Liquid-liquid Equilibrium Determination and Data Correlation for 2,2,4-trimethyl Pentane - tripropylene Glycol Binary System

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Liquid-liquid equilibrium at temperatures between 293.16K and 353.1K for the mixture of 2,2,4-trimethylpentane + 2- [2- (2-Hydroxypropoxy) propoxy] -1-propanol was determined using the cloud point method. The measured data was used to estimate the binary interaction parameters of NRTL thermodynamic model, through non-linear regression using MATLAB® software. The binary interaction parameters resulting from regression were used further in a chemical simulation software (PRO/II 9.3) to determine the LLE for the studied mixture. The LLE calculation results obtained with the NRTL model were compared with the results of LLE calculations using the predictive thermodynamic model-UNIFAC. It was determined that the results of the calculation of the LLE using binary interaction parameters obtained through regression have a smaller deviation from the experimental data than the results of the calculation performed using the UNIFAC model. Moreover, the binary interaction parameters obtained from regression were utilized for the estimation of the solvency properties of tripropylene glycol considering the extraction of C_8 aromatics from a mixture containing 2,2,4-trimethyl pentane, ethylbenzene and xylenes.

Keywords: LLE, isooctane, tripropylene glycol, regression, NRTL

Aromatic hydrocarbon extraction from petroleum products is still a challenging and high-interest topic for the industry with special regard to the produced economic value and environmental protection. Current environmental protection standards regarding the aromatic content of petroleum products used as fuels are strict. Liquid-liquid extraction can be successfully used to produce aromatics from petrochemical products. Considering these issues, the researchers are testing new solvents which can be used in the separation of aromatics through liquid-liquid extraction processes and are proposing new processes for aromatic hydrocarbons separation from petroleum products.

In the literature there are many studies reporting equilibrium data between aromatic hydrocarbons and different solvents as sulfolane [1-3], N-methyl pyrrolidinone [4], ethylene glycols [3,5-7] and more recently, different ionic liquids [8,9]. Propylene glycols are part of a less studied category, but with a great potential to be used for the aromatic hydrocarbon extraction. The possibility of using propylene glycols as solvents is studied by a research group from our university. 1,2-propylene glycol was the first solvent studied [10], and the research continued with dipropylene glycol [11-13] and with tripropylene glycol [14]. But propylene glycols application as solvents is not limited to aromatics extraction, they can be used for gas dehydration [15] or alcohols extraction as mentioned by Bumbac and Dumitrescu [16].

The testing of the newly proposed solvents includes the determination of the phase equilibrium in the systems solvent + nonaromatic hydrocarbons and solvent + aromatic hydrocarbons, mathematical modelling of the experimental data with a suitable thermodynamic model and the utilization of the complete thermodynamic model for the calculation of the solvent properties as capacity (solvation power) and selectivity. This paper brings into attention experimental data of liquid-liquid equilibrium for the binary system 2,2,4-trimethylpentane (isooctane) + 2- [2- (2-Hydroxypropoxy) propoxy] -1-propanol (tripropylene glycol - TPG) as well as information on experimental data processing by regression with NRTL thermodynamic model. In the previous lab experiments, it was observed that inferior aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes) are totally miscible with TPG, and as consequence, the vapor-liquid equilibrium data for the binary systems formed by aromatics mentioned above and the solvent TPG was determined and are presented in a separate article, which is dedicated exclusively to modelling the vapor-liquid equilibrium data [14].

The liquid-liquid equilibrium is calculated through a variety of thermodynamic models. A review of these models provided the following aspects:

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-Non-random two-liquid equation, NRTL**,** makes use of the local composition concept, while avoiding the Wilson equation's inability to predict liquid-liquid phase separation [17]. The resulting equation has been quite successful in correlating a wide variety of systems. It is useful for strongly non-ideal mixtures and for partially miscible systems. Minimum three parameters are necessary for each binary system.

-Universal quasi-chemical equation, UNIQUAC**,** was developed based on statistical-mechanical considerations and the lattice-based quasi chemical model of Guggenheim [18]. Local compositions are used in this equation. Local surface-area fractions are the primary composition variables. Each molecule *i* is characterized by a volume parameter and a surface-area parameter. The excess Gibbs energy is divided into a combinatorial and a residual part. The combinatorial part depends only on the sizes and shapes of the individual molecules; it contains no binary parameters. The residual part, which accounts for the energetic interactions, has two adjustable binary parameters.

-Universal functional activity coefficient method, UNIFAC**,** is based on the UNIQUAC model [19,20]. The UNIFAC method estimates activity coefficients based on the group contribution concept following the Analytical Solution of Groups. Interactions between two molecules are assumed to be a function of group-group interactions. Group-group interaction data are obtained from reduction of experimental data for binary component pairs.

-Lyngby modified UNIFAC, UFT1, displays the binary interaction parameter of the UNIFAC model into three-parameter, by using temperature dependent form [21].

-Dortmund modified UNIFAC, UFT2, is similarly with UFT1, but this method uses a Taylor series for calculate the adjustable parameters [22].

-Modified UNIFAC method, UFT3, is similarly with UFT1, but the adjustable parameters are calculated using a linear temperature function [23,24].

In some cases, the thermodynamic models for liquid-liquid equilibrium cannot be applied and used in the simulation software for chemical processes due to the lack of the binary interaction coefficients, or due to the errors introduced by the calculation algorithms of these coefficients. In this situation, one of the possible solutions is based on the use of the experimental liquid-liquid equilibrium data and their processing by using an existing thermodynamic model from the software's library. The coefficients of the thermodynamic model will be determined based on the selected thermodynamic model and using nonlinear regression. The studied mixture, 2,2,4-trimethyl pentane (isooctane) + tripropylene glycol (TPG), is found in this situation.

To solve the problem of the equilibrium calculation for the mixture TPG + isooctane, the authors approached three objectives:

a)Liquid-liquid equilibrium experiments for the isooctane mixture - tripropylene glycol;

b)Numerical processing of the experimental data using the equations of NRTL thermodynamic model and multiple nonlinear regression;

c)The validation of the NRTL model by comparing the experimental equilibrium data with the numerical results obtained with the PRO/II simulator (results obtained with the customized NRTL model, completed with the binary interaction coefficients, calculated at the previous step).

Experimental part

The studied mixture is formed from two components: 2,2,4-trimethyl pentane and tripropylene glycol. In all experimental determination of phase equilibrium, the composition of the binary mixture is expressed in terms of molar fractions of the more volatile compound. For the mixture considered in this work, the more volatile compound is 2,2,4-trimethylpentrane (isooctane).

The hydrocarbon – 2,2,4-trimethyl pentane (isooctane), was purchased from Merck Chemical GmbH, and was used with no further purification. The solvent used in experimental - TPG, comes from DOW Chemical Company, and was also used with no further purification. The purity of the compounds used in experimental part is presented in Table 1.

Liquid-liquid equilibrium determination for the TPG with 2,2,4-trimethylpentane was performed at atmospheric pressure, in a glass equilibrium cell (with volume of 100 cm^3) to determine the cloud point, the procedure being similar as described by Nicolae and Oprea [11]. The main compound (the component in high quantity in the mixture), previously weighed is introduced in the equilibrium cell, and the other compound is introduced in the cell with a syringe also previously weighed. The adding of the second component begins only when the desired temperature in the equilibrium cell is reached, and continues drop by drop, until the mixture becomes opalescent. After the cloud point apparition, the syringe is weighed again, this way the quantity of the second compound added in the equilibrium cell being determined by difference. This way, adding 2,2,4-trimethyl pentane to main component – TPG, and adding TPG to the main component- 2,2,4-trimethyl pentane, each compound becomes, alternatively, the dominant phase in the equilibrium cell, and the mutual solubility curves of the mixture are determined. The procedure is repeated at least three times, to remove the systematic errors. The equilibrium cell was maintained at constant temperature with a Haake bath, and the temperature in the equilibrium cell was measured with Digital thermometer VWR®, LLC, NIST Traceable® (± 0.05% accuracy, 0.001 °C resolution). The equilibrium cell used in experimental is displayed in Figure 1.

