Liquid-liquid equilibria for ternary systems polyoxymethylene dimethyl ethers + para-xylene + water

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Abstract

Polyoxymethylene dimethyl ethers (PODE_n) are promising diesel additives which can be synthesized from formaldehyde and methanol. In this work, the ternary liquid-liquid equilibria (LLE) were analytically determined at 293.15 K and 313.15 K for the following systems: PODE₁+para-xylene(PX)+water, PODE₂+PX+water, PODE₃+PX+water, PODE₄+PX+water, respectively. The isothermal experimental results have shown a good linear fit in Hand plots and the Othmer-Tobias. The design of the solvent extraction equipment for extracting PODE_n from aqueous solution requires an appropriate model for the liquid-liquid phase equilibrium. The well-known NRTL and UNIQUAC thermodynamic models were applied to correlate the experimental data, and the results indicate that the UNIQUAC model gives a better agreement.

Keywords: Polyoxymethylene dimethyl ether; Water; Para-xylene; Liquid-liquid equilibria

1. Introduction

As environmental issues become more urgent, the development of efficient diesel additives for reduction of emissions of particular materials (PM) and NO_x is highly desirable. Oxygenated compounds such as methanol, dimethyl ether (DME) and methylal are known to reduce soot formation during combustion when they are added into diesel fuels [1, 2]. However, due to the lower cetane number and high vapor pressure of DME [4], methanol [5], and methylal [6], they are not suitable for incorporation into diesel directly without modification of the engine's infrastructure. To overcome these disadvantages, a more attractive solution polyoxymethylene dimethyl ethers (PODE_n, CH₃O(CH₂O)_nCH₃) is being used as a diesel fuel additive. PODE₃₋₄ are believed to be the most appreciate constituents as diesel fuel additives among all PODE_n compounds [2, 3], which can be blended into diesel without structural changes of diesel engine.

Generally, PODE_n are synthesized from two routes [7]: one is methylal + trioxane (or paraformaldehyde) and the other is methanol + formaldehyde (FA). However, the first route is believed to be not appropriate for PODE_n synthesis in industrial production due to the high cost of raw materials; therefore, the second route has been found as an alternative way for the production of PODE_n and it is of great importance from the industrial view due to its lower raw materials' cost. However, this reaction system brings serious problems in separation process.

It is difficult to obtain highly purified desired products (e.g., PODE₃₋₄) from the reaction products in the presence of water [7-11]. Above a certain temperature, water reacts with the PODE_n in an acid-catalyzed reaction forming alcohols, such as the reaction of PODE₁ with water to form hemiformal, i.e., CH₃OCH₂OH (or poly- hemiformals, i.e., CH₃O(CH₂O)_nCH₂OH) and methanol [8-11].

During the PODE_n synthesis reactions process, based on the report of J. Burger [8], high concentration formaldehyde solution is always used to improve the selectivity of PODE₃₋₄, according to the following reactions:

Reactions 3 and 4 are reversible in acidic conditions and lead to an equilibrium chain distribution which mainly depends on the formaldehyde concentration in the reaction. Increasing the formaldehyde concentration shifts the distribution to longer chains, but the formaldehyde solution with high concentration is easy to be polymerized, which forms paraformaldehyde as white solid blocking pipelines.

These problems have brought great difficulty in the distillation operation, and made it hard to obtain pure products in PODE synthesis process. In addition, how to recycle massive formaldehyde in educts as raw material for reaction should also be considered.

