Liquid-liquid equilibrium for ternary systems, methyl isobutyl ketone +(catechol , resorcinol and hydroquinone) + water at 333.15 K, 343.15 K and 353.15 K

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ABSTRACT

Liquid-liquid equilibrium (LLE) data are vital to extraction process design and optimization. To provide fundamental data for the extracting process of dihydric phenol from wastewater, experimental liquid liquid equilibrium data for ternary systems {methyl isobutyl ketone + catechol + water}, {methyl isobutyl ketone + resorcinol + water} and {methyl isobutyl ketone + hydroquinone + water} were determined at 333.15 K, 343.15 K and 353.15 K under atmospheric pressure. The NRTL and UNIQUAC models were used to correlate the experimental data and relevant binary interaction parameters were yielded. The experimental data were successfully correlated with the two models, and the root mean square deviations (RMSD) between the calculated and experimental values were less than 2%. Moreover, NRTL model performed slightly better than UNIQUAC model since the RMSD was smaller. Distribution coefficient and selectivity were employed to assess methyl isobutyl ketone's extraction capacity, which indicate that, methyl isobutyl ketone is a desirable extractant with

extraction performance and physiochemical properties outperforming other extractants.

Keywords: Liquid-liquid equilibrium; Methyl isobutyl ketone; Catechol; Resorcinol; Hydroquinone

1. Introduction

Gasification and low temperature distillation process for low quality coal produce wastewater with high concentration of phenol and ammonia, which contains organic pollutants such as volatile phenols (e.g. phenol, cresols), non-volatile phenols (e.g. dihydric phenols and trihydric phenols), etc[1]. Non-volatile phenols such as catechol, resorcinol and hydroquinone are highly toxic, and the lethality (intra-abdominal injection, 100% death in 2 hour) of dihydric phenols for *Dicentrarchus labrax* is 5.8 mg/100g [2]. It is because of all these undesirable ecological effects of phenols that, strict regulations have been placed on their concentration in surface water around many countries (e.g. less than 0.5 ppm) [3] and there has been long standing effort to remove phenols from industrial wastewaters before discharging them to the environment.

Solvent extraction is the most common method to treat high concentration phenol and ammonia wastewater in chemical industries, which mainly includes following steps: firstly, removing coal tar and sludge from wastewater; secondly, sending high concentration phenol and ammonia wastewater to a stripper with side-draw to remove ammonia and sour gas simultaneously [4]; thirdly, after exchanging with the hot feeding stream and cooling with circulating water, sewage effluent from stripper bottom will flow into an extraction tower and countercurrent extract with extracting agent [5, 6]. After extraction, solvent recovered from the extraction or the raffinate phase are sent back to the extraction column for recycling. Most LLE or solvent extraction study of phenols were carried out below 328 K, since the industrial treatment of phenolic wastewater have normally been performed in this temperature range. This usually lead to a severe problem that, the paraffin wax (melting point range between 328 K and 335 K) in the wastewater would clog the extraction device [7]. Such problem is critical for treating wastewater in the coal gasification or distillation industry [1], which forces some commercial plants (e.g. Harbin Coal Chemical Industry Co. Ltd. in China [4, 6]) elevate the extraction temperature to above 333 K with ketones as the extractant. Therefore, to study the

liquid-liquid equilibrium of ketone-phenols-water systems above 333 K is of great significance for industrial wastewater treatment [8].

