1 **Measurement, correlation and COSMO-SAC prediction of**
2 **liquid-liquid equilibrium for the ternary systems, mesityl oxide +**
3 ***o*-, *m*-, *p*-cresol + water, at 333.2K and 353.2 K**

4 *Shaoming Zhou, Libo Li, Youchang Wang, Yun Chen**

5 *Department of Chemistry and Chemical Engineering, South China University of Technology,*

6 *Guangzhou, 510640, P.R.China*

7 **Abstract:** In this work, liquid-liquid equilibrium (LLE) data for the ternary systems, mesityl
8 oxide + *o*-, *m*-, *p*-cresol + water, were determined at 333.2 K and 353.2 K under 101 kPa. The
9 high distribution coefficient and selectivity calculated by the experimental tie-line data
10 indicate excellent efficiency for mesityl oxide extracting cresols from aqueous solutions. The
11 NRTL and UNIQUAC models were used to correlate the experimental LLE data, with root
12 mean square deviations (RMSDs) below 2.1% and 1.5%, respectively. The COSMO-SAC
13 model was also employed to calculate the LLE data, which agreed with the experimental
14 results quite well.

15 **Keywords:** Liquid-liquid equilibrium; mesityl oxide; cresol; NRTL; UNIQUAC;
16 COSMO-SAC;

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19 *Corresponding author. Tel: +8613632384249; E-mail address: yunchen@scut.edu.cn.
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1. Introduction

Coal gasification, a clean and high efficient coal utilization technology, is playing an significant role in the energy-hungry world due to the increasing demand of natural gas[1,2]. However, the widely used coal gasification processes[3], e.g. lurgi coal gasification process, usually generates a great amount of wastewater, which contains highly concentrated phenolic compounds and other toxic compounds[1,4]. With high toxicity even at low concentration, phenolic compounds cause serious damage to human beings, animals and plants if discharging without treatment[5]. Cresols are the primary phenolic compounds in the coal gasification wastewater[6], and are listed as priority pollutants by the EU and the USA-EPA[7]. Removing cresols from water with conventional recovery process, e.g. distillation or evaporation, is not energy efficient in the industry because of the high boiling point of cresols and the high heat of evaporation of water [8]. Other newly developed methods to remove cresols, e.g. adsorption[9,10], biodegradation[1,11] and chemical oxidation[12], also suffer from various flaws. For instance, adsorption is only applied in treating low concentrated phenolic effluents (less than 200 ppm) due to the high price of activated carbon, the most widely used adsorbents [13]. Biodegradation alone can not be used to treat phenolic wastewater because: (1) microorganisms would be poisoned by the highly concentrated phenolic compounds, (2) degrading cresols is quite time-consuming, which usually takes a few days. Chemical oxidation, a destructive treatment, cannot recycle cresols, which are important industrial materials widely used as antioxidants, herbicides, surfactants, dyes and pigments[14].

Liquid-liquid extraction has been used to recovered polar compounds from aqueous solutions[15,16], showing a series of advantages over other phenolic wastewater treatment methods, such as high throughput, versatility, low energy cost and high commercial efficiency. Such method has been used to treat industrial phenolic wastewater in USA[17], South Africa[17] and China[17-19]. The key problem to design a liquid-liquid extraction process is to develop an appropriate extractant with low water solubility, low price and high efficiency to separate cresols from water. However, such study or data is quite scarce at present, with just a few solvents (or extractants) having been reported [20-24]: at 298.2 K, the distribution

coefficient (D) and selectivity (S) of methyl tert-butyl ether for cresols are 800~1200 and 3500~13700, those of methyl isopropyl ketone are 390~1450 and 1300~7800 and those of methyl propyl ketone are 530~1450 and 1900~8900. As a polar organic solvent, Mesityl oxide have shown high efficiency in extracting phenol from the aqueous solution[26]. In addition, it is usually easier to extract cresols from aqueous solutions than to extract phenol [24,25, 27-29]. Therefore, it is of practical significance to study the performance of mesityl oxide to extract cresols from wastewater. In industrial practice, especially in coal gasification plants, the operation temperature of the extraction column is often above 333 K, so that the extraction installation would not be clogged by the paraffin (melting point ranges from 328.5 K to 335.15 K) in the wastewater. However, the LLE equilibrium data for phenolic compounds above 333 K are very scarce at present, not to mention data for cresols [25]. Hence, in this work, the extraction performance of mesityl oxide for cresols was investigated above 333 K.

