



STUDY OF QUATERNARY LIQUID-LIQUID EQUILIBRIA FOR SYSTEMS (WATER / METHANOL / CYCLOHEXANOL+TOLUENE): EXPERIMENTAL AND MODELLING

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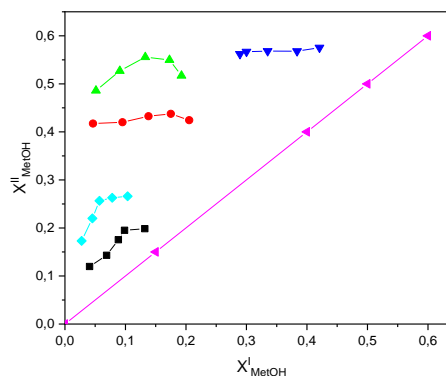
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The experimental liquid-liquid equilibrium (LLE) data for the extraction of methanol from aqueous solution using mixed solvents (toluene + cyclohexanol) at 291.15 K and atmospheric pressure at the ratios (0, 0.25, 0.4, 0.6, 0.8, 1) was studied. The values of the solvent ratio 0 and 1 led us to study the liquid-liquid equilibrium of the ternary systems (water/methanol/cyclohexanol) and (water/methanol/toluene). The compositions of the coexisting phases were determined by the cloud point method. The tie line data for ternary and quaternary systems were correlated by NRTL model. The Othmer-Tobias and Hand correlations were also tested, to verify the reliability of the experimental tie lines data. The separation factor and the distribution coefficient were calculated from the experimental data to evaluate the effect of using mixed solvents. It was found that the ratio $M = 0.4$ is the best suited for the liquid-liquid extraction of methanol from water.



INTRODUCTION

The separation of alcohol/water mixtures is of great importance in theoretical and industrial applications.¹ Although the ethanol/water separation is already well applied and disseminated at the industrial level representing as a consolidated technique, the methanol/water separation remains a challenge. There are

relatively limited studies examining the separation of methanol from water, this can be explained by the fact that the characteristics of water and methanol are fairly similar, and the non-ideal behaviour of the water and methanol molecules.² Methanol is an important raw material in the chemical industry and is a good solvent, it is also regarded as an alternative source of fuel.^{3,4}

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In the pharmaceutical industry, the fact that the cooling water circuit can be polluted by methanol due to a malfunction is a real problem. However, this pollution should be removed.² Pure alcohols and their mixtures significantly affect the structure of water, and exhibit particular anomalies in various physico-chemical properties.⁵ Understanding this mechanism is of great interest given the growing importance of water-based separation technologies.

The separation of methanol from aqueous mixture is feasible by distillation but the use of solvents makes it possible to study their separation by extraction. The use of solvent is an energy-saving process.¹ The pervaporation process can be also used for the separation of methanol–water mixture,² however, this process is still expensive.⁶ Therefore the use of liquid-liquid extraction is integrated and is mainly guided by its efficiency and low energy costs.

The study of a liquid-liquid equilibrium (LLE) of ternary and quaternary, pseudo-ternary, systems in liquid-liquid extraction processes was a very important subject in the last years. In this study LLE data for (water/methanol/cyclohexanol) and (water/methanol/toluene) ternaries are reported, and it is seen that cyclohexanol has low distribution coefficient and separation factor values compared with toluene. In view of the significant influence of solvents in the extraction of alcohols from aqueous solution, it is interesting to study the LLE of quaternary mixtures {water + methanol + (mixed solvent)}. So the mixtures of cyclohexanol and toluene were used as mixed solvent in order to show the trend of the distribution coefficient and separation factor, extraction improvement, for this mixed solvent.

The present work is focused on the determination of experimental data of quaternary system: water/methanol/cyclohexanol+toluene at 291.15 K and atmospheric pressure. In accordance with the literature review, data on solubility and liquid-liquid equilibrium (LLE) in the quaternary system water/methanol/cyclohexanol+toluene at 291.15 K are not available. These data will enable more detailed characterisation of the thermodynamic and phase properties of this system.

The representation of a system with four constituents requires a spatial diagram (tetrahedral). It is possible to group the constituents according to their chemical properties and to consider the complex mixture as a mixture of groups whose number is limited, which makes it possible to reduce to ternary systems.⁷

EXPERIMENTAL

Reagents

Methanol with a mass purity (by supplier) of 99.5% was purchased from Honeywell. Toluene with a purity of 99.8% was purchased from Labosi and cyclohexanol with purity and 99.5 %, was purchased from Biochem. Detailed information of reagents used in this study is presented in Table 1.