Liquid-liquid equilibria (LLE) data are essential for designing or optimizing an extraction process[9-11]. LLE data of some ternary solvent-dihydric phenols-water systems have been published in recent years. Lei et al.[12] measurement the LLE data of the quaternary system, {2-methoxy-2-methylpropane + phenol + hydroquinone + water}, at 313.15K. Xu et al.[13] studied the quaternary system of {water + isopropyl ether + phenol + hydroquinone} at 319.15K. Lv et al.[14] reported the LLE data of the systems {MIPK + hydroquinone + water} and {MIPK + resorcinol + water} 298.15K, 313.15K and 323.15K. However, these solvents have some shortcomings when they are used to extract phenols in industry, especially at moderate temperatures. The extraction efficiency (e.g. distribution coefficient or selectivity) of 2-methoxy-2-methylpropane (boiling point 328.15K) and isopropyl ether (boiling point 341.15K) for dihydric phenols are quite low (distribution coefficient are less than 10). Additionally, they are not suitable for extraction at moderate temperatures due to their low boiling points. Methyl isobutyl ketone (MIBK, boiling point 389.15K) is a desirable solvent because of its desirable physical properties and high extraction efficiency for dihydric phenols. The LLE data of the ternary systems, {methyl isobutyl ketone + 1,2-benzenediol + water}, {methyl isobutyl ketone + *m*-Benzenediol + water} at 298.15K, 308.15K and 318.15K, {methyl isobutyl ketone + hydroquinone + water} at 298.15K, 303.15K and 323.15K, and the quaternary system, {methyl isobutyl ketone + phenol + hydroquinone + water}, have been reported by Yang et al.[15-18]. Wang et al. studied the systems {methyl isobutyl ketone + *m*-, *o*-, *p*-cresol + water} at 333.15K, 343.15 K, 353.15 K and system {methyl isobutyl ketone + phenol + water} at 333.15K, 343.15 K, 353.15 K [19, 7]. However, those of the ternary systems, {methyl isobutyl ketone + catechol, resorcinol and hydroquinone + water}, above 333.15 K have not been published yet.

In this work, liquid-liquid equilibrium data for ternary systems, {MIBK + catechol + water}, {MIBK + resorcinol + water} and {MIBK + hydroquinone + water}, were measured at 333.15K, 343.15K and 353.15K under atmospheric pressure. These LLE data were used to calculate binary interaction parameters with the NRTL[20] and UNIQUAC[21] models.

2 Experimental

2.1 Materials

The purity and source of chemical reagents in this work are listed in Table 1. These chemicals were used without further purification since their purity had been verified with analysis methods listed in Table 1. Distilled water was used throughout all experiments.

2.2 Apparatus and procedure

A 100 mL glass equilibrium cell, a thermostatically controlled bath, a magnetic agitator, an analytical balance and gas chromatography were used in this work to measure the LLE data for the ternary systems, {MIBK + catechol + water}, {MIBK + resorcinol + water} and {MIBK + hydroquinone + water} at (333.15, 343.15 and 353.15) K under atmospheric pressure. The mixture of MIBK, catechol, resorcinol or hydroquinone and water was loaded into a glass equilibrium cell and was agitated vigorously for more than 2 h to mix thoroughly, then was left to settle for at least 20 h to reach the phase equilibrium. The temperature of the mixture in the cell was kept constant by using a thermostatic bath with a fluctuation of 0.1 K.

After the ternary mixture formed two phases, a sample was taken from each phase using a syringe and was analyzed by a gas chromatography (GC 6820, Agilent Technologies) equipped with a flame ionization detector (FID, with a sensitivity of 10 -100 ppb) and a DB-5MS capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 μ m). The initial oven temperature was held at 313.15 K for 2 min and then increased to 443.15 K at a rate of 30 K $\cdot$ min⁻¹. The detector and injector temperatures were held at 523.15 K and 533.15 K, respectively. The nitrogen was used as the carrier gas with a rate of 30 ml $\cdot$ min⁻¹. The solvent used in the GC analysis was methanol to dilute the samples.

The composition of the sample was determined by an internal standard method, where *n*-butyl acetate was used as the internal standard for MIBK and *n*-octanol for catechol, resorcinol and hydroquinone. The mole fraction of water was calculated from deducting those of the other two components (MIBK and dihydric phenols) from 1. The samples and internal standards were weighed by an analytical balance (Shimadzu AUW220D) with an accuracy of 0.1mg. Each sample was GC analyzed for at least 3 times, with a standard deviation of less than 0.2 %, thus the average value was reported.