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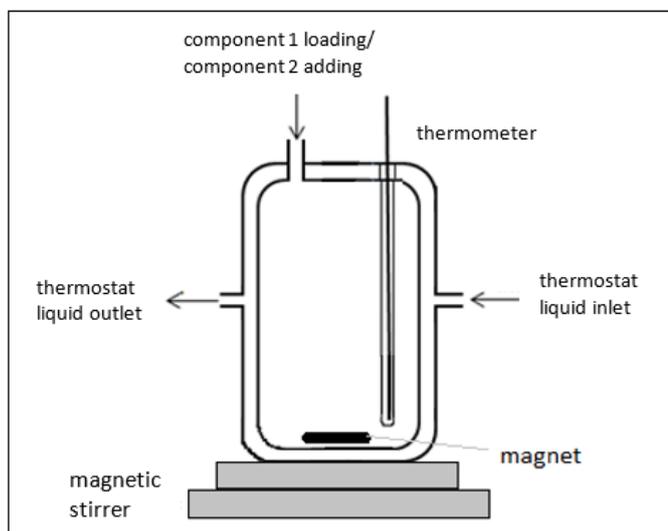
Fig. 1 Equilibrium cell used in the experimental determination of liquid-liquid equilibrium [25]

Table 1
PROPERTIES OF THE CHEMICALS USED IN EXPERIMENTAL

Chemical name, acronym, CAS number	Chemical structure	Mass fraction purity	Source
2,2,4-trimethylpentane, iC$_8$, 111-65-9		> 0.995	Merck KGaA, Germany
Tripropylene glycol, TPG, 24800-44-0		0.9993	Dow Chemical, Germany

The experiment was performed using the compounds presented in Table 1. The results are displayed in Table 2. The complete data referring to liquid -liquid equilibrium determinations are presented in the *Supplementary material- LLE data isooctane -TPG*. The mutual solubility curves, which are displayed in Figure 2, were plotted based on these results.

Table 2
EXPERIMENTAL (LIQUID-LIQUID) EQUILIBRIUM DATA FOR THE SYSTEM
2,2,4 –TRIMETHYL PENTANE (1) + 2- [2- (2-HYDROXYPROPOXY) PROPOXY] -1-PROPANOL (2)
AT TEMPERATURES T BETWEEN 293.16 K AND 353.1 K, AND PRESSURE P=0.1MPa[a]

T/K	Hydrocarbon rich phase		Solvent rich phase	
	x_1^I	x_2^I	x_1^{II}	x_2^{II}
293.16	0.99314	0.00686	0.15796	0.84204
296.14	0.99031	0.00969	0.16895	0.83105
298.22	0.98937	0.01063	0.17568	0.82432
303.16	0.98628	0.01372	0.19169	0.80831
308.16	0.98106	0.01894	0.20604	0.79396
313.12	0.97561	0.02439	0.22201	0.77799
318.20	0.96928	0.03072	0.23779	0.76221
323.16	0.96181	0.03819	0.25379	0.74621
328.12	0.95452	0.04548	0.27405	0.72595
333.06	0.94404	0.05596	0.29741	0.70259
338.12	0.93281	0.06719	0.32175	0.67825
341.19	0.92074	0.07926	0.34153	0.65847
343.14	0.91346	0.08654	0.35378	0.64622
345.15	0.90500	0.09500	0.36936	0.63064
348.19	0.88648	0.11352	0.39632	0.60368
350.70	0.87177	0.12823	0.42235	0.57765
353.10	0.84276	0.15724	0.45700	0.54300

[a] standard uncertainty is u(T)=0.0376, u(p)=10kPa; combined uncertainty u$_c$(x)=0.0003, Uc=0.00051
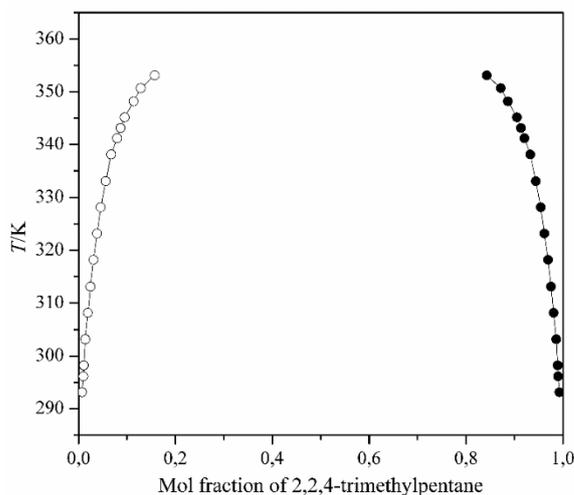
Fig. 2 Mutual solubility of the mixture TPG-2,2,4-trimethylpentane at temperature T: ○- mol fraction of 2,2,4-trimethylpentane in TPG rich phase; ● – mol fraction of 2,2,4-trimethylpentane in hydrocarbon rich phase

Calculation

The system from Figure 3 is considered for modelling of liquid-liquid equilibrium through NRTL thermodynamic model. Both phase *I* and phase *II* are liquid, multicomponent phases, with distinct compositions. According to the general definition of phase equilibrium, these two phases are in thermodynamic equilibrium when the temperature is the same in both phases, and the composition of each phase is constant. In addition, two liquid phases are in thermodynamic equilibrium when the chemical potential of each component *i* from phase *I* is equal with the chemical potential of the same component *i* in the phase *II*.
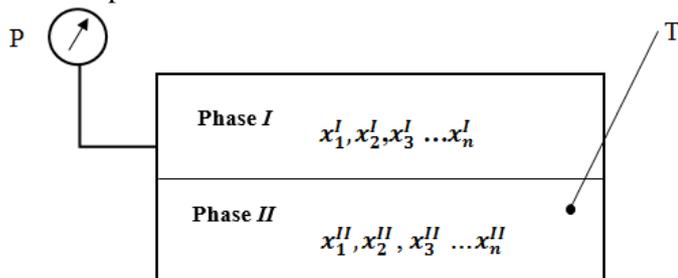

Fig. 3 The phase equilibrium problem in case of liquid-liquid equilibrium [25]

Let us consider the case of extract and raffinate phases in equilibrium, in an extractor, during the liquid-liquid extraction process. If we denote the raffinate phase as phase *I* and the extract phase as phase *II*, the equilibrium equation for any component *i*, can be described in fugacity terms [17] as in eq. (1):

$$f_i^I = f_i^{II} \tag{1}$$

Taking into account fugacity definition and considering the same standard state, the equilibrium relation can be written as eq. (2) [17]:

$$\gamma_i^I \cdot x_i^I = \gamma_i^{II} \cdot x_i^{II} \tag{2}$$

Calculation of the activity coefficient in liquid phase γ_i, can be realized with different functions, but the most utilized function is the excess Gibbs free energy g^E.

$$g^E = \mathcal{F}\left(x_i, xg_{ij}, \tau_{ij}, G_{ij}\right) \tag{3}$$

This function implies the interaction energies g_{ij} between the molecular species *i* and *j*, the global compositions of component *i* in both phases x_i^I, x_i^{II} and also, the adjustable binary parameters τ_{ij} and G_{ij}. Rewriting the eq. (2) in the terms of the $\mathcal{F}$ function is obtained:

$$\mathcal{F}_1(x_1^I, g_{12}, \tau_{12}, G_{12})x_1^I = \mathcal{F}_1(x_1^{II}, g_{12}, \tau_{12}, G_{12})x_1^{II} \tag{4}$$
$$\mathcal{F}_2(x_2^I, g_{21}, \tau_{21}, G_{21})x_2^I = \mathcal{F}_2(x_2^{II}, g_{21}, \tau_{21}, G_{21})x_2^{II} \tag{5}$$

The most well-known equation of equilibrium for the calculation of the thermodynamic function Gibbs free energy is the Non-Random-Two –Liquids (NRTL) equation, which for a binary mixture can be described in the general form as in eq. (6) [26]:

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \tag{6}$$

The activity coefficients γ_i associated to liquid –liquid equilibrium of a binary mixture can be calculated using the NRTL model, based on the general equation [18]:

$$\ln \gamma_i = \frac{g^E}{RT} \tag{7}$$

Using eq. (7) to write the equations of the activity coefficients of the two components, in both liquid phases, are obtained the expressions of liquid activity coefficients, eq. (8) – (11):

$$\ln \gamma_1^I = (x_2^I)^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1^I + x_2^I G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2^I + x_1^I G_{12})^2} \right] \tag{8}$$

$$\ln \gamma_2^I = (x_1^I)^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2^I + x_1^I G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1^I + x_2^I G_{21})^2} \right] \tag{9}$$

$$\ln \gamma_1^{II} = (x_2^{II})^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1^{II} + x_2^{II} G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2^{II} + x_1^{II} G_{12})^2} \right] \tag{10}$$

$$\ln \gamma_2^{II} = (x_1^{II})^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2^{II} + x_1^{II} G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1^{II} + x_2^{II} G_{21})^2} \right] \tag{11}$$