In the present work, the liquid-liquid equilibrium (LLE) data of the mesityl oxide + *o*-, *m*-, *p*-cresol + water ternary systems and corresponding distribution coefficients and selectivities were determined at 333.2 K and 353.2 K, under 101kPa. LLE data were correlated by the non-random two liquid (NRTL)[30] and universal quasi-chemical (UNIQUAC)[31] models. The conductor-like screening model for segment activity coefficient (COSMO-SAC)[32], a quantum chemical based prediction model, was also employed to predict the liquid-liquid equilibrium data.

2. COSMO-SAC model

2.1. COSMO-SAC

COSMO-SAC model, derived from the conductor-like screening model (COSMO) model[33], was first proposed by Lin[34] and Sandler[34] to predict activity coefficients in solutions. In 2007, Wang and Sandler[35] improved the definition of hydrogen bond to predict the thermodynamic properties of both pure and mixture solvents. Later, Hsieh[32] proposed a refinement COSMO-SAC(2010) model, which considers the electrostatic interaction parameter as temperature-dependent. Recently, COSMO-SAC has been used for phase equilibrium prediction, solubility calculation and solvent screening [36-38]. There are

two steps to calculate the thermodynamic activity coefficients by the COSMO-SAC model. First, calculate the COSMO file, mainly including the segment information, the surface area and the total volume of the molecules by the density functional theory and the COSMO calculation, then calculate the three-dimensional screening charge density distribution by averaging the original charge density in the COSMO file[32] and use this information to calculate the σ -profile $p(\sigma)$. The sigma profile of hydrogen bond atom $p^{hb}(\sigma)$ and the sigma profile of non-hydrogen bond atom $p^{nhb}(\sigma)$ are calculated separately to obtain the $p(\sigma)$ of pure compound as proposed by Lin et al.[39]. Second, calculate the activity coefficients of each pure compound and mixture by using the σ -profile $p(\sigma)$. The details of the COSMO-SAC model can be found in other publications[32,40,41] and in the Appendix. The COSMO-SAC universal parameter for the effective contact area a_{eff} in this work is $6.55\text{\AA}^2$, while the hydrogen bonding coefficient c_{hb} is $100\text{ kcal}\text{\AA}^4\text{mol}^{-1}\text{e}^{-2}$.

2.2. Tie lines prediction

In this work, the COSMO-SAC method combined with the Rachford-Rice algorithm[42] was used to predict the tie line data for the mesityl oxide + *o*-, *m*-, *p*-cresol + water ternary systems.

3. Experimental section

3.1. Materials and experimental procedure

The chemical reagents used in this work are listed in Table 1. All the chemicals were of high purity (>99 wt. %) and were confirmed by gas chromatography and no other obvious peaks of impurity were detected. The deionized water was used throughout this work.

The measurement of tie lines for the ternary systems, mesityl oxide + *o*-, *m*-, *p*-cresol + water, were carried out at 333.2 K and 353.15 K under 101 kPa. A certain amount of mesityl oxide, cresols and water were fed into a customized 100 ml glass vessel and were agitated vigorously by using a magnetic stirrer for 2 h. After agitation, the vessels were left to settle for more than 20 h for the system to reach phase equilibrium. A thermostatic bath with an accuracy of $\pm 0.1\text{ K}$ was used to control the temperature.

3.2. Analysis

Samples of both layers were extracted by using a syringe, and then analyzed by using a gas

chromatography (GC6820, Agilent Technologies) equipped with a flame ionization detector (FID) and a DB-5MS capillary column (30m×0.32mm×0.25μm). The column temperature was controlled by a temperature-controlled program: beginning at 313.2 K for 2 min, and then from 313.2 K to 436.2 K at 30 K·min⁻¹, finally at 436.2 K for 2 min. The temperature of the detector and the injector was kept at 543.2 K and 523.2 K, respectively. Nitrogen was used as the carrier gas, and the flow rate was maintained at 30 ml·min⁻¹. The mass fraction of mesityl oxide and cresols were calculated by using an internal standard method, with *n*-propyl acetate as the internal standard for mesityl oxide and 1,3,5-trimethylbenzene for cresols. Each sample was performed at least three times, and the resulting standard deviation was less than 0.2%. Thus, the mean value of mole fraction was reported in this work. The uncertainties of the experimental tie lines were calculated according to the GUM and NIST guidelines[43].