3 Results and discussion

The experimental tie line data for the studied systems, {MIBK + catechol + water}, {MIBK

+ resorcinol + water} and {MIBK + hydroquinone + water}, were determined at (333.15, 343.15 and 353.15) K under atmospheric pressure. The extraction efficiency of MIBK for catechol, resorcinol and hydroquinone is assessed by distribution coefficient (D) and separation factor (S), defined as follows:

$$D = \frac{x_{21}}{x_{23}} \quad (1)$$

$$S = D \frac{x_{33}}{x_{31}} \quad (2)$$

where x_{21} and x_{23} are diphenols mole fraction in the organic and the aqueous phases, respectively, x_{31} and x_{33} are water mole fraction in the organic and the aqueous phases, respectively. Tables 2-4 summarize the LLE data (expressed in mole fraction), distribution coefficient and selectivity for studied systems at different temperatures. Figs 4-9 show that the influence of temperature on the distribution coefficient and selectivity, and the distribution coefficient and selectivity at 333.15K, 343.15K, 353.15K were compared to low temperature (298.15K, 313.15K, 323.15K) [18] for the system {methyl isobutyl ketone + hydroquinone + water}. These tables and figures indicate that for the ternary system, at the same temperature, with the increase of diphenols in the aqueous phase, the distribution coefficient and selectivity decreases. On the other hand, the distribution coefficient and selectivity decreases slightly as the system temperature increases. In addition, the influence of temperature on LLE data is insignificant, in other words, temperature affect LLE data very slightly.

The NRTL and UNIQUAC models were used to correlate the experimental data and to yield binary interaction parameters. Figs 1-3 show the triangle phase diagrams of experimental data and corresponding calculated results at studied temperatures. All these figures show that, the calculated results are in good agreement with experimental data, which confirms both NRTL and UNIQUAC models are suitable for simulating the processes of extracting catechol, resorcinol or hydroquinone with MIBK at studied temperatures.

The root-mean-square deviation (RMSD) between experimental and calculated mole fractions was calculated according to the following equation:

$$\text{RMSD} = \left[\frac{\sum_{i=1}^3 \sum_{j=1}^2 \sum_{k=1}^n (x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2}{6n} \right]^{1/2} \quad (3)$$

where subscripts i, j and k refer to the components, the phases and the tie-lines, respectively, n is the number of tie lines, x^{exp} and x^{cal} are the experimental mole fraction and calculated mole fraction respectively. RMSD values for the three studied systems at 333.15K, 343.15K and 353.15K K are shown in Table 6, which are all less than 0.02. This indicates these two models show good representation of the tie-line data for the studied systems. The NRTL model is more accurate than the UNIQUAC model with even smaller RMSD. The binary interaction parameters (g_{ij} - g_{jj} and g_{ji} - g_{ii} , u_{ij} - u_{jj} and u_{ij} - u_{ji}) were obtained by minimizing the objective function (OF) :

$$\text{OF} = \sum_{i=1}^3 \sum_{j=1}^2 \sum_{k=1}^n \left[\frac{(T_k^{\text{exp}} - T_k^{\text{cal}})^2}{\sigma_T^2} + \frac{(x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2}{\sigma_x^2} \right] \quad (4)$$

where T^{exp} and T^{cal} are the experimental and calculated temperature respectively, σ_T and σ_x denote the standard deviation of the temperature and the mole fraction. The binary interaction parameters of the NRTL and UNIQUAC models and non-randomness parameters (α_{ij}) of the NRTL model for the ternary systems are shown in Table 6. The UNIQUAC structural parameters (r and q) taken from the literature [22, 23] are shown in Table 5.