The parameters $\tau_{12}, G_{12}, \tau_{21}, G_{21}$ are adjustable parameters and are calculated as functions of the binary interaction parameters $b_{12}, b_{21}, \alpha_{12}$ and the temperature T:

$$\tau_{12} = \frac{g_{12} - g_{11}}{RT} = \frac{b_{12}}{T} \tag{12}$$
$$\tau_{21} = \frac{g_{21} - g_{22}}{RT} = \frac{b_{21}}{T} \tag{13}$$
$$G_{12} = exp(-\alpha_{12} \tau_{12}) \tag{14}$$
$$G_{21} = exp(-\alpha_{12} \tau_{21}) \tag{15}$$

If the notion of distribution constant is introduced and defined as the ratio between the concentration of the component i in the extract phase (phase II) and the concentration of the same component in the raffinate phase (phase I), there is obtained:

$$K_i = \frac{x_i^{II}}{x_i^I} = \frac{\gamma_i^I}{\gamma_i^{II}} \tag{16}$$

An algorithm containing the equations specific to NRTL thermodynamic model was employed for the regression of the experimental data in the MATLAB® software. The resulting NRTL parameters are presented in Table 3. The following procedure was applied:

- the distribution coefficients K_1^{expt} and K_2^{expt} were calculated for each component as ratio between the experimental concentrations of the isooctane in the glycol rich phase, and hydrocarbon rich phase K_1, and respectively as ratio between the experimental concentrations of the TPG in the glycol rich phase, and hydrocarbon rich phase K_2 (eq. 17);

- the values of distribution coefficients K_1 and K_2 calculated in the previous step were fitted in the NRTL model with three binary interaction parameters using the MATLAB® implementation of equations (8) – (24);

- the differences between the experimental and calculated distribution coefficients K_i^{expt} and K_i^{calc} were calculated in the final step to evaluate the accuracy of the regression.

The effort of the authors was focused to define the objective function necessary to determinate the binary interaction parameters of the thermodynamic model used to calculate the liquid-liquid equilibrium. The distribution coefficient of the component 1 in both liquid phases is calculated by starting from the experimentally determined composition of the two phases:

$$K^{expt} = \frac{x_i^{II}}{x_i^I} \tag{17}$$

From experimental data, for each value of temperature and using eq. (18) – (24), there is obtained the *calculated* distribution coefficient K^{calc}.

$$\tau_{12} = \frac{b_{12}}{T} \tag{18}$$

$$\tau_{21} = \frac{b_{21}}{T} \tag{19}$$

$$G_{12} = exp(-\alpha_{12}\tau_{12}) \tag{20}$$

$$G_{21} = exp(-\alpha_{12}\tau_{21}) \tag{21}$$

$$\gamma_1^I = exp\left\{(x_2^I)^2\left[\tau_{21}\left(\frac{G_{21}}{x_1^I+x_2^IG_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2^I+x_1^IG_{12})^2}\right]\right\} \tag{22}$$

$$\gamma_1^{II} = exp\left\{(x_2^{II})^2\left[\tau_{21}\left(\frac{G_{21}}{x_1^{II}+x_2^{II}G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2^{II}+x_1^{II}G_{12})^2}\right]\right\} \tag{23}$$

$$K^{calc} = \frac{\gamma_1^I}{\gamma_1^{II}} \tag{24}$$

The determination of the constants b_{12}, b_{21}, α_{12} of the mathematical model of liquid-liquid equilibrium is realized by minimization of the objective function.

$$F_{ob}(b_{12}, b_{21}, \alpha_{12}) = \sum_{j=1}^{m}[K^{expt} - K^{calc}]^2 \tag{25}$$

To be able to minimize the objective function (eq. 25) a package of MATLAB scripts was developed. The operation of the MATLAB script is based on a sequential algorithm with the following steps:
-reading input data from file;
-computing the optimal solution;
-calculating the statistical quantities.

Since the number of results is significant, we chose to store the input data and the results in text files, in the working directory.

The reading of the input file is realized by the script ReadInput.m. The user has to introduce the filename where data is stored, then the MATLAB® engine reads the file contents and store it in vector type variables. The input file should have three space-separated columns corresponding to variables: temperature, T, molar fraction of isooctane in solvent rich phase (extract), x_1^{II}, molar fraction of isooctane in hydrocarbon rich phase (raffinate), x_1^I, as it can be observed in the Input.txt file from Supplementary material.

After reading the input data the algorithm identifies the optimal value of the binary interaction parameters, by using *fminsearch* function of MATLAB®. *fminsearch* is a specific function of MATLAB programming language that is designed to find the minimum of a scalar function of several variables, implementing unconstrained nonlinear optimization [27]. Basically, this function implements the simplex search method presented by Lagarias and collaborators [28].

The optimal values determined by using the developed MATLAB program are presented in Table 3. The value of the objective function in the optimal point is 1.46×10^{-5}.

Table 3
OPTIMAL VALUES OF THE VARIABLES OF THE FUNCTION DISPLAYED IN EQ. (25)

Variable	Optimal value
b_{12}	923.20076
b_{21}	-52.42663
α_{12}	0.10871

The last step of the proposed algorithm consists in evaluating its performance by comparing computed values and experimental data. We analyzed the performance by using statistical data, respectively the values of the distribution coefficient calculated with the experimental compositions - K_j^{expt}, and the distribution coefficient calculated with the compositions estimated with the thermodynamic model - K_j^{calc}, as presented in Table 4.

For this reason, we built another MATLAB script file – fktest.m – that implements the function fktest. It receives as input the optimal values and calculates the distributions coefficients and the deviations, which are saved in a results file.

According to these results, the mean value of the deviation between experimental data and the estimated data based on the optimal solution is 0.29%, and the maximum deviation is 1.36%. These values of the absolute deviation validate the use of the optimization algorithm and the determined optimal solution.

Table 4
COMPARATIVE RESULTS OF THE OPTIMIZATION ALGORITHM IN TERMS OF DISTRIBUTION COEFFICIENT K_j

	K_j^{expt}	K_j^{calc}	$K_j^{expt} - K_j^{calc}$	$\left\|\dfrac{K_j^{expt} - K_j^{calc}}{K_j^{expt}}\right\| \times 100$
1	0.1590513	0.1612269	-0.0021756	1.3678763
2	0.1706006	0.1710942	-0.0004936	0.2893472
3	0.1775661	0.1775368	0.0000293	0.0164982
4	0.1943608	0.1934220	0.0009388	0.4830350
5	0.2100206	0.2088957	0.0011249	0.5356367
6	0.2275603	0.2262905	0.0012698	0.5579913
7	0.2453234	0.2444313	0.0008921	0.3636343
8	0.2638663	0.2634536	0.0004126	0.1563770
9	0.2871096	0.2871706	-0.0000610	0.0212429
10	0.3150417	0.3152624	-0.0002207	0.0700638
11	0.3449288	0.3460251	-0.0010963	0.3178463
12	0.3709235	0.3715401	-0.0006166	0.1662300
13	0.3872978	0.3879491	-0.0006512	0.1681521
14	0.4081335	0.4088167	-0.0006833	0.1674107
15	0.4470760	0.4470032	0.0000727	0.0162654
16	0.4844763	0.4847474	-0.0002711	0.0559576
17	0.5422738	0.5407446	0.0015292	0.2819921

The standard deviation is calculated for all values displayed in Table 4 by using eq. (26) and the obtained value is: $\sigma = 0.000239$:

$$\sigma = \frac{\sqrt{\sum_{i=1}^{n}\left(K_i^{expt} - K_i^{calc}\right)^2}}{n-1} \qquad (26)$$

From Table 4 it can be observed that the calculated and the experimental values of the distribution coefficient are very close, fact demonstrated by the errors with values lower than 1%. Also, the standard deviations for the two types of coefficients are small, proving the coherence of the obtained results.

The used optimization algorithm requires the defining of an initial solution. In this context we studied the dependence of the optimal solution versus initial solution. Thereby, the values of the initial solution were varied as presented in Table 5. An output file containing more than 300 values was generated and the optimal solution was the same. These results confirm once again the consistency of the utilized optimization algorithm.

