences of the mass ratio of cyclopentane on [C<sub>2</sub>mim][Ac], temperature, and initial *m*-cresol content on the separation performance of *m*-cresol were investigated.

**2.3.1. Effect of Mass Ratio of Cyclopentane to [C<sub>2</sub>mim][Ac] on Separation.** The cyclopentane-to-[C<sub>2</sub>mim][Ac] mass ratio in the range from 0.0 to 3.0 are investigated, and the results are shown in Figure 8. As demonstrated in Figure 8a, as the cyclopentane-to-[C<sub>2</sub>mim][Ac] mass ratio increases from 0.0 to 3.0, the distribution coefficient of *m*-cresol ( $D_1$ ) decreases first from 75.7 to 56.6 and then increases to 84.8, while the distribution coefficient of cumene ( $D_2$ ) gradually decreases from 0.20 to 0.08. According to the change of  $D_1$  and  $D_2$ , the selectivity ( $S$ ) is greatly improved from 378.0 to 1058.5. As shown in Figure 8b, the extraction ratio of *m*-cresol ( $E\%$ ) is slightly decreased from 99.9 to 98.9%, while the entrainment of cumene ( $N\%$ ) declines evidently from 39.5 to 5.8%. The results show that the purity of *m*-cresol in the [C<sub>2</sub>mim][Ac]–cyclopentane solvent is higher than that in pure [C<sub>2</sub>mim][Ac] solvent.

To interpret the reason for improving the purity and selectivity of *m*-cresol carefully, the expression of selectivity is shown in eq 1

$$S = D_1/D_2 = \frac{(w_1^{\text{IL}}/w_1^{\text{sol}})}{(w_2^{\text{IL}}/w_2^{\text{sol}})} = \frac{(w_1^{\text{IL}}/w_2^{\text{IL}})}{(w_1^{\text{sol}}/w_2^{\text{sol}})} = \frac{(w_1/w_2)^{\text{IL}}}{(w_1/w_2)^{\text{sol}}} \quad (1)$$

where  $(w_1/w_2)^{\text{IL}}$  and  $(w_1/w_2)^{\text{sol}}$  represent the mass fraction ratios of *m*-cresol to cumene in the IL phase and the organic solvent phase, respectively.



**Figure 8.** Effect of cyclopentane-to-[C<sub>2</sub>mim][Ac] mass ratio on the separation performances in the double-solvent system. (a) Distribution coefficient of *m*-cresol ( $D_1$ ) and cumene ( $D_2$ ) and selectivity to *m*-cresol ( $S$ ). (b) Extraction ratio of *m*-cresol ( $E\%$ ) and entrainment of cumene ( $N\%$ ).

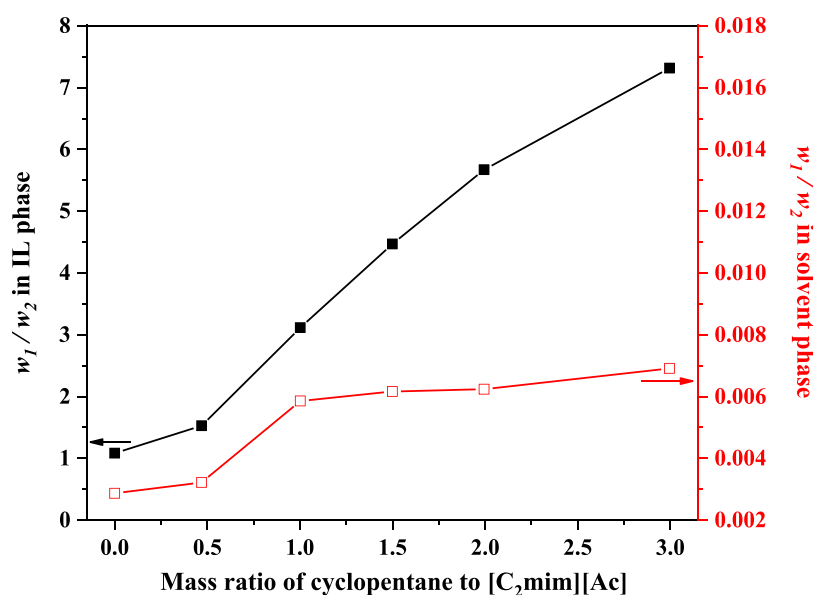
As shown in Figure 9, the mass fraction ratio of *m*-cresol to cumene is obviously increased from 1.08 to 7.31 in the IL phase with the increase in the cyclopentane-to-[C<sub>2</sub>mim][Ac] mass ratio but slowly increased from 0.0029 to 0.0069 in the solvent phase, about 6.77 and 2.38 times compared with individual [C<sub>2</sub>mim][Ac] solvent. Therefore, the obvious enlargement of the mass fraction ratio of *m*-cresol to cumene in the IL phase gives rise to the higher purity and selectivity of *m*-cresol.