There have been reported a couple of other LLE studies on dihydric phenols: e.g. {MIBK + catechol /resorcinol + water} at 298.15K, 308.15K and 318.15K [15, 16] and {MIBK + hydroquinone + water} at 298.15K, 313.15K and 323.15K[17]. Taking into account the available experimental data, the extraction efficiency of MIBK for hydroquinone was compared with MIPK in details. At 323.15K, the distribution coefficient and selectivity of MIBK for hydroquinone are considerably higher than MIPK (Fig.S1&S2). The distribution coefficient and selectivity of MIBK at 343.15K are lower than those at 323.15K, indicating higher temperature usually decrease the extraction efficiency, thus to screen a proper extractant is even more important for higher temperature extraction. The energy consumption and operation cost of extracting hydroquinone with MIBK were also considerably lower than MIPK, due to its higher extraction efficiency (table S1&S2). All these results show MIBK

should be even more promising than MIPK in extracting dihydric phenols such as hydroquinone.

4. Conclusions

The phase diagrams of the ternary systems, {MIBK + catechol + water}, {MIBK + resorcinol + water} and {MIBK + hydroquinone + water}, were measured at (333.15, 343.15 and 353.15) K under atmospheric pressure. These LLE data were correlated by using the NRTL and UNIQUAC models, which both described the phase behavior of the studied systems very accurately and yielded relevant binary interaction parameters among MIBK, water, and catechol, resorcinol or hydroquinone. MIBK was shown to be a very promising extractant than MIPK to recover dihydric phenols by comparing the distribution coefficient, selectivity, energy consumption and cost for the systems {MIBK + hydroquinone + water} at 323.15K and 343.15K, {MIPK + hydroquinone + water} at 323.15K.

Acknowledgments

Financial support from Project of the Science & Technology New Star of Pearl River in Guangzhou (2011J2200056), the Fundamental Research Funds for the Central Universities, SCUT (2014ZZ0057 and 2015ZM046), Guangdong Science Foundation (2014A030310260) and National Science Foundation of China (20906028 and 21506066) are gratefully acknowledged.

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Caption of Tables and Figures

Tables

Table 1 Source and purity of the materials studied.

Table 2 LLE data (mole fraction) for {MIBK(1) + catechol(2) + water(3)} at (333.15, 343.15, 353.15) K and pressure $p=0.1\text{Mpa}$.^a

Table 3 LLE data (mole fraction) for {MIBK(1) + resorcinol(2) + water(3)} at (333.15, 343.15, 353.15) K and pressure $p=0.1\text{Mpa}$.^a

Table 4 LLE data (mole fraction) for {MIBK(1) + hydroquinone(2) + water(3)} at (333.15, 343.15, 353.15) K and pressure $p=0.1\text{Mpa}$.^a

Table 5 UNIQUAC Structural (Area and Volume) Parameters

Table 6 Binary Interaction Parameters of NRTL and UNIQUAC Model for the studied systems at different temperatures.

Figures

Fig. 1. LLE phase diagram for LLE data of {MIBK(1) + catechol (2) + water (3)} at 333.15 K and atmospheric pressure: □-□, experimental data; ●, calculated data from NRTL model; Δ, calculated data from UNIQUAC model.

Fig. 2. LLE phase diagram for LLE data of {MIBK(1) + resorcinol (2) + water (3)} at 333.15 K and atmospheric pressure: □-□, experimental data; ●, calculated data from NRTL model; Δ, calculated data from UNIQUAC model.

Fig. 3. LLE phase diagram for LLE data of {MIBK(1) + hydroquinone (2) + water (3)} at 333.15 K and atmospheric pressure: □-□, experimental data; ●, calculated data from NRTL model; Δ, calculated data from UNIQUAC model.

Fig. 4. Distribution coefficient of catechol versus its mole fraction in aqueous phase at different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 5. Selectivity of catechol versus its mole fraction in aqueous phase at different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 6. Distribution coefficient of resorcinol versus its mole fraction in aqueous at phase different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 7. Selectivity of resorcinol versus its mole fraction in aqueous phase at different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 8. Distribution coefficient of hydroquinone versus its mole fraction in aqueous phase at different temperatures: □, 298.15 K; ○, 313.15 K; Δ, 323.15 K; ■, 333.15 K; ●, 343.15 K; ▲, 353.15 K.