Table 5
THE VARIATION DOMAIN OF THE VARIABLES

Variable	Minimal value	Maximal value
b_{12}	1000	3000
b_{21}	-1000	0
α_{12}	0.00	1

Results and discussions

Data correlation

Simultation of the liquid-liquid equilibria at the experimental temperatures specified in Table 2 were realized by using PRO/II simulation software. In order to verify the consistency of the binary parameters of NRTL model obtained through regression of the experimental data, the liquid-liquid equilibrium calculations were realized.

A flash fed with various mixtures was simulated at the experimental temperatures in PRO/II. The flash configuration is displayed in Fig. 4. Modelling of liquid-liquid equilibrium was realized using eight thermodynamic models available in the databank of the software, as specified in Table 8. The 9th model, the NRTL model uses the binary interaction parameters b_{12}, b_{21} and α_{12}, that are determined by optimization of the objective function described by the eq. (25) and which are displayed in Table 3.
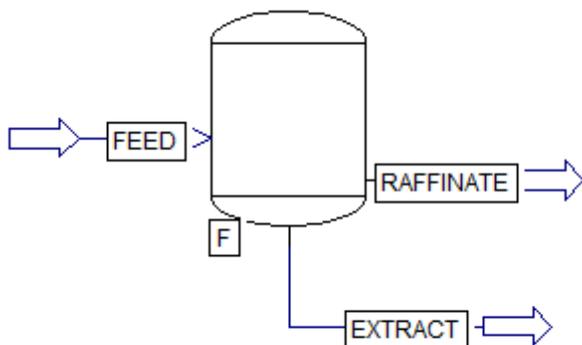
Fig. 4 The flash used in the liquid-liquid checking calculations

In Figure 4 the liquid phase named *Raffinate* refers at the 2,2,4-trimethyl pentane rich phase, while the liquid phase named *Extract* refers to the TPG rich phase.

The results of the liquid-liquid calculations in PRO/II with UNIFAC and NRTL model completed with binary interaction parameters resulted from regression are displayed in Table 6 and Table 7.

Table 6

THE EXPERIMENTAL $x_1^{II\,expt}$ AND CALCULATED $x_1^{II\,calc}$ VALUES OF CONCENTRATION EXPRESSED IN MOLAR FRACTION OF 2,2,4-TRIMETHYLPENTANE AND THE CALCULATED CONCENTRATION OF TPG $x_2^{II\,calc}$ WITH UNIFAC MODEL, AT TEMPERATURES T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\,expt}$	$x_1^{II\,calc}$	$x_2^{II\,calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\,expt}$	$x_1^{I\,calc}$	$x_2^{I\,calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.07214	0.92786	-0.08582	-54.33	0.99314	0.99883	0.00117	0.00568	0.57
296.05	0.16895	0.07326	0.92674	-0.09569	-56.64	0.99031	0.99874	0.00126	0.00843	0.85
298.22	0.17568	0.07411	0.92589	-0.10157	-57.82	0.98937	0.99867	0.00133	0.00931	0.94
303.16	0.19169	0.07607	0.92393	-0.11562	-60.32	0.98628	0.99851	0.00149	0.01223	1.24
308.16	0.20604	0.07810	0.92190	-0.12794	-62.09	0.98106	0.99833	0.00167	0.01727	1.76
313.12	0.22201	0.08016	0.91984	-0.14185	-63.89	0.97561	0.99814	0.00186	0.02252	2.31
318.2	0.23779	0.08232	0.91768	-0.15547	-65.38	0.96928	0.99792	0.00208	0.02864	2.95
323.16	0.25379	0.08446	0.91554	-0.16933	-66.72	0.96181	0.99770	0.00230	0.03589	3.73
328.12	0.27405	0.08665	0.91335	-0.18740	-68.38	0.95452	0.99746	0.00254	0.04294	4.50
333.06	0.29741	0.08887	0.91113	-0.20854	-70.12	0.94404	0.99720	0.00280	0.05317	5.63
338.12	0.32175	0.09119	0.90881	-0.23056	-71.66	0.93281	0.99693	0.00307	0.06411	6.87
341.19	0.34153	0.09262	0.90738	-0.24890	-72.88	0.92074	0.99675	0.00325	0.07600	8.25
343.14	0.35378	0.09354	0.90646	-0.26024	-73.56	0.91346	0.99663	0.00337	0.08317	9.10
345.15	0.36936	0.09449	0.90551	-0.27487	-74.42	0.90500	0.99651	0.00349	0.09150	10.11
348.19	0.39632	0.09594	0.90406	-0.30038	-75.79	0.88648	0.99631	0.00369	0.10984	12.39
350.7	0.42235	0.09715	0.90285	-0.32520	-77.00	0.87177	0.99615	0.00385	0.12438	14.27
353.1	0.45700	0.09832	0.90168	-0.35868	-78.49	0.84276	0.99599	0.00401	0.15323	18.18
Mean of the relative deviation					67.62					6.10

Table 7

THE EXPERIMENTAL $x_1^{II\,expt}$ AND CALCULATED $x_1^{II\,calc}$ VALUES OF CONCENTRATION EXPRESSED IN MOLAR FRACTION OF 2,2,4-TRIMETHYLPENTANE AND THE CALCULATED CONCENTRATION OF TPG $x_2^{II\,calc}$ WITH NRTL MODEL (COMPLETED WITH CALCULATED BINARY INTERACTION PARAMETERS), AT TEMPERATURES T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\,expt}$	$x_1^{II\,calc}$	$x_2^{II\,calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\,expt}$	$x_1^{I\,calc}$	$x_2^{I\,calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.22757	0.77243	0.06960	44.06	0.99314	0.91870	0.08130	-0.0744	-8.10
296.05	0.16895	0.23287	0.76713	0.06392	37.83	0.99031	0.91515	0.08485	-0.0752	-8.21
298.22	0.17568	0.23693	0.76307	0.06125	34.87	0.98937	0.91241	0.08759	-0.0770	-8.43
303.16	0.19169	0.24647	0.75353	0.05477	28.57	0.98628	0.90590	0.09410	-0.0804	-8.87
308.16	0.20604	0.25654	0.74346	0.05050	24.51	0.98106	0.89889	0.10111	-0.0822	-9.14
313.12	0.22201	0.26700	0.73300	0.04499	20.27	0.97561	0.89148	0.10852	-0.0841	-9.44
318.2	0.23779	0.27823	0.72177	0.04044	17.01	0.96928	0.88339	0.11661	-0.0859	-9.72
323.16	0.25379	0.28974	0.71026	0.03595	14.17	0.96181	0.87495	0.12505	-0.0869	-9.93

328.12	0.27405	0.30186	0.69814	0.02781	10.15	0.95452	0.86591	0.13409	-0.0886	-10.23
333.06	0.29741	0.31460	0.68540	0.01719	5.78	0.94404	0.85624	0.14376	-0.0878	-10.25
338.12	0.32175	0.32843	0.67157	0.00668	2.08	0.93281	0.84556	0.15444	-0.0872	-10.32
341.19	0.34153	0.33726	0.66274	-0.00426	-1.25	0.92074	0.83865	0.16135	-0.0821	-9.79
343.14	0.35378	0.34306	0.65694	-0.01072	-3.03	0.91346	0.83407	0.16593	-0.0794	-9.52
345.15	0.36936	0.34920	0.65080	-0.02016	-5.46	0.90500	0.82919	0.17081	-0.0758	-9.14
348.19	0.39632	0.35883	0.64117	-0.03749	-9.46	0.88648	0.82146	0.17854	-0.0650	-7.91
350.7	0.42235	0.36713	0.63287	-0.05522	-13.07	0.87177	0.81474	0.18526	-0.0570	-7.00
353.1	0.45700	0.37538	0.62462	-0.08162	-17.86	0.84276	0.80799	0.19201	-0.0348	-4.30
Mean of the relative deviation					17.02					8.84

The numerical results of mean of the relative deviation for all the thermodynamic models considered are displayed in Table 8.