**2.3.2. Effect of Temperature on Separation.** The effects of temperature on the mutual solubility and separation performance of [C<sub>2</sub>mim][Ac]-cyclopentane double solvent are demonstrated in Figure 10. As seen in Figure 10a, when the temperature increases from 25 to 65 °C, the solubility of cyclopentane in [C<sub>2</sub>mim][Ac] increases from 0.0962 to 0.1148 g/g, while the solubility of [C<sub>2</sub>mim][Ac] in cyclopentane increases from  $7.375 \times 10^{-5}$  to  $5.915 \times 10^{-4}$  g/g. It can be

concluded that a higher temperature can result in higher mutual solubility of cyclopentane with [C<sub>2</sub>mim][Ac]. From Figure 10b, the values of  $D_1$ ,  $D_2$ , and  $S$  at 25 °C are 78.6, 0.09, and 916.3, respectively, while the values of  $D_1$ ,  $D_2$ , and  $S$  at 65 °C are 58.8, 0.17, and 344.0, respectively. An increase in temperature can reduce the separation performance of the [C<sub>2</sub>mim][Ac]-cyclopentane double solvent, which is unfavorable for the separation process. Therefore, room temperature is the most suitable temperature for the separation of *m*-cresol from model oil.

**2.3.3. Effect of Initial *m*-Cresol Content on Separation.** Due to the different contents of phenolic compounds in different oils, it is essential to investigate the effect of initial *m*-cresol content on *m*-cresol separation. The initial *m*-cresol content in the range from 15% to 40% was studied in Figure 11. With the increase in the initial *m*-cresol content from 15 to 40%,  $D_1$  is gradually reduced from 141.0 to 92.5 and  $D_2$  is





**Figure 9.** Effect of cyclopentane-to-[C<sub>2</sub>mim][Ac] mass ratio on the mass fraction ratio of *m*-cresol to cumene in the IL phase and the solvent phase in the double-solvent system.

increased incrementally from 0.05 to 0.11. The changes in  $D_1$  and  $D_2$  lead to the decrease in  $S$  from 2821.1 to 840.7. In conclusion, the low content of phenols in LTCT easily delivers high-purity phenol products.

### 3. CONCLUSIONS

In this work, the multi-index evaluation method was used to screen the organic solvent in a [C<sub>2</sub>mim][Ac]–organic solvent double-solvent system for oil–phenol mixture separation. Eighteen organic solvents were screened through interaction energy, mutual solubility, distribution coefficient, and selectivity as screening indexes by COSMO-RS calculation. Among them, alkane and cycloalkane demonstrate strong interaction with cumene and low mutual solubility with [C<sub>2</sub>mim][Ac]. Meanwhile, alkane and cycloalkane have high distribution coefficient and selectivity for *m*-cresol, as well as low distribution coefficient for cumene at infinite dilution. The double-solvent extraction experiments verify that the screening method is useful and accurate. Furthermore, the distribution coefficient and entrainment of cumene are the lowest when cyclopentane is used as an organic solvent in the double-solvent extraction experiments. The analyses of  $\sigma$ -profile and  $\sigma$ -potential indicate that a strong nonpolar molecule and hydrogen bond repulsive interaction of cyclopentane lead to its low cumene entrainment and low mutual solubility with [C<sub>2</sub>mim][Ac]. The entrainment of cumene evidently declines from 39.5 to 5.8%, and the selectivity to *m*-cresol improves from 378.0 to 1058.5 when the cyclopentane-to-[C<sub>2</sub>mim][Ac] mass ratio increases from 0.0 to 3.0. The room temperature and the lower initial phenol content are more conducive to removing neutral oil and improving phenol selectivity.