Fig. 9. Selectivity of hydroquinone versus its mole fraction in aqueous phase at different temperatures: □, 298.15 K; ○, 313.15 K; Δ, 323.15 K; ■, 333.15 K; ●, 343.15 K; ▲, 353.15 K.

Table 1

Source and purity of the materials studied.

Component	Source	Stated fraction purity	Mass	Purification method	Analysis method
methanol	Xiya Reagent	≥0.99		None	GC ^a
catechol	Xiya Reagent	≥0.99		None	GC ^a
resorcinol	Xiya Reagent	≥0.99		None	GC ^a
hydroquinone	Xiya Reagent	≥0.99		None	GC ^a
n-butyl acetate	Xiya Reagent	≥0.99		None	GC ^a
n-octanol	Xiya Reagent	≥0.99		None	GC ^a
methyl isobutyl ketone	Xiya Reagent	≥0.99		None	GC ^a

^a Gas chromatography

Table 2

LLE data (mole fraction) for {MIBK(1) + catechol(2) + water(3)} at (333.15, 343.15, 353.15) K and pressure $p=0.1\text{Mpa}$.^a

T/K	Organic Phase			Aqueous phase			D	S
	x_1	x_2	x_3	x_1	x_2	x_3		
333.15	0.3423	0.1486	0.5091	0.0010	0.0036	0.9955	41	80
	0.4009	0.1269	0.4722	0.0010	0.0028	0.9962	45	95
	0.4270	0.1168	0.4562	0.0011	0.0025	0.9964	47	103
	0.4632	0.1024	0.4344	0.0012	0.0020	0.9967	51	117
	0.4912	0.0910	0.4178	0.0014	0.0017	0.9969	54	129
	0.5342	0.0789	0.3869	0.0015	0.0014	0.9970	56	144
	0.5514	0.0655	0.3831	0.0016	0.0012	0.9972	55	143
	0.6012	0.0470	0.3517	0.0018	0.0008	0.9974	59	167
	0.6675	0.0211	0.3114	0.0020	0.0003	0.9977	70	224
	0.8109	0.0000	0.1891	0.0023	0.0000	0.9977		
343.15	0.3225	0.1411	0.5364	0.0010	0.0040	0.9951	35	65
	0.3838	0.1208	0.4954	0.0010	0.0029	0.9961	42	84
	0.4088	0.1121	0.4791	0.0011	0.0026	0.9963	43	89
	0.4397	0.1010	0.4593	0.0011	0.0022	0.9967	46	100
	0.4693	0.0901	0.4406	0.0012	0.0019	0.9969	47	106
	0.5012	0.0780	0.4208	0.0014	0.0015	0.9971	52	123
	0.5258	0.0685	0.4057	0.0015	0.0013	0.9973	53	130
	0.5732	0.0466	0.3801	0.0017	0.0008	0.9975	58	152
	0.6521	0.0236	0.3243	0.0018	0.0004	0.9978	59	182
	0.7410	0.0000	0.2590	0.0022	0.0000	0.9978		
353.15	0.3099	0.1399	0.5502	0.0009	0.0043	0.9947	33	60
	0.3719	0.1238	0.5043	0.0010	0.0033	0.9957	38	75
	0.3981	0.1126	0.4892	0.0011	0.0029	0.9961	39	79
	0.4227	0.1020	0.4754	0.0011	0.0025	0.9964	41	86
	0.4639	0.0951	0.4410	0.0012	0.0022	0.9966	43	97
	0.4882	0.0843	0.4275	0.0013	0.0018	0.9969	47	110
	0.5186	0.0705	0.4109	0.0014	0.0015	0.9971	47	114
	0.5597	0.0514	0.3888	0.0015	0.0010	0.9975	51	131
	0.6224	0.0271	0.3505	0.0018	0.0005	0.9977	54	154
	0.6924	0.0000	0.3076	0.0019	0.0000	0.9981		