Solvent extraction process was therefore developed by introducing para-xylene as an extracting solvent. In proper solvent extraction, water could be separated from reaction products to inhibit reactions 1 and 2. On the other hand, massive formaldehyde could be recycled in water-rich phase, which associates strongly with water in oligomers as followings [10, 12]:

LLE data are valuable in studies of the applicability of activity coefficient. A reliable thermodynamic model for a good system description is important for equipment modeling, development and design [13]. Although there is a growing industrial interest in the separation

processes associated in PODE_n production, there are few experimental LLE data on these systems. M. Albert [14] measured the LLE of (water+methylal(PODE_1)) and (water+methanol+methylal), and related data were correlated well using the UNIQUAC model. C. Kuhnert [10] modeled the LLE of ternary system (formaldehyde+water+methylal) well by revised UNIFAC. No experimental data of $\text{PODE}_{n>1}$ could be obtained from current literatures. Some investigations have been carried out on hydrophobic solvents which influence separation effectiveness, immiscibility region, and LLE behavior of ternary systems. Several aromatic compounds have been chosen because of their low solubility in aqueous phase [15-18].

Additionally, due to the complexity of compositions in PODE_n reaction system, the boiling point of the lightest component PODE_1 is only 315.15 K [14] in ambient pressure. To recycle raw material PODE_1 as much as possible, the actual extraction temperature should not exceed the highest temperature limit of 315.15 K, while the lower operation temperature will lead to much higher extraction cost. The operation temperature range between 293.15 K and 313.15 K in PODE_n extraction plant is more economical.

As no available literature data on liquid-liquid phase equilibrium of multicomponent mixtures (PODE_n +water) and extraction solvent para-xylene, this contribution reported experimental results of the phase equilibrium in such mixtures: liquid-liquid equilibrium of ternary systems (PODE_1 +PX+water), (PODE_2 +PX+water), (PODE_3 +PX+water) and (PODE_4 +PX+water) at temperatures 293.15 K and 313.15 K. All experimental liquid-liquid phase equilibrium data were correlated by applying the NRTL [19] and UNIQUAC [20] models to fit the extraction process.

2. Experiment section

2.1. Materials and Sample Preparation

The materials used for the experiments were methylal, ethanol, para-xylene, PODE₂₋₄. The detailed information about the suppliers and the mass fraction of the used chemical reagents were shown in Table 1. Molecular sieves with a pore diameter of 0.4 nm were used to dry the above chemicals.

PODE₂₋₄ were synthesized by the reaction of methanol + formaldehyde. Para-xylene was used as an extraction solvent to extract PODE_n from the reaction products, and then PODE₂₋₄ in extraction phase were obtained by fractional distillation depending on the different boiling points.

2.2. Apparatus and Procedure

The liquid-liquid equilibrium was determined by taking samples from the equilibrated coexisting liquid phases in a thermostated flask, which is present in figure 1. Heat-conducting medium from circulating thermostatic bath ensured isothermal conditions for experiment process. Additionally, a thermometer with an uncertainty of 0.1 K was applied to measure the temperature in the flasks. All experiments were operated at $P=101.3$ kPa with an uncertainty of 1 kPa. The equilibration of the phases was achieved by stirring with magnetic bars for half an hour and left at rest for 2 hours. In order to determine the equilibrium time, preliminary experiments were carried out using KF titration and gas chromatograph for quantitative analysis. Preliminary tests showed that these times are adequate to achieve the phase equilibrium. In this work, no variation of composition with stirring time was established more than half an hour, such as 1 hour, 2 hours, 3 hours, 5 hours, 8 hours, 24 hours. Therefore, it was found reasonable to assume that the time is enough for the phase equilibrium. When the equilibrium was achieved, the system was separated into two clear, transparent phases with a well-defined interface and finally, the samples of organic phase were sucked by syringes from the upper layer and that of water-rich phase from a sampling tap at the bottom of the cell, and then analyzed at least three times by gas

chromatography and KF titration (for details, see the section Analytical Methods). The mass fractions values are the average ones.

2.3. Analytical Methods

To determine the water content, samples taken from the conjugated phases were quantified by volumetric one-component KF titration method. (KF titrator from Mettler Toledo, Model V30). The titrator was calibrated with standard solution of sodium tartrate. It is estimated that the standard uncertainty for the water content (mass fraction) of an analyzed sample did not exceed 0.0005.