4. Results and discussion

4.1. Ternary tie-line data

The experiment tie-line data with mole fraction of the systems, mesityl oxide + *o*-, *m*-, *p*-cresol + water, at 333.2 and 353.2 K are listed in Tables S1-S3 in supporting information, and are shown in Figs.1-2. These data show low solubilities of cresols and mesityl oxide in water, indicating promising potential for of mesityl oxide to extract cresols. Seen from Figs.1-2, the slopes of all tie lines are positive, which indicates the distribution coefficients of cresols in mesityl oxide are larger than 1. The distribution coefficient (*D*) and selectivity (*S*) are calculated as follows:

$$D = \frac{x_2^o}{x_2^w} \quad (1)$$

$$S = \frac{x_2^o \cdot x_3^w}{x_2^w \cdot x_3^o} \quad (2)$$

where x_i^o and x_i^w denote the mole fraction of component *i* in organic phase and aqueous phase, respectively. The resulting distribution coefficients (>210.5) and selectivities (>354) listed in Tables S1-S3 are quite high, indicating that, to separate cresols from aqueous

solutions by using mesityl oxide as an extractant is feasible and economical. Fig.3 shows the distribution coefficient (D) and selectivity(S) as functions of the cresol mole fraction in the aqueous phase at 333.2 K and 353.2 K. Seen from this figure, both D and S values decline with cresol concentration in the raffinate phase increasing, but are still quite high even when cresol mole fraction in the raffinate phase is above 0.0012. This indicates the high application potential of extracting cresols with mesityl oxide from highly concentrated phenolic effluents. According to this figure, both D and S slightly decrease when the temperature rises.

In comparison with other extractants, mesityl oxide's extraction efficiency for cresols are quite better than toluene and heptane[20], and the reason may be that, mesityl oxide could interact with cresols quite strongly with hydrogen bonds. Mesityl oxide's physical proprieties (eg: boiling point is 402.2 K and water solubility is 2.8g/100g water at 293.2 K) are more desirable than methyl tert-butyl ether (MTBE) (eg: boiling point is 328.4 K and water solubility is 4.3g/100g water at 293.2 K) which forms azeotropic mixtures with water at 328.2K. A further comparison of D and S of mesityl oxide with methyl isobutyl ketone (MIBK)[25] are shown in Fig.S1-S3, which indicates the extraction efficiency of mesityl oxide and MIBK for cresols are quite close. All these results indicate that, a mesityl oxide-based extraction process to remove cresols from effluents is quite feasible.

The high reliability of the experimental tie-line data was checked by Bachman [44] and Hand [45] equation and the details and results were listed in supporting information.

Thermodynamic models correlations

The NRTL and UNIQUAC models were used to evaluate the activity coefficients and then combined with phase equilibrium expression to correlate the experimental tie lines in this work. The non-randomness parameters (α_{ij}) for the NRTL model was fixed to 0.2 for the binary pairs contained water and fixed to 0.3 for (mesityl oxide + cresols) binary pairs. The UNIQUAC structural parameters for all the compounds used in this work were taken from literature[46], and were shown in Table 1. The activity coefficient in the NRTL model for component i in multicomponent system is expressed as follows:

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{i=1}^n x_i \tau_{ij} G_{ij}}{\sum_{k=1}^n G_{kj} x_k} \right) \quad (3)$$

1

2 here $G_{ji} = \exp(-\alpha_{ji} \tau_{ji})$, $G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$, $\tau_{ji} = (g_{ji} - g_{ii}) / RT$, and

3 $\tau_{ij} = (g_{ij} - g_{jj}) / RT$.

4 The activity coefficient by the UNIQUAC model for component i in multicomponent system
5 is expressed as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (4)$$

6

7 here γ_i^C denotes combinatorial activity coefficient and γ_i^R refer to residual activity coefficient,

8 defined as equation (5) and (6), respectively.