### 4. CALCULATION AND EXPERIMENTAL DESCRIPTION

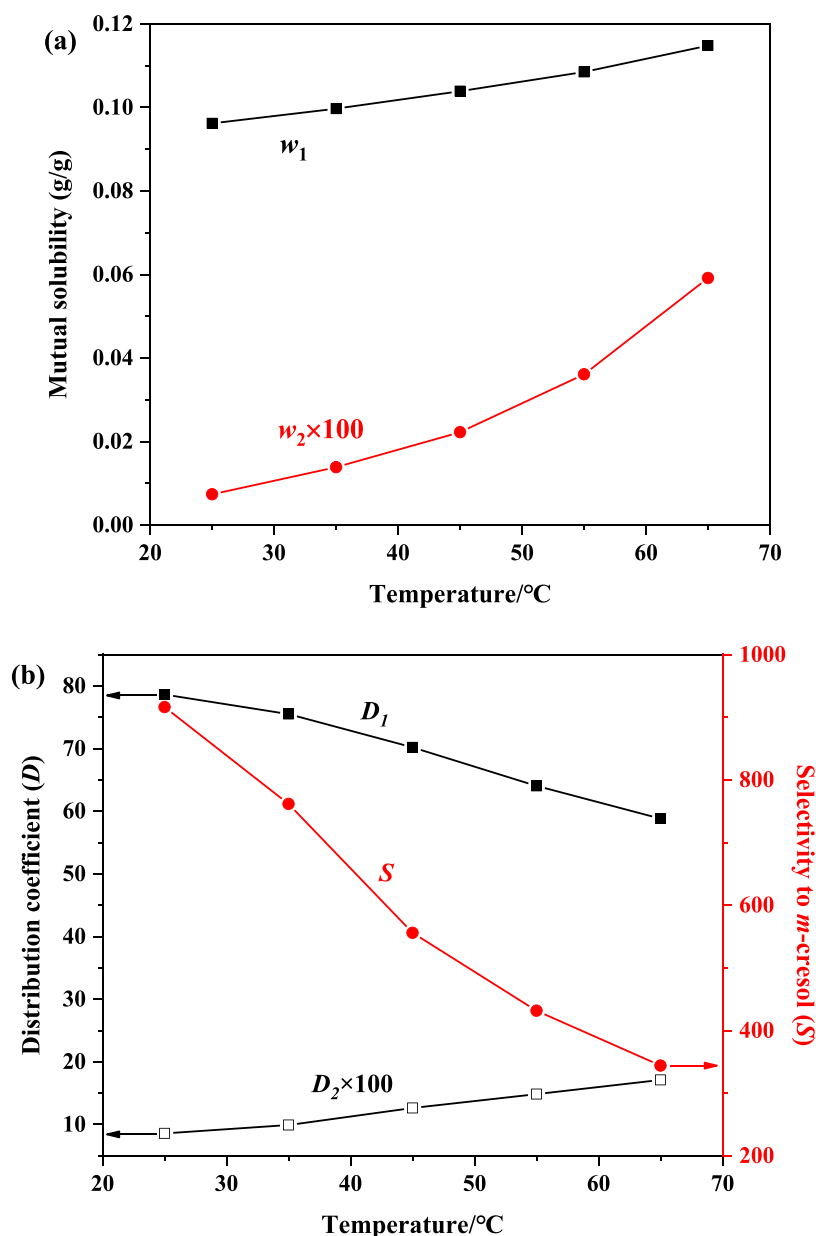
**4.1. COSMO-RS Calculation.** **4.1.1. Screening Indexes and Principles.** The COSMO-RS model can calculate the thermodynamic properties of liquid or liquid mixtures only by molecular information and without requiring any experimental data.<sup>19–21</sup> Among them, interaction energy, mutual solubility, distribution coefficient, and selectivity are used to screen the