Concentration of para-xylene and PODE_n were determined using gas chromatograph by applying an internal standard. Ethanol was used as the internal standard. The standard uncertainties of para-xylene and PODE_n in mass fraction were determined to be 0.004 and 0.005, respectively. The gas chromatograph from Perkin Elmer (Clarus 580) was equipped with elite-wax fused silica capillary column (30 m×0.32 mm×0.25 μm). A flame ionization detector (FID) was utilized with high purity nitrogen as a carrier gas, and the flow rate of nitrogen was kept constant at 40 ml·min⁻¹. The injector and detector temperatures were maintained at 523.15 K. The column submitted to the following temperature program: initial temperature 318.15 K for 3 min, temperature ramp 20 K·min⁻¹, and final temperature of 493.15 K for 3 min.

During the internal standard preparing process, all weighting was operated by using BEL electronic analytical balance (mark-720) with an accuracy of ±0.0001 g.

3. Results and discussion

3.1. Experimental LLE data

The experimental tie-line data for the ternary systems of (PODE_n+ para-xylene+ water) were determined at $T = (293.15, 313.15)$ K, $P = 101.3$ kPa. The measured data for the ternary

systems at each temperature were listed in table 2, and ternary phase diagrams were shown in Figures 4 to 7.

As can be observed in table 2, the phase equilibrium data of each corresponding experimental tie line show a little variation over temperature range of 293.15 K and 313.15 K. As expected, in contrast to the water content in residual phase, there is only a small quantity of water in the para-xylene-rich liquid phase, and the maximum mass fraction is less than 0.025, the vast majorities are less than 0.010, which greatly decreases the influences from water for distillation process. Mass fractions of PX in aqueous phase below 0.0007 are approximate to zero, which means the majority of PX could be recycled with a small solvent loss in the aqueous phase.

Distribution coefficients (D_{pode}) listed in Table 2 were calculated to evaluate the extracting capability of the solvent PX for the separation of PODE_n from aqueous solutions. Distribution coefficient of PODE_n is defined as the ratio of PODE_n mass fraction in organic phase (W_I^I) to that in aqueous phase (W_I^{II}) as the following equation:

$$D_{pode} = W_I^I / W_I^{II} \quad (7)$$

Figure 2, 3 present distribution coefficients of PODE_n as a function of the mass fraction PODE_n in the organic phase at the same temperature $T=293.15$ K and $T=313.15$ K, respectively. Distribution coefficients are not constant over the whole two-phase region, which vary between (2.049, 3.723) at $T=293.15$ K and (1.821, 4.796) at $T=313.15$ K for the systems reported here. In Table 2 the PODE_n mass fractions in the organic phase are much larger than that in aqueous phase. These results indicate using solvent PX to extract PODE_n from the aqueous phase is feasible at $T=(293.15, 313.15)$ K.

As can be seen from ternary phase diagrams in the Figures 4 to 7, the LLE experimental data for (PODE_n + PX + water) are not consistent with the change of the chain length. The slopes

of tie-lines for PODE₁ are similar to that of PODE₄, but much different from those for PODE₂ and PODE₃, which are also similar between each other. Also, the water content in the organic phase changes irregularly with the growth of the chain length. More research work need to be done on the intrinsic changes and interactions between molecules in the ternary system (PODE_n + PX + water) with the change of the chain length to clarify the reasons for this phenomenon.

In the Figure 4a and Figure 4b, it is seen for (PODE₁ + PX + water) that the change trend of the slopes of tie-lines at two different temperatures is more obvious than the other systems. When the mass fraction of PODE₁ in aqueous phase exceeds about 0.101, the slopes of tie-lines increase much more significantly at higher temperature 313.15 K under same PODE₁ concentrations in aqueous phase. This phenomenon indicates that temperature has great impact on promoting extraction of PODE₁ from aqueous solution, especially for system richer in PODE₁.