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \left(\frac{z}{2} \right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^n x_j l_j \quad (5)$$

$$\ln \gamma_i^R = q_i \left[1 - \ln \left(\sum_{j=1}^n \theta_j \tau_{ji} \right) - \sum_{j=1}^n \frac{\theta_j \tau_{ij}}{\sum_{k=1}^n \theta_k \tau_{kj}} \right] \quad (6)$$

9

10 here $\phi_i = x_i r_i / (\sum_{i=1}^n x_i r_i)$, $\theta_i = x_i q_i / (\sum_{i=1}^n x_i q_i)$, $l_j = (z/2)(r_j - q_j) - (r_j - 1)$,

11 $\tau_{ji} = \exp[-(u_{ji} - u_{ii}) / RT]$, $\tau_{ij} = \exp[-(u_{ij} - u_{jj}) / RT]$. z is the coordination

12 number and is fixed to 10. ϕ_i and θ_i are the segment fraction and area fraction. The binary

13 interaction parameters (g_{ij} - g_{jj} and g_{ji} - g_{ii} for NRTL, u_{ij} - u_{jj} and u_{ji} - u_{ii} for UNIQUAC) were

14 obtained by minimizing the objection function (OF) and shown in table 2:

$$\text{OF} = \sum_{i=1}^3 \sum_{j=1}^2 \sum_{k=1}^n (x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2 \quad (7)$$

where x_{ijk}^{exp} and x_{ijk}^{cal} denote the mole fraction of the component i in the phase j for the kth experimental and calculated tie-line, respectively. The RMSD values between experimental LLE data and calculated LLE data listed in Table 2 are less than 2.1%, which indicate that all the ternary systems were adequately correlated by using those thermodynamic models. This good agreement can be further observed in Figs 1-2, which were compared with the experimental LLE data.

4.2. Sigma-profiles analysis

The hydrogen bond σ -profiles ($p^{hb}(\sigma)$) and non-hydrogen bond σ -profiles ($p^{nhb}(\sigma)$) of all compounds in the studied ternary system were plotted in Fig 4. Seen from Fig 4(a), the hydrogen bond σ -profile of water has two strong peaks within $0.01\text{e}/\text{\AA}^2$ and $0.02\text{e}/\text{\AA}^2$ and two peaks within $-0.02\text{e}/\text{\AA}^2$ and $-0.01\text{e}/\text{\AA}^2$, indicating water is strong for hydrogen bond interactions and can be classified as a strong polar compound. Hydrogen bonding interaction was caused by the symmetrical peak on positive and negative σ of water, explaining its high boiling point. The $p^{hb}(\sigma)$ of *o*-, *m*-, *p*-cresol show two peaks, one ranges from $0.01\text{e}/\text{\AA}^2$ to $0.015\text{e}/\text{\AA}^2$ and the other one ranges from $-0.02\text{e}/\text{\AA}^2$ to $-0.01\text{e}/\text{\AA}^2$. The negative (positive) σ of cresols forms hydrogen bonding interaction with the positive (negative) screening charge density of water, which may lead to the higher water-solubility of cresols than methylbenzene. The $p^{hb}(\sigma)$ of mesityl oxide have one peak at $0.012\text{e}/\text{\AA}^2$, which leads to favorable hydrogen bonding interaction with the positive screening charge of cresols. This might explain why mesityl oxide or other ketones show higher distribution coefficient and selectivity for cresols than alkane (eg: heptane or octane)[20]. Seen from Fig.4(b), due to a large number of nonpolar groups, mesityl oxide and all three cresols show strong peaks around $0.00\text{e}/\text{\AA}^2$. A high peak of mesityl oxide at $-0.004\text{e}/\text{\AA}^2$ interacts with the peaks of *o*- or *m*- or *p*-cresol between 0.00 and $0.05\text{e}/\text{\AA}^2$ through electrostatic force. The strong interactions between mesityl oxide and *o*- or *m*- or *p*-cresol indicate the high efficiency for mesityl oxide to extract cresols from effluents.

4.3. COSMO-SAC predictions

The tie-line data of the ternary systems, mesityl oxide + *o*-, *m*-, *p*-cresol + water, were predicted by using the COSMO-SAC model. The mole fractions of tie-line data at both phases

predicted by the COSMO-SAC model are listed in Tables S4-S6 in supporting information and shown in Figs.5-6 with comparison with corresponding experimental data. Seen from these figures, the COSMO-SAC model well predict the positive slopes, indicating high efficiency of mesityl oxide to extract cresols from water. The agreement between the COSMO-SAC predictions and the experimental data are better in the aqueous phase than in the organic phase. The RMSD values were shown in Table 3, indicating the COSMO-SAC predictions are quite close to the experimental tie lines.