suitable organic solvent.<sup>34,35</sup> The organic solvent itself should have a suitable molecular weight and boiling point. In this work, eighteen organic solvents, such as alkane, cycloalkane, alkene, alkyne, aromatic hydrocarbon, oxygenated solvent, and chlorinated solvent, including *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, cyclohexane, 1-octene, 1-octyne, benzene, toluene, 1-methylnaphthalene, tetralin, diethyl ether, isopropyl ether, diethyl carbonate, carbon disulfide, carbon tetrachloride, and tetrachloroethylene, were screened by the COSMO-RS model. The specific information of eighteen organic solvents is shown in Table S1 (Supporting Information). The suitable organic solvent should satisfy the following three conditions: (1) strong interaction between the organic solvent and neutral oil but weak interaction between organic solvent and phenols, (2) the low mutual solubility of [C<sub>2</sub>mim][Ac] and organic solvent, and (3) the high distribution coefficient and selectivity of phenols but the low distribution coefficient of neutral oil in the double solvent.

**4.1.2. Calculation Details.** Generally, the calculation process of COSMO-RS involves two steps. First, the screening charge density ( $\sigma$ -profile) of the involved compounds should be obtained from the database or quantum chemical calculation. Among them, the  $\sigma$ -profiles of 1-octene, 1-octyne, 1-methylnaphthalene, and diethyl carbonate were calculated by TmoleX software (Version 4.4.0N) at the BP86/TZVP level, and the  $\sigma$ -profiles of other compounds were chosen from the database of COSMOthermX software (Version 18.0.0) with the BP\_TZVP\_18 parameterization.<sup>36,37</sup>

Then, on the basis of the  $\sigma$ -profiles, the interaction energy could be estimated through the statistical thermodynamic method using COSMOthermX software, which included the misfit energy, the hydrogen bonding (HB) energy, and the van der Waals (vdW) energy. The relevant calculation method and details can be found in the literature.<sup>25,38</sup> The mass-based mutual solubility can be calculated from the mole-based mutual solubility by

$$w_1 = \frac{x_1 \times MW_{\text{sol}}}{(1 - x_1) \times MW_{\text{IL}}} \quad (2)$$



**Figure 10.** Effect of temperature on the mutual solubility and separation performance in the double-solvent system. (a) Solubility of cyclopentane in  $[\text{C}_2\text{mim}][\text{Ac}]$  and  $[\text{C}_2\text{mim}][\text{Ac}]$  in cyclopentane. (b) Distribution coefficient of *m*-cresol ( $D_1$ ) and cumene ( $D_2$ ) and selectivity to *m*-cresol ( $S$ ).

$$w_2 = \frac{x_2 \times \text{MW}_{\text{IL}}}{(1 - x_2) \times \text{MW}_{\text{sol}}} \quad (3)$$

where  $w_1$  and  $w_2$  are the mass-based solubilities of an organic solvent in IL and IL in an organic solvent, respectively;  $x_1$  and  $x_2$  are the mole-based solubilities of an organic solvent in IL and IL in an organic solvent, respectively; and  $\text{MW}_{\text{sol}}$  and  $\text{MW}_{\text{IL}}$  are the molar mass of organic solvent and IL, respectively.