The binary endpoints (water + PODE₁) from literature [14] have been added into the ternary diagrams in the Figure 4a and Figure 4b. It is seen that water shows a solubility of 0.0432 and 0.0491 mass fraction in PODE₁ at $T=293.15$ K and 313.15 K, respectively. Immiscibility region available for extraction operation is established by the connection of experimental data and endpoint of (water + PODE₁). As no significant difference of solubility is observed for the water in the PODE₁ with the temperature, the immiscibility region size is less affected by temperature.

3.2. LLE Correlation

The experimental LLE data of the ternary systems (PODE_n + PX + water) were correlated using the NRTL and UNIQUAC models. According to the experimental LLE data, the systems have small mutual solubilities within the application scope of NRTL and UNIQUAC. Both thermodynamic models based on local composition are applicable to partially miscible systems and complex polar, nonpolar mixtures [19-20].

In the LLE calculation, temperature, pressure and a mixture of known global composition were specified, and the corresponding compositions of the two liquid phases present in equilibrium at the given temperature and pressure must be determined. The calculation was carried out by solving the thermodynamic criteria and mass balance equation

$$\sum_{i=1}^3 x_i^I = 1 \text{ and } \sum_{i=1}^3 x_i^{II} = 1 \quad (8)$$

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad (9)$$

Where I and II represent the equilibrium phases; i denotes the number of components; x denotes the mole fraction of liquid phase; and γ denotes the activity coefficient given by NRTL or UNIQUAC model; the mole fraction x_i can be determined using the following equations:

$$x_i = \frac{W_i/M_i}{\sum_{i=1}^3 W_i/M_i} \quad (10)$$

In this work, the optimum binary interaction parameters were obtained by fitting experimental LLE data to two thermodynamic models. During the regression process of NRTL model, according to the rules of Renon and Prausnitz [19], NRTL non-randomness parameters $\alpha_{ij(\text{water-PODEn})}$ and $\alpha_{ij(\text{water-PX})}$ were fixed to 0.2, $\alpha_{ij(\text{PX-PODEn})}$ to 0.3. The UNIQUAC structural parameters r (molecular-geometric volume) and q (molecular-geometric surface) were taken from the Bondi method. The values r and q used in the UNIQUAC equation were present in table 3.

The corresponding binary interaction parameters were obtained by minimizing the difference between the experimental and calculated mass fractions for each ternary system. The composition-based objective function [22] (OF) in iterative optimization procedure used was

$$\text{OF} = \min \left\{ \sum_{k=1}^n \sum_{i=1}^3 \left[(W_i^{I,exp} - W_i^{I,cal})^2 + (W_i^{II,exp} - W_i^{II,cal})^2 \right] / 2ni \right\}^{0.5} \quad (11)$$

Where W_i^I and W_i^{II} indicate the mass fractions of component i in phases organic phase I and

aqueous phase *II*, respectively. The subscripts *k* and *n* denote the number and total numbers of tie-lines, while the superscripts “exp” and “cal” refer to the experimental and calculated values of the liquid phase concentration.

The optimization of the binary model parameters and quality of the correlation can be evaluated by the root-mean square deviation (RMSD). The RMSD value was calculated based on the difference between the experimental and calculated data according to the following equation [16, 23, 24]:

$$\text{RMSD} = \min \left\{ \sum_{k=1}^n \sum_{i=1}^3 \left[(W_i^{I,\text{exp}} - W_i^{I,\text{cal}})^2 + (W_i^{II,\text{exp}} - W_i^{II,\text{cal}})^2 \right] / 6n \right\}^{0.5} \quad (12)$$

The RMSD values in the correlation by NRTL and UNIQUAC models along with regressed binary interaction parameters for the four investigated ternary subsystems are listed in table 4. As can be seen in table 4, the RMSD values for the ternary systems correlated by NRTL range from 0.024 to 0.053. In contrast, the deviations of the UNIQUAC model regressions for each system are relatively smaller. The RMSD values for four systems are within the range from 0.012 to 0.026, suggesting a better performance by the UNIQUAC equation, which shows a great agreement with the observed correlation results of ternary phase diagrams for each system.