^a Standard uncertainties u are $u(T) = 0.1\text{ K}$, $u(p)=1\text{kPa}$, $u(x)=0.0008$

Table 3

LLE data (mole fraction) for {MIBK(1) + resorcinol(2) + water(3)} at (333.15, 343.15, 353.15) K and pressure $p=0.1\text{Mpa}$.^a

T/K	Organic Phase			Aqueous phase			D	S
	x_1	x_2	x_3	x_1	x_2	x_3		
333.15	0.4106	0.1470	0.4424	0.0010	0.0034	0.9956	43	97
	0.4722	0.1238	0.4040	0.0010	0.0026	0.9963	48	118
	0.5004	0.1130	0.3866	0.0012	0.0023	0.9966	49	126
	0.5251	0.1019	0.3730	0.0012	0.0020	0.9968	51	136
	0.5495	0.0879	0.3625	0.0014	0.0017	0.9969	52	143
	0.5873	0.0712	0.3416	0.0016	0.0013	0.9972	55	161
	0.6197	0.0602	0.3201	0.0017	0.0010	0.9973	60	187
	0.6901	0.0412	0.2687	0.0018	0.0007	0.9975	59	219
	0.7325	0.0231	0.2444	0.0019	0.0004	0.9977	58	237
	0.8109	0.0000	0.1891	0.0023	0.0000	0.9977		
343.15	0.3796	0.1509	0.4695	0.0010	0.0039	0.9952	39	83
	0.4310	0.1320	0.4370	0.0010	0.0031	0.9958	43	98
	0.4606	0.1216	0.4177	0.0011	0.0028	0.9961	43	103
	0.4837	0.1087	0.4076	0.0012	0.0024	0.9964	45	110
	0.5083	0.0960	0.3957	0.0014	0.0020	0.9966	48	121
	0.5333	0.0869	0.3798	0.0015	0.0018	0.9968	48	126
	0.5849	0.0616	0.3535	0.0017	0.0012	0.9971	51	144
	0.6494	0.0412	0.3094	0.0018	0.0007	0.9974	59	190
	0.6808	0.0284	0.2908	0.0019	0.0005	0.9976	57	196
	0.7410	0.0000	0.2590	0.0022	0.0000	0.9978		
353.15	0.3752	0.1519	0.4729	0.0009	0.0041	0.9949	37	78
	0.4114	0.1303	0.4584	0.0010	0.0034	0.9956	38	83
	0.4406	0.1189	0.4405	0.0011	0.0030	0.9959	40	90
	0.4572	0.1078	0.4350	0.0012	0.0027	0.9962	40	92
	0.4865	0.0967	0.4168	0.0014	0.0023	0.9963	42	100
	0.5131	0.0904	0.3965	0.0015	0.0020	0.9965	45	113
	0.5597	0.0675	0.3728	0.0016	0.0015	0.9970	45	120
	0.6140	0.0438	0.3422	0.0017	0.0008	0.9975	55	160
	0.6533	0.0307	0.3160	0.0018	0.0006	0.9976	51	161
	0.6924	0.0000	0.3076	0.0019	0.0000	0.9981		

^a Standard uncertainties u are $u(T) = 0.1\text{ K}$, $u(p)=1\text{kPa}$, $u(x)=0.0008$

Table 4

LLE data (mole fraction) for {MIBK(1) + hydroquinonel(2) + water(3)} at (333.15, 343.15, 353.15) K and pressure $p=0.1\text{Mpa}$.^a