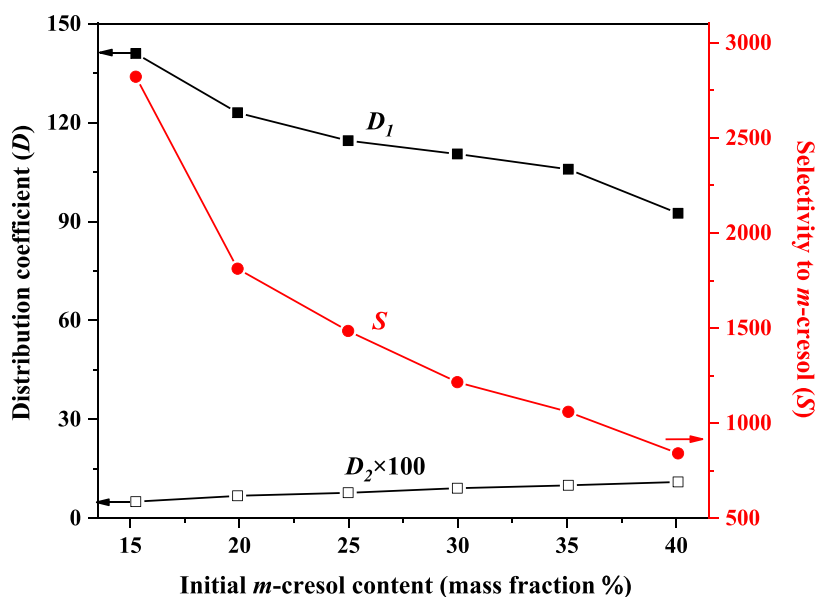
The distribution coefficient ( $\beta^\infty$ ) and selectivity ( $S^\infty$ ) of the extract at infinite dilution can be calculated through infinite-dilution activity coefficient from COSMO-RS by

$$\beta_i^\infty = (1/\gamma_i^\infty)^{\text{IL}} / (1/\gamma_i^\infty)^{\text{sol}} \quad (4)$$

$$S^\infty = \beta_1^\infty / \beta_2^\infty \quad (5)$$

where  $(\gamma_i^\infty)^{\text{IL}}$  and  $(\gamma_i^\infty)^{\text{sol}}$  are the infinite dilution activity coefficient of compound  $i$  in the IL phase and the organic solvent phase, respectively, where  $\beta_1^\infty$  and  $\beta_2^\infty$  refer to the distribution coefficient of *m*-cresol and cumene, respectively. The accuracy of COSMO-RS involved the calculation of solubility, and the infinite dilution activity coefficient has been proved in the previous literature.<sup>20,39–41</sup>

**4.2. Experiments.** **4.2.1. Chemical Materials.** IL  $[\text{C}_2\text{mim}][\text{Ac}]$  ( $\geq 99.0$  wt %), *m*-cresol ( $\geq 99.0$  wt %), cumene ( $\geq 99.0$  wt %), *o*-nitrotoluene ( $\geq 99.0$  wt %), *n*-hexane ( $\geq 98.0$  wt %), *n*-heptane ( $\geq 99.0$  wt %), *n*-octane ( $\geq 99.0$  wt %), cyclopentane ( $\geq 98.0$  wt %), cyclohexane ( $\geq 99.5$  wt %), tetralin ( $\geq 98.5$  wt %), and isopropyl ether ( $\geq 99.0$  wt %) were purchased from Shanghai Macklin Biochemical Co., Ltd. Absolute alcohol ( $\geq 99.5$  wt %) and *n*-pentane ( $\geq 98.0$  wt %) were purchased from Modern Oriental (Beijing) Technology Development Co., Ltd.  $[\text{C}_2\text{mim}][\text{Ac}]$  was dried in vacuum at



**Figure 11.** Effect of initial *m*-cresol content (mass fraction) in model oil on the distribution coefficient of *m*-cresol ( $D_1$ ) and cumene ( $D_2$ ) and the selectivity to *m*-cresol ( $S$ ) in the double-solvent system.

80 °C for 24 h before use to remove moisture as far as possible (<1000 mg/kg with 870 KF Titrino plus Karl Fischer Moisture Titrator, Switzerland). The other chemicals in the experiments were used without further purification.

**4.2.2. Mutual Solubility Measurement.** In a typical experiment, 10 g of organic solvent and 10 g of IL  $[C_2mim][Ac]$  were weighed using an analytical balance (AE124C within  $\pm 0.0001$  g, China) and added into a 50 mL screw-capped glass bottle. The mixture was magnetically stirred for 30 min at 25 °C in a thermostatic water bath equipped with a magnetic stirring system (HWCL-3 within  $\pm 0.1$  °C, China). Then, the mixture was settled for 1 h to ensure thermodynamic equilibrium. After settling, the organic solvent and IL phases were carefully separated with syringes. The solubility of  $[C_2mim][Ac]$  in the organic solvent was analyzed by the increase in nitrogen content in the organic solvent before and after  $[C_2mim][Ac]$  was dissolved, which was measured using a chemiluminescence nitrogen analyzer (Antek 9000 within  $\pm 0.02$ ). The solubility of organic solvent in  $[C_2mim][Ac]$  was determined using the gravimetric method by weighing the mass reduction of  $[C_2mim][Ac]$  phase before and after evaporation.