Table 8
THE RESULTS OBTAINED IN LIQUID-LIQUID EQUILIBRIUM SIMULATION

No.	Thermodynamic model	The mean of the relative errors of the isooctane concentration in the mixture	
		Extract phase	Raffinate phase
1	UNIFAC	67.62	6.10
2	UNIFAC (temperature dependent)-T1	48.88	6.20
3	UNIFAC (temperature dependent)-T2	60.84	6.30
4	UNIFAC (temperature dependent)-T3	37.03	6.21
5	UNIQUAC (filled with UNIFAC Lingby)	25.56	5.72
6	UNIQUAC (filled with UNIFAC Dortmund)	87.76	4.29
7	NRTL (filled with UNIFAC Lingby)	28.55	5.89
8	NRTL (filled with UNIFAC Dortmund)	86.41	4.35
9	NRTL (regressed parameters from experimental data)	17.02	8.84

The composition of the extract phase, calculated with the existing thermodynamic models (from the software library), has a maximum mean deviation of 87.76% versus the experimental data. The composition of the same phase, calculated using the NRTL model completed with the determined binary interaction through the regression of the experimental data, has a mean deviation of 17.02% versus the same experimental data. As consequence, we can assert that the NRTL model completed with the binary interaction parameters determined from regression fits better the experimental data than the other thermodynamic models displayed in Table 8.

Tripropylene glycol solvency properties estimation
Further, the solvency properties of the TPG - capacity and selectivity - were calculated. In order to do this, a mixture of paraffinic and aromatic hydrocarbons containing 8 atoms of carbon (isooctane, ethylbenzene, o-, m- and p-xylene) was considered to be extracted with tripropylene glycol. The simulation software PRO/II was utilized to calculate the liquid − liquid extraction process. The thermodynamic model NRTL was completed with the binary interaction parameters specific to the binary 2,2,4-trimethyl pentane + TPG previously determined. The binary interaction parameters for the aromatics compound remained set to default (zero), as the aromatic compounds are completely miscible with TPG, as it was concluded by Fendu [14]. The single stage extraction process was calculated using a flash fed with a stream containing the mixture of hydrocarbons, and which has two products streams: Extract and Raffinate. The solvent mass ratio was varied from 1:1 to 2,5:1 and the extraction temperature was varied from 293.15K to 313.15K. The composition of the hydrocarbon mixture which feeds the flash and the operation conditions of the flash are displayed Table 9.

Table 9
FEED COMPOSITION AND OPERATING CONDITIONS IN THE EXTRACTOR

Component	Feed composition, mass fraction	Solvent ratio, mass	T/K	p/kPa
2,2,4-trimethyl pentane	0.8	1:1	293.15– 313.15	101.3
Ethylbenzene	0.05	1.5:1		
o-xylene	0.05	2:1		
m-xylene	0.05	2.5:1		
p-xylene	0.05			

The solvation capacity of TPG (expressed as distribution coefficient K) and selectivity - β were calculated based on the results of the single stage extraction simulations. The distribution coefficient was calculated with eq. (27) and (28) and the compositions of the *Extract* and *Raffinate* phases, while the selectivity was calculated with eq. (29).

$$K_{NAr} = \frac{X_{NAr,E}}{X_{NAr,R}} \qquad (27)$$

Where: $X_{NAr,E}$ - the concentration of non-aromatics hydrocarbons in the *Extract* phase;
$X_{NAr,R}$ - the concentration of non-aromatics hydrocarbons in the *Raffinate* phase.

$$K_{Ar} = \frac{X_{Ar,E}}{X_{Ar,R}} \qquad (28)$$

Where: $X_{Ar,E}$ - the concentration of aromatics hydrocarbons in the *Extract* phase;
$X_{Ar,R}$ - the concentration of non-aromatics hydrocarbons in the *Raffinate* phase.

$$\beta = \frac{K_{Ar}}{K_{NAr}} \qquad (29)$$

The results of the solvent properties calculations were plotted. The capacity of the TPG solvent for isooctane is displayed in Fig. 5, while the capacity of the solvent for the aromatics is displayed in Fig. 6 and Fig. 7.
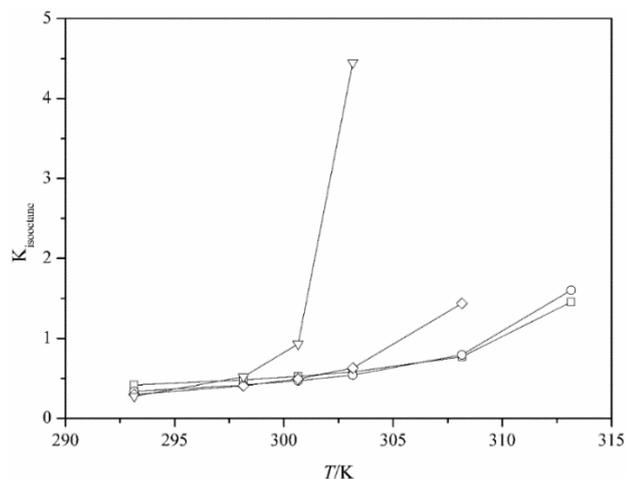
Fig. 5 The variation of the capacity of TPG for isooctane $K_{isooctane}$ with temperature, at different solvent ratio (mass): □- solvent ratio 1:1; ○- solvent ratio 1.5:1 ;◇- solvent ratio 2:1; ▽- solvent ratio 2.5:1.
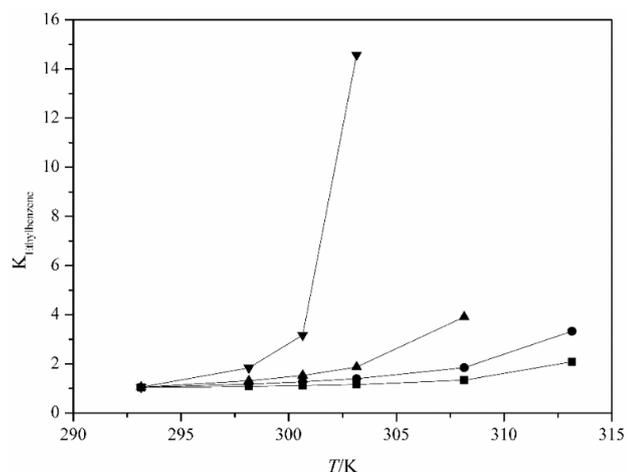
Fig. 6 The variation of the capacity of TPG for ethylbenzene, $K_{ethylbenzene}$ with temperature, at different solvent ratio: ■- solvent ratio 1:1; ●- solvent ratio 1.5:1; ▲- solvent ratio 2:1; ▼- solvent ratio 2.5:1.
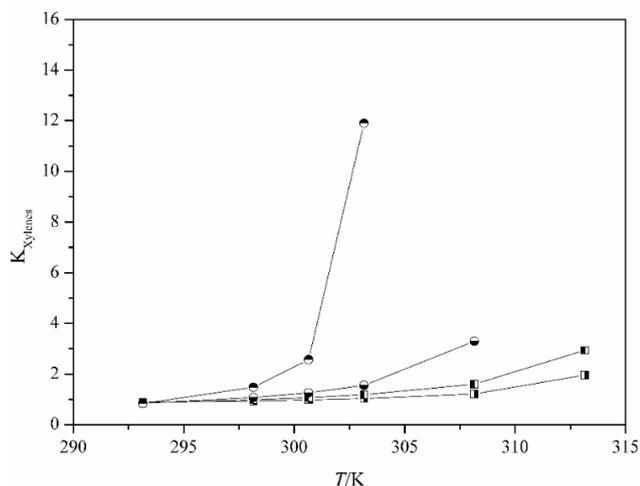
Fig. 7 The variation of the capacity of TPG for Xylenes, $K_{xylenes}$ with temperature, at different solvent ratio (mass): ▪- solvent ratio 1:1; ▫- solvent ratio 1.5:1; ●- solvent ratio 2:1; ○- solvent ratio 2.5:1.

The solvation capacity of TPG is increasing with the temperature increasing in the extractor and with the solvent ratio as it can be observed in Figure, 5, Figure 6 anf Figure 7. Also, it can be seen that the capacity of TPG for isooctane is lower than capacity of TPG for ethylbenzene and xylenes.