Experimental Procedure

The binodal curves and the tie line data were determined using the titration, cloud point method.¹ The right-hand of the binodal curve was constructed by shaking vigorously a known volumes of a binary mixtures of (water, methanol) with the mixed solvent (toluene + cyclohexanol) at 291.15 K under atmospheric pressure for 2hours, until the transformation of the mixture into a cloud, turbid, mixture. The mixtures were made by weighing using a Kern analytical balance model (ABJ220-4NM, accurate to ± 0.0001 g). Stirring of the mixture is carried out in a glass equilibrium cell with a magnetic stirrer and an isothermal fluid jacket for circulating water from a controlled temperature bath to maintain the desired temperature, in the equilibrium cell, within ± 0.1 K. For the construction of the left-hand a mixture of mixed solvent-methanol was titrated with water until the appearance of a permanent turbidity. The refractive index (n_D) of the turbid mixtures was measured using a refractometer type HI 96801 ± 0.2 Brix and taken as a function of the composition.

The tie lines data were determined using the same equilibrium container. Known volumes of a mixture (water+ methanol + mixed solvent) were prepared and subjected to a vigorous shaking in the equilibrium. The mixture was left to settle for 24 h until obtaining two clear phases with a separate interface.⁸ Samples of both phases were taken and analysed by refractometry to determine their composition. All the experiments were repeated on three separate times to obtain an average value and converted to molar fraction.

To ensure the reproducibility of the measures, it is necessary to calculate the standard uncertainty of the composition. The standard uncertainty formula is defined as follows:^{9,10}

$$S^2 = \frac{\sum_{j=1}^n (q_j - \bar{q})^2}{n - 1} \quad (1)$$

$$u = \left(\frac{S^2}{n}\right)^{0.5} \quad (2)$$

where: S is the experimental standard deviation, u represents the standard uncertainty, n is the number of the experiments, q_j indicates the j^{th} experimental value, \bar{q} refers to the average values of the experiments.

The mixed solvent (cyclohexanol+ toluene) for the quaternary systems is represented by the ratio M , and its expression is given by:¹¹

$$M = \frac{\omega_1}{\omega_1 + \omega_2} = \frac{m_1}{m_1 + m_2} \quad (3)$$

where m_1 and m_2 are the amount of toluene and cyclohexanol, respectively.

The ratio M took the values 0; 0.25; 0.4; 0.6; 0.8; 1. While $M = 0$ and $M = 1$ represents the ternary systems: cyclohexanol/methanol/water and toluene/methanol/water respectively.

Table 1

Properties of pure component

Component	Molecular weight (g/mol)	Density (g/cm ³)	Refractive index (<i>n_D</i>)	
			Exp	Lit
Methanol	32.04	0.792	1.33572	1.32880 ¹
Cyclohexanol	100.16	0.950	1.45965	1.46570 ¹²
Toluene	92.14	0.870	1.49412	1.49410 ¹³
Water	18.02	1.000	1.33299	1.33340 ¹

RESULTS AND DISCUSSION

Experimental values

The composition of the measured points of binodal, solubility, curves for the water-methanol-mixed solvent (toluene + cyclohexanol) were determined experimentally at temperature 291.15 K and reported in

Table 2 (for $M = 0$, $M = 0.25$, $M = 0.4$, $M = 0.6$ and $M = 1$). The experimental tie-line data for the studied systems are given in Table 3, in which x_i^I and x_i^{II} refer to mole fraction of the i component in the aqueous and organic phase, respectively. The liquid-liquid phase diagrams (binodal curves, and tie lines data) of the systems for $M = 0$, $M = 0.25$, $M = 0.4$, $M = 0.6$ and $M = 1$ are plotted respectively in Figs. 1–5.