5. Conclusion

Liquid-liquid equilibrium data were measured for mesityl oxide + *o*-, *m*-, *p*-cresol + water ternary systems at 333.2 K and 353.2 K under 101 kPa. The distribution coefficient and selectivity calculated from the experimental LLE data show that, mesityl oxide is a promising solvent to extract cresols from aqueous solutions. The NRTL and UNIQUAC activity coefficient models were used to correlate the experimental LLE data. The RMSD between experimental LLE data and the NRTL or UNIQUAC results are below 2.1% or 1.5%, respectively. The binary interaction parameters of the NRTL or UNIQUAC models were also calculated to help designing or optimizing an industrial process to extract cresols from effluents. The LLE data were also predicted by the COSMO-SAC model, and the resulting RMSDs from the experimental data range from 4.88% to 5.90% for *o*-cresol, from 4.41% to 6.45% for *m*-cresol, and from 5.09% to 5.44% for *p*-cresol.

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Appendix

COSMO-SAC model

In COSMO-SAC model, the activity coefficient of solute i in the solution S ($\gamma_{i/S}$) is calculated from:

$$\ln \gamma_{i/S} = \frac{\Delta G_{i/S}^{*res} - \Delta G_{i/i}^{*res}}{RT} + \ln \gamma_{i/S}^{comb}$$

where ΔG^{*res} refers to the restoring solvation free energy, γ^{comb} denotes the combinatorial contribution activity coefficient and calculated using the Staverman-Guggenheim model.

After COSMO calculation, the surface of a molecule is dissected to small segments and the screening charges are obtained for each segment. The next equation was used to average these charges to obtain the apparent screening charge which was used in the COSMO-SAC model.

$$\sigma_m = \frac{\sum \sigma_n^* \frac{r_n^2 r_{eff}^2}{r_n^2 + r_{eff}^2} \exp(-f \frac{d_{mn}^2}{r_n^2 + r_{eff}^2})}{\sum \frac{r_n^2 r_{eff}^2}{r_n^2 + r_{eff}^2} \exp(-f \frac{d_{mn}^2}{r_n^2 + r_{eff}^2})}$$

here σ and σ^* represent the charge density after and before this process. The empirical parameter f is 3.57; σ_n denotes the charge density of segment; r_n is the radius of segment n ; and d_{mn} is the distance between segments m and n .

The σ -profile ($p(\sigma)$) is defined as following equation to describe the probability of finding a surface segment with screening charge density σ .

$$p_i(\sigma) = \frac{A_i(\sigma)}{A_i}$$

where $A_i(\sigma)$ refers to the surface area with a charge density of value σ , and A_i is the total surface area of species i . The mixture σ -profile is calculated from:

$$p_s(\sigma) = \frac{\sum_i x_i A_i p_i(\sigma)}{\sum_i x_i A_i}$$

In order to describe the hydrogen-bonding interaction accurately, the σ -profile was including hydrogen-bonding σ -profile ($p^{hb}(\sigma)$) and non-hydrogen bonding σ -profile ($p^{nhb}(\sigma)$), proposed

1 by Lin et al.

$$2 \quad p_i(\sigma) = p_i^{hb}(\sigma) + p_i^{nhb}(\sigma)$$

$$3 \quad \text{Where} \quad p_i^{hb}(\sigma) = p^{HB}(\sigma) \times (A_i^{hb}(\sigma) / A_i) \quad \text{and}$$

$$4 \quad p_i^{nhb}(\sigma) = [1 - p^{HB}(\sigma)] \times (A_i^{hb}(\sigma) / A_i) + (A_i^{nhb}(\sigma) / A_i) \quad . \quad p^{HB}(\sigma) \quad \text{denotes a}$$

5 Gaussian-type function to describe the probability of forming a hydrogen bonding for the
6 hydrogen bonding segments.

$$7 \quad p^{HB}(\sigma) = 1 - \exp\left(-\frac{\sigma^2}{2\sigma_0^2}\right)$$

8 where $\sigma_0 = 0.0007 \text{ e/\AA}^2$.

9 The restoring free energy is determined from:

$$10 \quad \frac{\Delta G_{i/j}^{*res}}{RT} = n_i \sum_s \sum_{\sigma_n}^{nhb,hb} p_i^s(\sigma_m^s) \ln \Gamma_j^s(\sigma_m^s)$$

11 where n_i is the total number of segments in a single molecule of total surface area A_i .