The selectivity of TPG for aromatics hydrocarbons ethylbenzene and xylenes (o-, m-, p-) in presence of the isoparaffinic hydrocarbon 2,2,4-trimethylpentane is calculated at different temperatures and solvent ratio. The results are plotted and are displayed in Fig. 8 and Fig. 9.
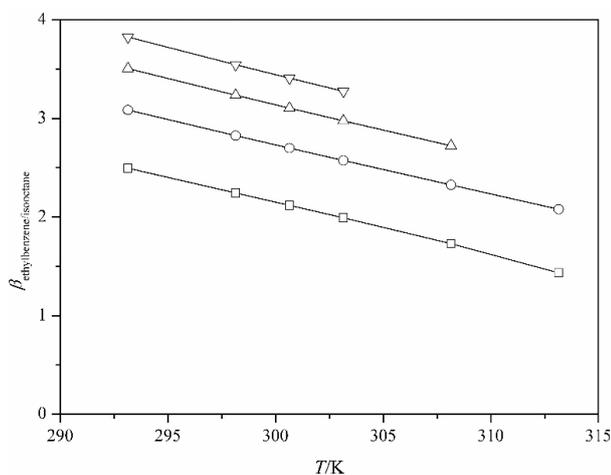
Fig. 8 The variation of the selectivity $\beta_{ethylbenzene/isooctane}$ of TPG for ethylbenzene in the presence of isooctane with temperature, at different solvent ratio (mass): □- solvent ratio 1:1; ○- solvent ratio 1.5:1; △- solvent ratio 2:1; ▽- solvent ratio 2.5:1.
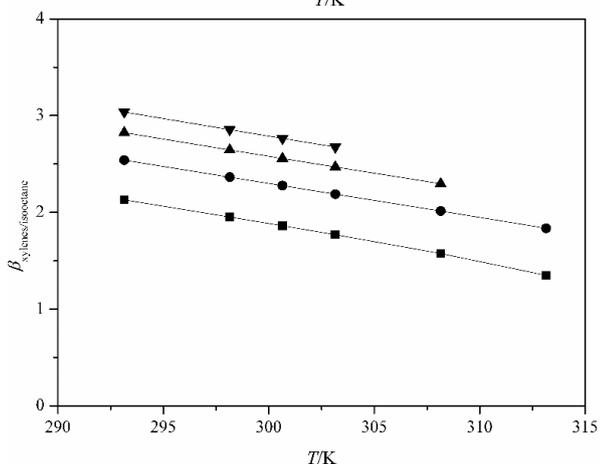
Fig. 9 The variation of the selectivity $\beta_{xylenes/isooctane}$ of TPG for xylenes in the presence of isooctane with temperature, at different solvent ratio (mass): ■- solvent ratio 1:1; ●- solvent ratio 1.5:1; ▲- solvent ratio 2:1; ▼- solvent ratio 2.5:1.

The selectivity of TPG for aromatics is increasing with the solvent ratio, but it is decreasing with the temperature rising. The TPG selectivity for ethylbenzene is higher than the selectivity of TPG for xylenes as can be seen in Fig. 8 and Fig. 9.

Comparing the values obtained for these properties of TPG with those obtained for DPG by Nicolae [13], we can conclude that TPG has a higher capacity than DPG, but its selectivity is significantly lower than the DPG selectivity for aromatics with 8 atoms of carbon.

Conclusions

The liquid-liquid equilibrium data for the binary mixture 2,2,4-trimethyl pentane + tripropylene glycol was determined using the cloud point method, at atmospheric pressure and temperatures between 293 K and 353 K.

The experimental equilibrium data were regressed using the mathematical model of the NRTL thermodynamic model and MATLAB software. An optimization function was used to determine the values of the binary interaction parameters of the NRTL model, specific to the binary mixture TPG + 2,2,4-trimethyl pentane. The consistency of the regression results was verified by comparing the liquid-liquid equilibrium calculations results with the experimental data. This step was performed not only for the NRTL model completed with the binary interaction parameters obtained from regression, but for other eight thermodynamic models widely used for the prediction and calculation of the liquid-liquid equilibrium. The results of the liquid-liquid equilibrium calculation (performed in PRO/II software) in terms of the mean of the relative errors of the 2,2,4-trimethyl pentane concentration in the mixture, showed a minimum for the thermodynamic model NRTL completed with the binary interaction parameters obtained from regression, compared with the results obtained with the other thermodynamic models considered.

The solvency properties (capacity and selectivity) were calculated for TPG. The calculations were achieved considering the extraction of aromatics hydrocarbons using as solvent TPG, from a mixture containing isooctane, ethylbenzene, o-xylene, m-xylene and p-xylene and was concluded that TPG has a greater solvation capacity than DPG.

Abbreviations
LLE – liquid-liquid equilibrium, NRTL- non-random two liquids, TPG – tripropylene glycol, UNIQUAC – universal quasi chemical,

List of symbols
b - binary interaction parameters of the NRTL model
G - adjustable parameter which depends on the interaction energy between molecules of component i and component j.
P - pressure
R - universal gas constant (J mol^{-1} K^{-1})
T - temperature (K)
u - uncertainty
x - concentration of the component in liquid phase of the mixture expressed as molar fraction
F_{ob} - objective function
K_{Ar} - distribution coefficient, specific to aromatics hydrocarbons.
K_{Nar} - distribution coefficient, specific to non-aromatics hydrocarbons

Greek symbols
γ_i - activity coefficient
τ - adjustable parameter of the NRTL model
α - nonrandomness parameter of the NRTL model
σ - standard deviation
β - selectivity of the solvent

Subscripts
i, j - components i and j
$1, 2$ – components 1 and 2
ij - i-j pair interaction
ji - j-i pair interaction

Superscripts
I - first liquid phase
II - second liquid phase
$calc$ - calculated value
$expt$ - experimental value

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Table S1 The experimental $x_1^{II\,expt}$ and calculated $x_1^{II\,calc}$ values of concentration expressed in molar fraction of 2,2,4-trimethylpentane and the calculated concentration of TPG $x_2^{II\,calc}$ with UNIFAC -T1 model, at temperatures T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\,expt}$	$x_1^{II\,calc}$	$x_2^{II\,calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\,expt}$	$x_1^{I\,calc}$	$x_2^{I\,calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.10068	0.89932	-0.05728	-36.26	0.99314	0.99951	0.00049	0.00637	0.64
296.05	0.16895	0.10319	0.89681	-0.06575	-38.92	0.99031	0.99947	0.00053	0.00916	0.92
298.22	0.17568	0.10514	0.89486	-0.07054	-40.15	0.98937	0.99943	0.00057	0.01007	1.02
303.16	0.19169	0.10976	0.89024	-0.08193	-42.74	0.98628	0.99935	0.00065	0.01307	1.32
308.16	0.20604	0.11475	0.88525	-0.09129	-44.31	0.98106	0.99924	0.00076	0.01819	1.85
313.12	0.22201	0.12006	0.87994	-0.10195	-45.92	0.97561	0.99912	0.00088	0.02351	2.41
318.2	0.23779	0.12591	0.87409	-0.11188	-47.05	0.96928	0.99898	0.00102	0.02969	3.06
323.16	0.25379	0.13209	0.86791	-0.12170	-47.95	0.96181	0.99881	0.00119	0.03699	3.85
328.12	0.27405	0.13881	0.86119	-0.13524	-49.35	0.95452	0.99861	0.00139	0.04409	4.62
333.06	0.29741	0.14612	0.85388	-0.15129	-50.87	0.94404	0.99837	0.00163	0.05433	5.76
338.12	0.32175	0.15433	0.84567	-0.16742	-52.03	0.93281	0.99808	0.00192	0.06527	7.00
341.19	0.34153	0.15973	0.84027	-0.18180	-53.23	0.92074	0.99788	0.00212	0.07714	8.38
343.14	0.35378	0.16333	0.83667	-0.19045	-53.83	0.91346	0.99774	0.00226	0.08428	9.23
345.15	0.36936	0.16719	0.83281	-0.20217	-54.73	0.90500	0.99758	0.00242	0.09258	10.23
348.19	0.39632	0.17336	0.82664	-0.22297	-56.26	0.88648	0.99732	0.00268	0.11085	12.50
350.7	0.42235	0.17875	0.82125	-0.24360	-57.68	0.87177	0.99709	0.00291	0.12532	14.38
353.1	0.45700	0.18419	0.81581	-0.27281	-59.70	0.84276	0.99684	0.00316	0.15408	18.28
Mean of the relative deviation					48.88					6.20