In order to clearly illustrate that, ternary phase diagrams for each system at each temperature were present in Figures 4 to 7, and also presented the comparison of the calculated tie-lines from NRTL, UNIQUAC models with the experimental results. From Figures 4 to 7, a good coincidence between experimental and all calculated tie lines from UNIQUAC models can be observed. By comparison, the NRTL models show slight deviations in Figures 4, 5, 7, which are also acceptable in description of ternary phase diagrams, but for the system of PODE₃+PX+water in Figure 6.a and 6.b, the tie-lines calculated from NRTL don't fit well with the experimental lines and show relatively serious deviations. The result obtained by the

UNIQUAC model provided a better description of tie-lines for the ternary systems of (PODE_n+PX+water) at each temperature studied.

It indicates that the UNIQUAC models are more adequate to represent ternary systems, and capable of reproducing the LLE data of all studied systems, with a good agreement between experimental and calculated LLE data. Based on the reliable data, the complete set of UNIQUAC models binary interaction parameters can be used to describe the phase diagrams across the temperature range studied. The reliability of the UNIQUAC in the description of the phase equilibrium of (PODE_n+PX+water) makes it the suitable model for designing, optimizing, and operating PODE_n production plants.

3.3. Consistency of experimental tie-line data

The consistency of the tie-line data experimentally measured were tested by Hand correlations [16, 23, 24] and the Othmer-Tobias, equations (13) and (14):

$$\lg(W_1^H/W_3^H) = A + B \times \lg(W_1^L/W_2^L) \quad (13)$$

$$\ln \left[(1 - W_3^H) / W_3^H \right] = A' + B' \times \ln \left[(1 - W_2^L) / W_2^L \right] \quad (14)$$

Here W_1^H and W_3^H are the mass fractions of PODE_n and water in aqueous phase, respectively. W_1^L and W_2^L are the mass fractions of PODE_n and para-xylene in organic phase, respectively. Constants A , B , A' , B' are the parameters of the Hand correlations and the Othmer-Tobias, which could be obtained by linear fit.

The squared correlation coefficient (R^2) and the fitting parameters for the studied systems are presented in Table 5. The Hand plots and the Othmer-Tobias are shown in Figure 8 and 9, respectively. It can be seen that all plots display a linearity behavior, with R^2 being approximately unity. This clearly indicates the degree of consistency of the LLE experimental data in this study.

4. Conclusion

The liquid-liquid equilibria for the (PODE₁+PX+water), (PODE₂+PX+water), (PODE₃+PX+water), (PODE₄+PX+water) ternary systems were measured and modeled. The LLE data were determined at $T = (293.15, 313.15)$ K and $P = 101.3$ kPa. The Hand equations and the Othmer-Tobias demonstrated that the experimental values were consistent and reliable. Additionally, the NRTL and UNIQUAC models were used to correlate the experimental data and to calculate the phase compositions of the mixture. The UNIQUAC models exhibited a better correlation for the investigated systems with very small mutual solubilities and showed a decent fit to the experimental data.

Nomenclature

Abbreviations:

PODE _n	Polyoxymethylene dimethyl ethers
LLE	Liquid-Liquid Equilibria
PX	Para-xylene
FA	Formaldehyde
ME	Methanol
HF _n	poly-hemiformals
KF	Karl Fischer
FID	Flame Ionization Detector
NRTL	Non-Random Two Liquid
UNIQUAC	Universal Quasi-Chemical

Symbols and indices:

T	Temperature, K
D	Distribution coefficient
W	Mass Fraction
R^2	Squared Correlation Coefficient
α_{ij}	Nonrandomness Parameter in the NRTL equation
OF	Composition-Based Objective Function
RMSD	Root-Mean Square Deviation
g_{ij}	NRTL binary interaction parameter, cal/mol
u_{ij}	UNIQUAC binary interaction parameter, cal/mol
exp	Experimental Value
cal	Calculated Value
I	Organic Phase
II	Aqueous Phase
n	Number of Tie-Lines

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Table 1. Example Sample Table