12 Hence

$$13 \quad \ln(\gamma_{i/S}) = n_i \sum_s \sum_{\sigma_m}^{nhb,hb} p_i(\sigma_m^s) [\ln(\Gamma_s^s(\sigma_m^s)) - \ln(\Gamma_i^s(\sigma_m^s))] + \ln(\gamma_i^{SG})$$

14 where $\Gamma_s(\sigma_m)$ and $\Gamma_i(\sigma_m)$ denote the activity coefficient of segment m with a
15 charge density of σ_m in solvent and pure liquid, and expressed as following equations,
16 respectively.

$$17 \quad \ln(\Gamma_s^t(\sigma_m^t)) = -\ln\left[\sum_s \sum_{\sigma_n}^{nhb,hb} p_s(\sigma_n^s) \Gamma_s^s(\sigma_n^s) \exp\left(\frac{-\Delta W(\sigma_m^t, \sigma_n^s)}{RT}\right)\right]$$

$$18 \quad \ln(\Gamma_i^t(\sigma_m^t)) = -\ln\left[\sum_s \sum_{\sigma_n}^{nhb,hb} p_i(\sigma_n^s) \Gamma_i^s(\sigma_n^s) \exp\left(\frac{-\Delta W(\sigma_m^t, \sigma_n^s)}{RT}\right)\right]$$

19 where $\Delta W(\sigma_m^t, \sigma_n^s)$ is the segment exchange energy and determined by following
20 expression.

$$21 \quad \Delta W(\sigma_m^t, \sigma_n^s) = f_{pol} \left(\frac{0.3a_{eff}^{1.5}}{2\sigma_0} \right) (\sigma_m^t + \sigma_n^s)^2 - c_{hb}(\sigma_m^t, \sigma_n^s) (\sigma_m^t - \sigma_n^s)^2$$

22 where $f_{pol} = 0.6916$ and $\epsilon_0 = 2.395 \times 10^{-4} (\text{e}^2 \text{mol}/(\text{kcal}\text{\AA})).$

$$c_{hb}(\sigma_m^t, \sigma_n^s) = \begin{cases} chb, & \text{if } s=t=hb \text{ and } \sigma_m^t \times \sigma_n^s < 0 \\ 0, & \text{otherwise} \end{cases}.$$

2

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1   **Caption of tables**

2   Table 1. Supplier, purity and UNIQUAC parameters of the reagents used in this work.

3   Table 2. NRTL and UNIQUAC binary interaction parameters and RMSD values for the
4   studied systems, Mesityl oxide(1) + Cresol(2) + Water(3).

5   Table 3. RMSD values of COSMO-SAC predictions for the studied systems at 333.2 K and
6   353.2 K.

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2 Table 1. Supplier, purity and UNIQUAC parameters of the reagents used in this work.

component	Supplier	Mass fraction	UNIQUAC parameter	
			r	q
Mesityl oxide	Xiya Reagent	>0.99	4.43632	3.8600
<i>o</i> -Cresol	Xiya Reagent	>0.995	4.2867	3.2480
<i>m</i> -Cresol	Xiya Reagent	>0.995	4.2867	3.2480
<i>p</i> -Cresol	Xiya Reagent	>0.99	4.2867	3.2480
water		deionized water	0.9200	1.4000
<i>n</i> -propyl acetate	Xiya Reagent	>0.99	-	-
Methanol	Xiya Reagent	>0.99	-	-

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2 Table 2. NRTL and UNIQUAC binary interaction parameters and RMSD values for the
3 studied systems, Mesityl oxide(1) + Cresol(2) + Water(3).