Table S2 The experimental $x_1^{II\,expt}$ and calculated $x_1^{II\,calc}$ values of concentration expressed in molar fraction of 2,2,4-trimethylpentane and the calculated concentration of TPG $x_2^{II\,calc}$ with UNIFAC -T2 model, at temperatures T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\,expt}$	$x_1^{II\,calc}$	$x_2^{II\,calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\,expt}$	$x_1^{I\,calc}$	$x_2^{I\,calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.08152	0.91848	-0.07644	-48.39	0.99314	0.99992	0.00008	0.00678	0.68
296.05	0.16895	0.08290	0.91710	-0.08605	-50.93	0.99031	0.99991	0.00009	0.00959	0.97
298.22	0.17568	0.08399	0.91601	-0.09169	-52.19	0.98937	0.99990	0.00010	0.01053	1.06
303.16	0.19169	0.08665	0.91335	-0.10505	-54.80	0.98628	0.99986	0.00014	0.01358	1.38
308.16	0.20604	0.08962	0.91038	-0.11642	-56.50	0.98106	0.99982	0.00018	0.01876	1.91
313.12	0.22201	0.09288	0.90712	-0.12913	-58.16	0.97561	0.99977	0.00023	0.02415	2.48
318.2	0.23779	0.09657	0.90343	-0.14122	-59.39	0.96928	0.99970	0.00030	0.03041	3.14
323.16	0.25379	0.10054	0.89946	-0.15325	-60.38	0.96181	0.99961	0.00039	0.03780	3.93
328.12	0.27405	0.10492	0.89508	-0.16913	-61.71	0.95452	0.99950	0.00050	0.04498	4.71
333.06	0.29741	0.10973	0.89027	-0.18768	-63.10	0.94404	0.99936	0.00064	0.05532	5.86
338.12	0.32175	0.11518	0.88482	-0.20657	-64.20	0.93281	0.99919	0.00081	0.06638	7.12
341.19	0.34153	0.11876	0.88124	-0.22276	-65.23	0.92074	0.99906	0.00094	0.07831	8.51

343.14	0.35378	0.12116	0.87884	-0.23262	-65.75	0.91346	0.99897	0.00103	0.08550	9.36
345.15	0.36936	0.12373	0.87627	-0.24563	-66.50	0.90500	0.99887	0.00113	0.09386	10.37
348.19	0.39632	0.12782	0.87218	-0.26851	-67.75	0.88648	0.99869	0.00131	0.11221	12.66
350.7	0.42235	0.13139	0.86861	-0.29096	-68.89	0.87177	0.99853	0.00147	0.12677	14.54
353.1	0.45700	0.13498	0.86502	-0.32202	-70.46	0.84276	0.99836	0.00164	0.15561	18.46
Mean of the relative deviation					60.84					6.30

Table S3 The experimental $x_1^{II\ expt}$ and calculated $x_1^{II\ calc}$ values of concentration expressed in molar fraction of 2,2,4-trimethylpentane and the calculated concentration of TPG $x_2^{II\ calc}$ with UNIFAC -T3 model, at temperatures T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\ expt}$	$x_1^{II\ calc}$	$x_2^{II\ calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\ expt}$	$x_1^{I\ calc}$	$x_2^{I\ calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.14285	0.85715	-0.01511	-9.56	0.99314	0.99940	0.00060	0.00626	0.63
296.05	0.16895	0.14480	0.85520	-0.02415	-14.29	0.99031	0.99935	0.00065	0.00904	0.91
298.22	0.17568	0.14627	0.85373	-0.02941	-16.74	0.98937	0.99931	0.00069	0.00994	1.00
303.16	0.19169	0.14966	0.85034	-0.04203	-21.93	0.98628	0.99920	0.00080	0.01292	1.31
308.16	0.20604	0.15315	0.84685	-0.05289	-25.67	0.98106	0.99909	0.00091	0.01803	1.84
313.12	0.22201	0.15667	0.84333	-0.06534	-29.43	0.97561	0.99896	0.00104	0.02334	2.39
318.2	0.23779	0.16034	0.83966	-0.07745	-32.57	0.96928	0.99881	0.00119	0.02953	3.05
323.16	0.25379	0.16398	0.83602	-0.08981	-35.39	0.96181	0.99865	0.00135	0.03684	3.83
328.12	0.27405	0.16768	0.83232	-0.10637	-38.81	0.95452	0.99848	0.00152	0.04397	4.61
333.06	0.29741	0.17143	0.82857	-0.12599	-42.36	0.94404	0.99830	0.00170	0.05426	5.75
338.12	0.32175	0.17533	0.82467	-0.14643	-45.51	0.93281	0.99809	0.00191	0.06528	7.00
341.19	0.34153	0.17772	0.82228	-0.16380	-47.96	0.92074	0.99795	0.00205	0.07721	8.39
343.14	0.35378	0.17926	0.82074	-0.17452	-49.33	0.91346	0.99786	0.00214	0.08439	9.24
345.15	0.36936	0.18085	0.81915	-0.18851	-51.04	0.90500	0.99776	0.00224	0.09276	10.25
348.19	0.39632	0.18328	0.81672	-0.21304	-53.75	0.88648	0.99761	0.00239	0.11113	12.54
350.7	0.42235	0.18531	0.81469	-0.23704	-56.12	0.87177	0.99748	0.00252	0.12572	14.42
353.1	0.45700	0.18726	0.81274	-0.26975	-59.03	0.84276	0.99735	0.00265	0.15460	18.34
Mean of the relative deviation					37.03					6.21

Table S4 The experimental $x_1^{II\ expt}$ and calculated $x_1^{II\ calc}$ values of concentration expressed in molar fraction of 2,2,4-trimethylpentane and the calculated concentration of TPG $x_2^{II\ calc}$ with UNIQUAC model (filled with UNIFAC Lyngby), at temperatures T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\ expt}$	$x_1^{II\ calc}$	$x_2^{II\ calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\ expt}$	$x_1^{I\ calc}$	$x_2^{I\ calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.23429	0.76571	0.07633	48.32	0.99314	0.99662	0.00338	0.00348	0.35
296.05	0.16895	0.23475	0.76525	0.06580	38.95	0.99031	0.99644	0.00356	0.00612	0.62
298.22	0.17568	0.23513	0.76487	0.05945	33.84	0.98937	0.99629	0.00371	0.00692	0.70
303.16	0.19169	0.23612	0.76388	0.04443	23.18	0.98628	0.99595	0.00405	0.00967	0.98
308.16	0.20604	0.23729	0.76271	0.03125	15.16	0.98106	0.99558	0.00442	0.01453	1.48
313.12	0.22201	0.23860	0.76140	0.01659	7.47	0.97561	0.99519	0.00481	0.01958	2.01
318.2	0.23779	0.24009	0.75991	0.00230	0.97	0.96928	0.99477	0.00523	0.02549	2.63

T/K	$x_1^{II\,expt}$	$x_1^{II\,calc}$	$x_2^{II\,calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\,expt}$	$x_1^{I\,calc}$	$x_2^{I\,calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
323.16	0.25379	0.24169	0.75831	-0.01210	-4.77	0.96181	0.99433	0.00567	0.03252	3.38
328.12	0.27405	0.24343	0.75657	-0.03063	-11.18	0.95452	0.99387	0.00613	0.03935	4.12
333.06	0.29741	0.24528	0.75472	-0.05213	-17.53	0.94404	0.99339	0.00661	0.04935	5.23
338.12	0.32175	0.24731	0.75269	-0.07445	-23.14	0.93281	0.99286	0.00714	0.06005	6.44
341.19	0.34153	0.24860	0.75140	-0.09293	-27.21	0.92074	0.99253	0.00747	0.07178	7.80
343.14	0.35378	0.24944	0.75056	-0.10434	-29.49	0.91346	0.99231	0.00769	0.07885	8.63
345.15	0.36936	0.25033	0.74967	-0.11903	-32.23	0.90500	0.99208	0.00792	0.08708	9.62
348.19	0.39632	0.25171	0.74829	-0.14462	-36.49	0.88648	0.99173	0.00827	0.10525	11.87
350.7	0.42235	0.25288	0.74712	-0.16947	-40.13	0.87177	0.99143	0.00857	0.11966	13.73
353.1	0.45700	0.25402	0.74598	-0.20298	-44.42	0.84276	0.99113	0.00887	0.14837	17.61
Mean of the relative deviation					25.56					5.72