T/K	Organic Phase			Aqueous phase			D	S
	x_1	x_2	x_3	x_1	x_2	x_3		
333.15	0.4524	0.0986	0.4490	0.0012	0.0041	0.9946	24	53
	0.4773	0.0913	0.4314	0.0013	0.0036	0.9951	25	58
	0.4871	0.0885	0.4244	0.0014	0.0034	0.9952	26	61
	0.5143	0.0802	0.4055	0.0015	0.0029	0.9956	28	69
	0.5515	0.0684	0.3801	0.0016	0.0023	0.9961	30	79
	0.5906	0.0556	0.3538	0.0017	0.0017	0.9966	33	93
	0.6120	0.0483	0.3396	0.0018	0.0015	0.9968	32	94
	0.6543	0.0335	0.3122	0.0019	0.0009	0.9972	37	118
	0.7011	0.0165	0.2824	0.0020	0.0004	0.9976	41	145
	0.8109	0.0000	0.1891	0.0023	0.0000	0.9977		
343.15	0.4346	0.0976	0.4678	0.0012	0.0047	0.9941	21	45
	0.4546	0.0902	0.4551	0.0013	0.0041	0.9947	22	48
	0.4608	0.0880	0.4512	0.0014	0.0039	0.9947	23	51
	0.5074	0.0810	0.4117	0.0015	0.0033	0.9952	25	60
	0.5383	0.0692	0.3924	0.0016	0.0026	0.9958	27	69
	0.5734	0.0556	0.3710	0.0016	0.0020	0.9964	28	75
	0.5921	0.0482	0.3596	0.0017	0.0016	0.9966	30	83
	0.6226	0.0360	0.3415	0.0018	0.0012	0.9970	30	88
	0.6967	0.0189	0.2845	0.0019	0.0005	0.9976	38	133
	0.7410	0.0000	0.2590	0.0022	0.0000	0.9978		
353.15	0.4304	0.0985	0.4711	0.0012	0.0049	0.9939	20	42
	0.4520	0.0910	0.4569	0.0012	0.0044	0.9944	21	46
	0.4606	0.0874	0.4521	0.0013	0.0041	0.9945	21	46
	0.4951	0.0804	0.4245	0.0014	0.0036	0.9950	22	52
	0.5211	0.0689	0.4100	0.0016	0.0029	0.9955	24	58
	0.5499	0.0560	0.3941	0.0016	0.0023	0.9961	24	61
	0.5701	0.0517	0.3782	0.0017	0.0020	0.9963	26	68
	0.6182	0.0392	0.3426	0.0018	0.0014	0.9968	28	81
	0.6902	0.0207	0.2891	0.0019	0.0007	0.9975	30	104
	0.6924	0.0000	0.3076	0.0019	0.0000	0.9981		

^a Standard uncertainties u are $u(T) = 0.1\text{ K}$, $u(p)=1\text{kPa}$, $u(x)=0.0008$

Table 5

UNIQUAC Structural (Area and Volume) Parameters

component	r	q
water	0.9200	1.4000
MIBK	4.5967	3.9560
catechol	3.9156	3.0080
resorcinol	3.9156	3.0080
hydroquinonel	3.9156	3.0080

Table6

Binary Interaction Parameters of NRTL and UNIQUAC Model for the studied systems at different temperatures.