Chemical Name	Source	Purification Method	Mass Fraction	Purity Analysis Method
methylal	Shanghai BlueStar POM Co.	none	0.998	GC ^a
ethanol	Sinopharm Group Co.	none	0.995	GC
para-xylene	Sinopharm Group Co.	none	0.995	GC
KF reagent ^b	Sinopharm Group Co.	none	-	-
DI water ^c	Sino Polymer Co.	distillation	0.999	EC ^d
PODE ₂	synthesis	extraction and distillation	0.950 ^e	GC
PODE ₃	synthesis	extraction and distillation	0.951 ^e	GC
PODE ₄	synthesis	extraction and distillation	0.952 ^e	GC

^a Gas chromatograph.

^b Karl Fischer (KF) reagent for volumetric one-component KF titration

^c Deionized water

^dElectrical conductivity

^eThe main impurity in PODE_n is PODE_{n+1}. These impurities could be quantified by internal standard method.

Table 2. Experimental Liquid-Liquid Equilibrium Data (W_i^I : mass fraction of component i in organic phase I , W_i^{II} : mass fraction of component i in aqueous phase II) and distribution coefficients (D_{pode}) for the Ternary Systems (PODE_n+PX+water) at $T=(293.15, 313.15)$ K and $P=101.3$ kPa^a.

		PODE _n (1)+Para-xylene(2)+Water(3)						
		Organic phase mass fraction			Aqueous phase mass fraction			D_{pode}
PODE _n	T/K	W_1^I	W_2^I	W_3^I	W_1^{II}	W_2^{II}	W_3^{II}	
PODE ₁	293.15	0.489	0.499	0.012	0.145	0.000	0.855	3.37
		0.446	0.544	0.010	0.132	0.000	0.868	3.38
		0.355	0.639	0.007	0.101	0.000	0.899	3.51
		0.206	0.791	0.003	0.062	0.000	0.938	3.32
		0.135	0.863	0.002	0.039	0.000	0.961	3.46
		0.114	0.885	0.001	0.032	0.000	0.968	3.56
	313.15	0.675	0.301	0.024	0.149	0.000	0.851	4.53
		0.485	0.502	0.012	0.104	0.000	0.896	4.66
		0.372	0.621	0.007	0.078	0.000	0.922	4.77
		0.236	0.760	0.004	0.058	0.000	0.941	4.07
		0.153	0.844	0.002	0.038	0.000	0.962	4.03
		0.096	0.903	0.001	0.032	0.000	0.968	3.00
PODE ₂	293.15	0.576	0.415	0.009	0.220	0.000	0.780	2.62
		0.448	0.547	0.006	0.167	0.000	0.833	2.68
		0.417	0.578	0.005	0.155	0.000	0.845	2.69
		0.357	0.639	0.004	0.127	0.000	0.873	2.81
		0.273	0.724	0.003	0.094	0.000	0.906	2.90
		0.146	0.853	0.001	0.059	0.000	0.941	2.47
	313.15	0.551	0.440	0.009	0.193	0.000	0.808	2.85
		0.430	0.563	0.006	0.151	0.000	0.849	2.85
		0.387	0.608	0.005	0.134	0.000	0.866	2.89
		0.349	0.647	0.004	0.127	0.000	0.873	2.75
		0.271	0.727	0.003	0.104	0.000	0.896	2.61
		0.132	0.867	0.001	0.060	0.000	0.940	2.20
PODE ₃	293.15	0.686	0.293	0.020	0.233	0.000	0.767	2.94
		0.578	0.406	0.016	0.192	0.000	0.808	3.01
		0.453	0.535	0.012	0.163	0.000	0.836	2.78
		0.429	0.560	0.011	0.154	0.000	0.846	2.79
		0.273	0.720	0.007	0.124	0.000	0.875	2.20
		0.210	0.785	0.005	0.102	0.000	0.897	2.06