**4.2.3. Extraction Procedures.** In this experiment, the model oil was composed of a mixture of *m*-cresol and cumene, representing phenolic compounds and neutral oil components in LTCT, respectively. The extraction experiments were performed as follows. Certain amounts of model oil,  $[C_2mim][Ac]$ , and organic solvent according to a specific mass ratio were added to a 50 mL screw-capped glass bottle with a magnetic stirrer. Then, the bottle was covered and partially immersed in a thermostatic water bath and the mixture in the bottle was stirred for 30 min. After standing for 30 min, the upper dephenol oil phase and the lower IL phase were formed clearly. After that, the two phases were separated carefully by a separating funnel, and the composition of the two phases was detected by gas chromatography (GC-SP3420, China).

In a typical extraction process, 10 g of model oil (3 g of *m*-cresol + 7 g of cumene), 10 g of cyclopentane, and 5 g of

$[C_2mim][Ac]$  were added to a 50 mL bottle. Then, the mixture was magnetically stirred at 600 r/min for 30 min, and the temperature was controlled at 25 °C. Then, the mixture was made to stand for 30 min at 25 °C. After separating the two phases using a separating funnel, 0.5 mL of the upper dephenol oil phase and the lower IL phase were taken into a 10 mL screw-capped glass bottle by a pipette gun, respectively, and 0.5 mL of *o*-nitrotoluene as the internal standard was added in the bottle. The mass of the transferred liquids was accurately weighed. The mixture was diluted five times with absolute ethanol for GC analysis.

The concentrations of *m*-cresol, cumene, and organic solvent in each phase were analyzed by GC-SP3420. The GC was equipped with a KB-WAX (50 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) column and a flame ionization detector (FID). The temperature program of the GC was started at 80 °C, settled for 2 min, then increased at a rate of 10 °C/min until the temperature reached 200 °C and settled for 16 min. The temperature of FID and the injection port were set at 230 °C. All analyses were repeated at least three times.

**4.2.4. Evaluation Indexes.** The following indexes were used to evaluate the separation performance. The distribution coefficient ( $D$ ) is calculated by

$$D_i = w_i^{IL} / w_i^{sol} \quad (6)$$

where  $w_i^{IL}$  and  $w_i^{sol}$  are the mass concentrations of *m*-cresol or cumene in the IL phase and the organic solvent phase, respectively.

The selectivity ( $S$ ) to *m*-cresol is calculated by

$$S = D_1 / D_2 \quad (7)$$

where  $D_1$  and  $D_2$  are the distribution coefficients of *m*-cresol and cumene, respectively.

The extraction ratio ( $E\%$ ) of *m*-cresol in the double-solvent extraction process is calculated by

$$E\% = w_1^{IL} \cdot m^{IL} / m_1 \times 100\% \quad (8)$$

where  $w_i^{\text{IL}}$  is the mass concentration of *m*-cresol in the IL phase.  $m_i^{\text{IL}}$  and  $m_i$  are the weights of the IL phase and *m*-cresol in model oil, respectively.

The neutral oil entrainment (N%) of cumene and the organic solvent is calculated by

$$N_i\% = w_i^{\text{IL}} \cdot m_i^{\text{IL}} / m_i \times 100\% \quad (9)$$

where  $w_i^{\text{IL}}$  is the mass concentration of cumene or organic solvent in the IL phase and  $m_i$  is the weight of cumene in model oil or organic solvent.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03097>.

Details of eighteen organic solvents (PDF)

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<https://pubs.acs.org/10.1021/acsomega.2c03097>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank the financial support provided by the National Key Research and Development Program of China (2016YFB0600305).

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