Table S5 The experimental $x_1^{II\,expt}$ and calculated $x_1^{II\,calc}$ values of concentration expressed in molar fraction of 2,2,4-trimethylpentane and the calculated concentration of TPG $x_2^{II\,calc}$ with UNIQUAC model (filled with UNIFAC Dortmund), at temperatures T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\,expt}$	$x_1^{II\,calc}$	$x_2^{II\,calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\,expt}$	$x_1^{I\,calc}$	$x_2^{I\,calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.02147	0.97853	-0.13649	-86.41	0.99314	0.98616	0.01384	-0.00699	-0.70
296.05	0.16895	0.02241	0.97759	-0.14654	-86.74	0.99031	0.98560	0.01440	-0.00471	-0.48
298.22	0.17568	0.02313	0.97687	-0.15255	-86.84	0.98937	0.98518	0.01482	-0.00419	-0.42
303.16	0.19169	0.02481	0.97519	-0.16688	-87.06	0.98628	0.98417	0.01583	-0.00211	-0.21
308.16	0.20604	0.02660	0.97340	-0.17944	-87.09	0.98106	0.98311	0.01689	0.00205	0.21
313.12	0.22201	0.02844	0.97156	-0.19357	-87.19	0.97561	0.98201	0.01799	0.00640	0.66
318.2	0.23779	0.03042	0.96958	-0.20737	-87.21	0.96928	0.98084	0.01916	0.01156	1.19
323.16	0.25379	0.03242	0.96758	-0.22137	-87.22	0.96181	0.97965	0.02035	0.01783	1.85
328.12	0.27405	0.03451	0.96549	-0.23954	-87.41	0.95452	0.97841	0.02159	0.02389	2.50
333.06	0.29741	0.03667	0.96333	-0.26074	-87.67	0.94404	0.97712	0.02288	0.03309	3.50
338.12	0.32175	0.03897	0.96103	-0.28279	-87.89	0.93281	0.97576	0.02424	0.04295	4.60
341.19	0.34153	0.04040	0.95960	-0.30112	-88.17	0.92074	0.97490	0.02510	0.05416	5.88
343.14	0.35378	0.04133	0.95867	-0.31245	-88.32	0.91346	0.97435	0.02565	0.06088	6.66
345.15	0.36936	0.04230	0.95770	-0.32706	-88.55	0.90500	0.97377	0.02623	0.06876	7.60
348.19	0.39632	0.04380	0.95620	-0.35252	-88.95	0.88648	0.97287	0.02713	0.08640	9.75
350.7	0.42235	0.04506	0.95494	-0.37729	-89.33	0.87177	0.97212	0.02788	0.10036	11.51
353.1	0.45700	0.04628	0.95372	-0.41072	-89.87	0.84276	0.97139	0.02861	0.12863	15.26
Mean of the relative deviation					87.76					4.29

Table S6 The experimental $x_1^{II\,expt}$ and calculated $x_1^{II\,calc}$ values of concentration expressed in molar fraction of 2,2,4-trimethylpentane and the calculated concentration of TPG $x_2^{II\,calc}$ with NRTL model (filled with UNIFAC Lyngby), at temperatures T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\,expt}$	$x_1^{II\,calc}$	$x_2^{II\,calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\,expt}$	$x_1^{I\,calc}$	$x_2^{I\,calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.26367	0.73633	0.10571	66.92	0.99314	0.99773	0.00227	0.00458	0.46
296.05	0.16895	0.26349	0.73651	0.09455	55.96	0.99031	0.99758	0.00242	0.00727	0.73
298.22	0.17568	0.26340	0.73660	0.08772	49.93	0.98937	0.99747	0.00253	0.00810	0.82

303.16	0.19169	0.26330	0.73670	0.07161	37.36	0.98628	0.99720	0.00280	0.01092	1.11
308.16	0.20604	0.26337	0.73663	0.05733	27.83	0.98106	0.99690	0.00310	0.01585	1.62
313.12	0.22201	0.26360	0.73640	0.04159	18.73	0.97561	0.99659	0.00341	0.02098	2.15
318.2	0.23779	0.26398	0.73602	0.02619	11.01	0.96928	0.99625	0.00375	0.02696	2.78
323.16	0.25379	0.26449	0.73551	0.01070	4.22	0.96181	0.99589	0.00411	0.03407	3.54
328.12	0.27405	0.26514	0.73486	-0.00891	-3.25	0.95452	0.99550	0.00450	0.04099	4.29
333.06	0.29741	0.26591	0.73409	-0.03150	-10.59	0.94404	0.99510	0.00490	0.05106	5.41
338.12	0.32175	0.26683	0.73317	-0.05492	-17.07	0.93281	0.99466	0.00534	0.06185	6.63
341.19	0.34153	0.26745	0.73255	-0.07408	-21.69	0.92074	0.99437	0.00563	0.07363	8.00
343.14	0.35378	0.26786	0.73214	-0.08592	-24.29	0.91346	0.99419	0.00581	0.08073	8.84
345.15	0.36936	0.26831	0.73169	-0.10105	-27.36	0.90500	0.99400	0.00600	0.08899	9.83
348.19	0.39632	0.26902	0.73098	-0.12730	-32.12	0.88648	0.99369	0.00631	0.10722	12.09
350.7	0.42235	0.26964	0.73036	-0.15271	-36.16	0.87177	0.99344	0.00656	0.12167	13.96
353.1	0.45700	0.27026	0.72974	-0.18675	-40.86	0.84276	0.99318	0.00682	0.15043	17.85
Mean of the relative deviation					28.55					5.89

Table S7 The experimental $x_1^{II\ expt}$ and calculated $x_1^{II\ calc}$ values of concentration expressed in molar fraction of 2,2,4-trimethylpentane and the calculated concentration of TPG $x_2^{II\ calc}$ with NRTL model (filled with UNIFAC Dortmund), at temperatures T

	Solvent rich phase					Hydrocarbon rich phase				
T/K	$x_1^{II\ expt}$	$x_1^{II\ calc}$	$x_2^{II\ calc}$	standard deviation of x_1^{II}	relative deviation of x_1^{II}	$x_1^{I\ expt}$	$x_1^{I\ calc}$	$x_2^{I\ calc}$	standard deviation of x_1^{I}	relative deviation of x_1^{I}
293.16	0.15796	0.02568	0.97432	-0.13228	-83.74	0.99314	0.98792	0.01208	-0.00522	-0.53
296.05	0.16895	0.02657	0.97343	-0.14238	-84.27	0.99031	0.98735	0.01265	-0.00296	-0.30
298.22	0.17568	0.02725	0.97275	-0.14843	-84.49	0.98937	0.98691	0.01309	-0.00245	-0.25
303.16	0.19169	0.02884	0.97116	-0.16285	-84.95	0.98628	0.98587	0.01413	-0.00041	-0.04
308.16	0.20604	0.03051	0.96949	-0.17553	-85.19	0.98106	0.98477	0.01523	0.00371	0.38
313.12	0.22201	0.03222	0.96778	-0.18979	-85.49	0.97561	0.98362	0.01638	0.00800	0.82
318.2	0.23779	0.03404	0.96596	-0.20375	-85.69	0.96928	0.98238	0.01762	0.01309	1.35
323.16	0.25379	0.03587	0.96413	-0.21792	-85.86	0.96181	0.98111	0.01889	0.01930	2.01
328.12	0.27405	0.03777	0.96223	-0.23628	-86.22	0.95452	0.97979	0.02021	0.02528	2.65
333.06	0.29741	0.03972	0.96028	-0.25769	-86.64	0.94404	0.97842	0.02158	0.03438	3.64
338.12	0.32175	0.04179	0.95821	-0.27996	-87.01	0.93281	0.97695	0.02305	0.04414	4.73
341.19	0.34153	0.04308	0.95692	-0.29845	-87.39	0.92074	0.97602	0.02398	0.05528	6.00
343.14	0.35378	0.04391	0.95609	-0.30988	-87.59	0.91346	0.97542	0.02458	0.06196	6.78
345.15	0.36936	0.04477	0.95523	-0.32459	-87.88	0.90500	0.97480	0.02520	0.06979	7.71
348.19	0.39632	0.04611	0.95389	-0.35022	-88.37	0.88648	0.97383	0.02617	0.08735	9.85
350.7	0.42235	0.04722	0.95278	-0.37513	-88.82	0.87177	0.97301	0.02699	0.10124	11.61
353.1	0.45700	0.04831	0.95169	-0.40870	-89.43	0.84276	0.97221	0.02779	0.12946	15.36
Mean of the relative deviation					86.41					4.35