PODE ₄	313.15	0.675	0.304	0.022	0.208	0.000	0.791	3.25
		0.534	0.451	0.015	0.175	0.000	0.824	3.05
		0.464	0.524	0.012	0.160	0.000	0.840	2.90
		0.427	0.562	0.011	0.155	0.000	0.844	2.75
		0.276	0.718	0.006	0.121	0.000	0.879	2.28
	293.15	0.179	0.818	0.004	0.098	0.000	0.902	1.83
		0.685	0.306	0.009	0.197	0.000	0.802	3.48
		0.551	0.442	0.007	0.162	0.000	0.838	3.40
		0.514	0.479	0.007	0.144	0.000	0.856	3.57
		0.397	0.598	0.005	0.107	0.000	0.893	3.71
	313.15	0.234	0.763	0.003	0.065	0.000	0.934	3.60
		0.140	0.858	0.002	0.045	0.000	0.955	3.11
		0.541	0.452	0.007	0.134	0.000	0.865	4.04
		0.523	0.470	0.006	0.122	0.000	0.877	4.29
		0.450	0.546	0.005	0.109	0.000	0.890	4.13
		0.396	0.601	0.004	0.095	0.000	0.905	4.17
		0.238	0.760	0.001	0.072	0.000	0.928	3.31
		0.124	0.876	0.001	0.044	0.000	0.956	2.82

^a Standard uncertainties u are u(T)=0.1K, u(W₁)=0.005, u(W₂)=0.004, u(W₃)=0.0005, u(P)=1 kPa.

Table 3. Values of the UNIQUAC structural parameters r and q

Components	r	q
Water	0.9200	1.4000
PX	4.6579	3.5360
PODE ₁	2.9644	2.7160
PODE ₂	3.8827	3.4960
PODE ₃	4.8009	4.2760
PODE ₄	5.7192	5.0560

Table 4. NRTL and UNIQUAC model interaction parameters and root-mean square deviation (RMSD) for the ternary systems (PODE_n + PX + water) at $T=(293.15, 313.15)\text{K}$ and $P=101.3\text{ kPa}$.

Systems	NRTL parameters			RMSD
	i-j	$(g_{ij}-g_{ii})/R$	$(g_{ji}-g_{jj})/R$	
PODE ₁ (1)+PX(2)+water(3)	1 to 2	-334.37	472.65	0.033
	1 to 3	217.39	711.92	
	2 to 3	1434.07	2560.17	
PODE ₂ (1)+PX(2)+water(3)	1 to 2	-211.51	180.03	0.024
	1 to 3	229.63	604.20	
	2 to 3	1434.07	2560.17	
PODE ₃ (1)+PX(2)+water(3)	1 to 2	968.19	96.85	0.053
	1 to 3	-623.15	2070.12	
	2 to 3	1434.07	2560.17	
PODE ₄ (1)+PX(2)+water(3)	1 to 2	-449.99	745.59	0.031
	1 to 3	-6.85	917.94	
	2 to 3	1434.07	2560.17	
Systems	UNIQUAC parameters			RMSD
	i-j	$(u_{ij}-u_{ii})/R$	$(u_{j}-u_{jj})/R$	
PODE ₁ (1)+PX(2)+water(3)	1 to 2	317.96	-791.50	0.026
	1 to 3	-528.45	40.19	
	2 to 3	-1109.05	-341.27	
PODE ₂ (1)+PX(2)+water(3)	1 to 2	236.22	-424.95	0.012
	1 to 3	-579.06	94.64	
	2 to 3	-1109.05	-341.27	
PODE ₃ (1)+PX(2)+water(3)	1 to 2	151.75	-254.97	0.018
	1 to 3	-249.17	26.62	
	2 to 3	-1109.05	-341.27	
PODE ₄ (1)+PX(2)+water(3)	1 to 2	217.91	-391.36	0.021
	1 to 3	-580.17	114.89	
	2 to 3	-1109.05	-341.27	

Table 5. Coefficients and the Correlation Factor (R^2), Constants A , B , A' , B' of the Hand correlations and the Othmer-Tobias of Hand Equation and Othmer-Tobias for the Ternary Systems (PODE_n + PX + water) at

$T=(293.15, 313.15)\text{K}$ and $P=101.3\text{ kPa}$.