T/K	components	UNIQUAC			NRTL			RMSD
	$i-j$	$u_{ij}-u_{jj}$ /J·mol ⁻¹	$u_{ji}-u_{ii}$ /J·mol ⁻¹	RMSD	$g_{ij}-g_{jj}$ /J·mol ⁻¹	$g_{ji}-g_{ii}$ /J·mol ⁻¹	α_{ij}	
MIBK(1) + catechol(2) + water (3)								
333.15	1-2	-2411.22	1909.23	0.0040	-421.18	-1657.31	0.3	0.0032
	1-3	-677.09	-2706.21		-1271.2	18663.85	0.2	
	2-3	2648.51	-4907.92		-7102.65	18603.24	0.2	
343.15	1-2	-1954.54	1655.82	0.0045	-1135.11	-1481.30	0.3	0.0031
	1-3	-989.70	-2601.87		-1466.42	19553.86	0.2	
	2-3	2452.05	-4359.53		-7869.87	2340.06	0.2	
353.15	1-2	-618.31	853.18	0.0059	-1163.21	-1183.83	0.3	0.0041
	1-3	-587.22	-2989.38		-1748.52	20455.43	0.2	
	2-3	2192.57	-3725.75		-7919.5	19783.74	0.2	
MIBK(1) +resorcinol(2) + water (3)								
333.15	1-2	-4279.63	2683.93	0.0033	-341.87	-1653.07	0.3	0.0029
	1-3	-1574.75	-2184.50		-305.12	17889.73	0.2	
	2-3	2806.22	-5041.44		-7139.15	18695.69	0.2	
343.15	1-2	-2049.98	1687.74	0.0038	-1359.09	-908.72	0.3	0.0030
	1-3	-1038.67	-2552.56		-957.02	18954.92	0.2	
	2-3	2546.41	-4586.59		-6800.44	18038.55	0.2	
353.15	1-2	-618.31	853.18	0.0038	-2100.95	-69.42	0.3	0.0029
	1-3	-587.22	-2989.38		-1437.32	19979.95	0.2	
	2-3	2192.57	-3725.75		-6715.30	17990.50	0.2	
MIBK(1) +hydroquinone(2) + water (3)								
333.15	1-2	-1132.03	1530.44	0.0056	-2078.83	-2396.43	0.3	0.0028
	1-3	-950.54	-2478.65		-919.19	18215.14	0.2	
	2-3	2545.50	-3628.64		-7591.68	15320.04	0.2	
343.15	1-2	-1974.24	2009.66	0.0074	-1950.05	-2653.33	0.3	0.0034
	1-3	-785.51	-2710.94		-1049.31	18969.47	0.2	
	2-3	2955.05	-4672.55		-8338.28	16309.66	0.2	
353.15	1-2	-826.91	1215.09	0.0082	-1765.39	-1727.98	0.3	0.0038
	1-3	-595.78	-2959.12		-1218.75	19746.58	0.2	
	2-3	2585.90	-3858.11		-8454.17	17672.82	0.2

Fig. 1. LLE phase diagram for LLE data of {MIBK(1) + catechol (2) + water (3)} at 333.15 K and atmospheric pressure: □-□, experimental data; ●, calculated data from NRTL model; Δ, calculated data from UNIQUAC model.

Fig. 2. LLE phase diagram for LLE data of {MIBK(1) + resorcinol (2) + water (3)} at 333.15 K and atmospheric pressure: □-□, experimental data; ●, calculated data from NRTL model; △, calculated data from UNIQUAC model.

Fig. 3. LLE phase diagram for LLE data of {MIBK(1) + hydroquinone (2) + water (3)} at 333.15 K and atmospheric pressure: □-□, experimental data; ●, calculated data from NRTL model; Δ, calculated data from UNIQUAC model.

Fig. 4. Distribution coefficient of catechol versus its mole fraction in aqueous phase at different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 5. Selectivity of catechol versus its mole fraction in aqueous phase at different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 6. Distribution coefficient of resorcinol versus its mole fraction in aqueous at phase different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 7. Selectivity of resorcinol versus its mole fraction in aqueous phase at different temperatures: ■, 333.15 K; ○, 343.15 K; ▲, 353.15 K.

Fig. 8. Distribution coefficient of hydroquinone versus its mole fraction in aqueous phase at different temperatures: □, 298.15 K; ○, 313.15 K; △, 323.15 K; ■, 333.15 K; ●, 343.15 K; ▲, 353.15 K.

Fig. 9. Selectivity of hydroquinone versus its mole fraction in aqueous phase at different temperatures:
□, 298.15 K; ○, 313.15 K; △, 323.15 K; ■, 333.15 K; ●, 343.15 K; ▲, 353.15 K.