Table 2

The solubility curves (molar fractions) for the water (1)/methanol (2)/mixed solvent (cyclohexanol + toluene) (3) at 291.15 K^a

Water (1)/ methanol/ (2)/ cyclohexanol (3): ($M = 0$)			Water (1)/ methanol (2)/ cyclohexanol+ toluene (3): ($M = 0.25$)		
x_1	x_2	x_3	x_1	x_2	x_3
0.9770	0.0000	0.0230	0.8839	0.0000	0.1161
0.9266	0.0382	0.0352	0.8251	0.0551	0.1198
0.8861	0.0644	0.0495	0.7768	0.1038	0.1194
0.8613	0.0785	0.0602	0.7210	0.1405	0.1385
0.8593	0.0832	0.0575	0.6783	0.1727	0.1490
0.8145	0.1089	0.0766	0.6377	0.1989	0.1634
0.7768	0.1346	0.0886	0.5537	0.2467	0.1996
0.7480	0.1578	0.0942	0.5101	0.2576	0.2323
0.6909	0.1910	0.1181	0.4686	0.2684	0.2630
0.6337	0.2146	0.1517	0.4104	0.2742	0.3154
0.5948	0.2120	0.1932	0.3631	0.2647	0.3722
0.5561	0.2086	0.2353	0.3094	0.2413	0.4493
0.5113	0.1952	0.2935	0.2898	0.2152	0.4950
0.4951	0.1764	0.3285	0.2543	0.1812	0.5645
0.4722	0.1578	0.3700	0.2400	0.1544	0.6056
0.4529	0.1211	0.4260	0.2160	0.1202	0.6638
0.4373	0.0974	0.4653	0.1922	0.0856	0.7222
0.4192	0.0700	0.5108	0.1688	0.0626	0.7686
0.4000	0.0382	0.5618	0.1410	0.0302	0.8288
0.3915	0.0000	0.6085	0.1151	0.0000	0.8849
^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0013$, $u(x_2) = 0.0007$, $u(x_3) = 0.0006$.			^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0028$, $u(x_2) = 0.0010$, $u(x_3) = 0.0019$.		
Water (1)/ methanol/ (2)/ cyclohexanol+toluene (3): ($M = 0.4$)			Water (1)/ methanol/ (2)/ cyclohexanol+toluene (3): ($M = 0.6$)		
x_1	x_2	x_3	x_1	x_2	x_3
0.7617	0.0000	0.2383	0.8543	0.0000	0.1457
0.7064	0.0524	0.2412	0.7854	0.0583	0.1563
0.6517	0.1056	0.2427	0.7268	0.1079	0.1653
0.5801	0.1723	0.2475	0.6464	0.1646	0.1890
0.5021	0.2237	0.2742	0.5597	0.2494	0.1909
0.4336	0.2704	0.2960	0.4774	0.3190	0.2036
0.3672	0.2944	0.3384	0.4162	0.3708	0.2130
0.3150	0.3087	0.3763	0.3364	0.4246	0.2390
0.2802	0.3052	0.4146	0.3002	0.4012	0.2986

0.2214	0.2819	0.4967	0.2703	0.3611	0.3686
0.1987	0.2361	0.5652	0.2474	0.3307	0.4219
0.1717	0.1836	0.6447	0.2230	0.2732	0.5038
0.1633	0.1455	0.6912	0.1966	0.2335	0.5699
0.1348	0.0600	0.8052	0.1657	0.1845	0.6498
0.1259	0.0000	0.8741	0.1520	0.1354	0.7126
–	–	–	0.1188	0.0706	0.8106
			0.0890	0.0000	0.9110
^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0006$, $u(x_2) = 0.0002$, $u(x_3) = 0.0004$.			^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0050$, $u(x_2) = 0.0023$, $u(x_3) = 0.0030$.		
Water (1)/ methanol/ (2)/ toluene (3): ($M = 1$)					
x_1	x_2	x_3	x_1	x_2	x_3
0.9671	0	0.0329	0.5586	0.1818	0.2596
0.9127	0.0407	0.0466	0.5035	0.1794	0.3171
0.8375	0.1008	0.0617	0.4421	0.1723	0.3856
0.7900	0.1408	0.0692	0.3946	0.1465	0.4589
0.7520	0.1577	0.0903	0.3503	0.1249	0.5248
0.7162	0.1695	0.1143	0.3078	0.1028	0.5894
0.6838	0.1726	0.1436	0.2487	0.0739	0.6774
0.6475	0.1803	0.1722	0.1979	0.0441	0.7580
0.6053	0.1854	0.2093	0.1530	0.0227	0.8243
			0.1051	0.0000	0.8949
^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0039$, $u(x_2) = 0.0007$, $u(x_3) = 0.0035$.					