T	Hand correlation			Othmer-Tobias correlation		
	A	B	R^2	A'	B'	R^2
(PODE ₁ +PX+water)						
293.15 K	-0.750	0.794	0.995	-1.743	0.787	0.995
313.15 K	-0.944	0.566	0.991	-2.183	0.560	0.991
(PODE ₂ +PX+water)						
293.15 K	-0.647	0.739	0.995	-1.496	0.736	0.995
313.15 K	-0.679	0.622	0.998	-1.572	0.620	0.998
(PODE ₃ +PX+water)						
293.15 K	-0.682	0.435	0.994	-1.581	0.432	0.994
313.15 K	-0.703	0.384	0.996	-1.626	0.381	0.996
(PODE ₄ +PX+water)						
293.15 K	-0.808	0.656	0.993	-1.866	0.656	0.993
313.15 K	-0.865	0.543	0.989	-1.998	0.538	0.990

Figure 1. Schematic diagram of equilibrium flask

Figure 2. Distribution coefficient of PODE (D_{pode}) plotted against the mass fraction of PODE in the organic phase at $T=293.15\text{K}$. (■) PODE₁, (●) PODE₂, (▲) PODE₃, (▼) PODE₄.

Figure 3. Distribution coefficient of PODE (D_{pode}) plotted against the mass fraction of PODE in the organic phase at $T=313.15\text{K}$. (■) PODE₁, (●) PODE₂, (▲) PODE₃, (▼) PODE₄.

Figure 4.a. phase diagram for LLE of (PODE₁ + PX + water) system at $T=293.15$ K and $P=101.3$ kPa. (■) experimental points, (×) NRTL calculated points, (○) UNIQUAC calculated points. (▲) binary endpoints (water + PODE₁) from literature.

Figure 4.b. phase diagram for LLE of (PODE₁+ PX + water) system at $T=313.15$ K and $P=101.3$ kPa. (■) experimental points, (x) NRTL calculated points, (o) UNIQUAC calculated points. (▲) binary endpoints (water + PODE₁) from literature.

Figure 5.a. phase diagram for LLE of (PODE₂+ PX + water) system at $T=293.15$ K and $P=101.3$ kPa. (■) experimental points, (×) NRTL calculated points, (○) UNIQUAC calculated points.

Figure 5.b.phase diagram for LLE of (PODE₂+ PX + water) system at $T=313.15$ K and $P=101.3$ kPa. (■)

experimental points, (x) NRTL calculated points, (○) UNIQUAC calculated points.

Figure 6.a. phase diagram for LLE of (PODE₃+ PX + water) system at $T=293.15$ K and $P=101.3$ kPa. (■) experimental points, (×) NRTL calculated points, (○) UNIQUAC calculated points.

Figure 6.b.phase diagram for LLE of (PODE₃+ PX + water) system at $T=313.15\text{K}$ and $P=101.3\text{ kPa}$. (■) experimental points, (×) NRTL calculated points, (○) UNIQUAC calculated points.

Figure 7.a.phase diagram for LLE of (PODE₄+ PX + water) system at $T=293.15$ K and $P=101.3$ kPa. (■) experimental points, (x) NRTL calculated points, (○) UNIQUAC calculated points.

Figure 7.b.phase diagram for LLE of (PODE₄+ PX + water) system at $T=313.15$ K and $P=101.3$ kPa. (■)

experimental points, (x) NRTL calculated points, (○) UNIQUAC calculated points.

Figure 8. Hand plot for the ternary systems (PODE_n + para-xylene + water) at (■) $T=293.15$ K, (●) $T=313.15$ K and $P=101.3$ kPa.

Figure 9. Othmer-Tobias for the ternary systems (PODE_n + para-xylene + water) at (■) $T=293.15$ K, (●) $T=313.15$ K and $P=101.3$ kPa.