<i>T/K</i>	components		UNIQUAC			NRTL	
	<i>i-j</i>	<i>u_{ij}-u_{jj}'</i>	<i>u_{ji}-u_{ii}'</i>	RMSD	<i>g_{ij}-g_{jj}'</i>	<i>g_{ji}-g_{ii}'</i>	RMSD
		J/mol	J/mol		J/mol	J/mol	
Mesityl oxide (1) + <i>o</i> -Cresol (2) + Water (3)							
333.2	1-2	2289.9	-742.8	0.00755	-4061.7	-1954.9	0.00859
	1-3	-4399.3	-1196.8		2121.0	14677.8	
	2-3	1866.7	-4342.6		-5253.4	20097.3	
353.2	1-2	-5738.0	3283.3	0.01097	13194.9	-7733.6	0.01484
	1-3	-3065.0	-1680.8		493.7	16916.3	
	2-3	2908.7	-7215.7		-7260.0	25123.8	
Mesityl oxide (1) + <i>m</i> -Cresol (2) + Water (3)							
333.2	1-2	3035.8	-1755.1	0.00843	-5518.6	-741.0	0.00909
	1-3	-3340.5	-1632.1		1620.0	14641.0	
	2-3	1746.0	-4049.6		-4730.3	19021.7	
353.2	1-2	-6510.4	3383.9	0.01409	15299.8	-8032.9	0.02095
	1-3	-4341.5	-1354.3		1548.8	16178.0	
	2-3	2943.0	-7235.6		-7583.2	25337.0	
Mesityl oxide (1) + <i>p</i> -Cresol (2) + Water (3)							
333.2	1-2	1477.8	-259.2	0.00829	-3495.1	-1868.3	0.01048
	1-3	-3972.6	-1532.9		2131.5	14487.7	
	2-3	2150.5	-5259.6		-5366.5	20734.5	
353.2	1-2	-6678.0	3522.2	0.01508	-9294.3	8338.8	0.01047
	1-3	-2947.6	-1661.6		646.1	16487.4	
	2-3	2673.9	-6633.6		-5403.1	20623.3	

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3 Table 3. RMSD values of COSMO-SAC predictions for the studied systems at 333.2 K and
4 353.2 K.

T/K	RMSD
Mesityl oxide + <i>o</i>-cresol +water	
333.2	0.0488
353.2	0.0590
Mesityl oxide + <i>m</i>-cresol +water	
333.2	0.0441
353.2	0.0645
Mesityl oxide + <i>p</i>-cresol +water	
333.2	0.0509
353.2	0.0544

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Caption of figures

Figure 1. Ternary diagram for experimental LLE data and the corresponding NRTL and UNIQUAC calculated data of the ternary system, Mesityl oxide(1) + Cresol(2) + Water(3), at 333.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

Figure 2. Ternary diagram for experimental LLE data and the corresponding NRTL and UNIQUAC calculated data of the ternary system, Mesityl oxide(1) + Cresol(2) + Water(3), at 353.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

Figure 3. Distribution coefficient (D) and Selectivity (S) of *o*-, *m*-, *p*-cresol versus the mole fraction of *o*-, *m*-, *p*-cresol in aqueous phase at different temperatures, respectively.

Figure 4. Hydrogen bonding σ -profiles ($p^{hb}(\sigma)$) and non-hydrogen bonding σ -profiles ($p^{nhb}(\sigma)$) of the chemicals used in our work.

Figure 5. Experimental and COSMO-SAC predictions for the tie lines of the system, Mesityl oxide(1) + Cresols(2) + Water(3), at 333.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

Figure 6. Experimental and COSMO-SAC predictions for the tie lines of the system, Mesityl oxide(1) + Cresols(2) + Water(3), at 353.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

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6 Figure 1. Ternary diagram for experimental LLE data and the corresponding NRTL and
 7 UNIQUAC calculated data of the ternary system, Mesityl oxide(1) + Cresol(2) + Water(3), at
 8 333.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

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8 Figure 2. Ternary diagram for experimental LLE data and the corresponding NRTL and

9 UNIQUAC calculated data of the ternary system, Mesityl oxide(1) + Cresol(2) + Water(3), at

10 353.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

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4 Figure 3. Distribution coefficient (D) and Selectivity (S) of *o*-, *m*-, *p*-cresol versus the mole
5 fraction of *o*-, *m*-, *p*-cresol in aqueous phase at different temperatures, respectively.

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4 Figure 4. Hydrogen bonding σ -profiles ($p^{hb}(\sigma)$) and non-hydrogen bonding σ -profiles ($p^{nhb}(\sigma)$)
 5 of the chemicals used in our work.

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Figure 5. Experimental and COSMO-SAC predictions for the tie lines of the system, Mesityl oxide(1) + Cresols(2) + Water(3), at 333.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

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6 Figure 6. Experimental and COSMO-SAC predictions for the tie lines of the system, Mesityl
7 oxide(1) + Cresols(2) + Water(3), at 353.2 K; (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol.

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