Table 3

Experimental tie lines compositions of the five studied systems at 291.15 K^a

Aqueous phase			Organic phase			D_1	D_2	S
x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}			
water/methanol/cyclohexanol ($M = 0$)								
0.7927	0.1207	0.0866	0.4399	0.1089	0.4512	0.5549	0.9030	1.6274
0.8457	0.0925	0.0618	0.4361	0.1057	0.4582	0.5157	1.1429	2.2164
0.8579	0.0831	0.0590	0.4320	0.0919	0.4761	0.5035	1.10663	2.1977
0.8803	0.0651	0.0546	0.4230	0.0707	0.5063	0.4805	1.0849	2.2576
0.9189	0.0391	0.0420	0.4143	0.0563	0.5294	0.4508	1.4416	3.1980
^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0013$, $u(x_2) = 0.0015$, $u(x_3) = 0.0028$ in aqueous phase, $u(x_1) = 0.0017$, $u(x_2) = 0.0011$, $u(x_3) = 0.0028$ in organic phase.								
water/methanol/cyclohexanol + toluene ($M = 0.25$)								
0.6769	0.1750	0.1481	0.3536	0.2605	0.3859	0.5224	1.4890	2.8506
0.7100	0.1507	0.1393	0.3159	0.2457	0.4384	0.4448	1.6305	3.6654
0.7553	0.1211	0.1236	0.2931	0.2235	0.4834	0.3880	1.8461	4.7575
0.7966	0.0838	0.1196	0.2878	0.2085	0.5037	0.3613	2.4876	6.8847
0.8390	0.0409	0.1201	0.2624	0.1880	0.5496	0.3127	4.6013	14.7134
^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0044$, $u(x_2) = 0.0022$, $u(x_3) = 0.0065$ in aqueous phase, $u(x_1) = 0.0065$, $u(x_2) = 0.0011$, $u(x_3) = 0.0076$ in organic phase.								
water/methanol/cyclohexanol+toluene ($M = 0.4$)								
0.6080	0.1451	0.2469	0.2854	0.3056	0.4090	0.4695	2.1061	4.4860
0.6236	0.1303	0.2461	0.2364	0.2887	0.4749	0.3791	2.2160	5.8448
0.6576	0.1007	0.2417	0.2114	0.2644	0.5242	0.3215	2.6263	8.1702
0.6917	0.0690	0.2393	0.1805	0.2010	0.6185	0.2610	2.9140	11.1658
0.7222	0.0391	0.2387	0.1639	0.1548	0.6813	0.2269	3.9624	17.4654
^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0001$, $u(x_2) = 0.0004$, $u(x_3) = 0.0005$ in aqueous phase, $u(x_1) = 0.0002$, $u(x_2) = 0.0002$, $u(x_3) = 0.0004$ in organic phase.								
water/methanol/cyclohexanol+toluene ($M = 0.6$)								
0.4614	0.3352	0.2034	0.2914	0.3947	0.3139	0.6315	1.1776	1.8646
0.4932	0.3070	0.1998	0.2803	0.3686	0.3511	0.5684	1.2006	2.1122
0.5358	0.2700	0.1942	0.2617	0.3443	0.3940	0.4884	1.2752	2.6109
0.5621	0.2496	0.1883	0.2545	0.3331	0.4124	0.4527	1.3823	3.0535
0.5761	0.2345	0.1894	0.2437	0.3126	0.4437	0.4230	1.3334	3.1524
^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0011$, $u(x_2) = 0.0004$, $u(x_3) = 0.0015$ in aqueous phase, $u(x_1) = 0.0008$, $u(x_2) = 0.0002$, $u(x_3) = 0.0011$ in organic phase.								
water/methanol/toluene ($M = 1$)								

0.8433	0.0975	0.0592	0.3678	0.1333	0.4989	0.4361	1.3676	3.1356
0.8704	0.0737	0.0559	0.3422	0.1219	0.5359	0.3931	1.6551	4.2103
0.8971	0.0542	0.0487	0.3064	0.1058	0.5878	0.3416	1.9511	5.7124
0.9111	0.0432	0.0457	0.2535	0.0715	0.6750	0.2783	1.6546	5.9463
0.9307	0.0263	0.0430	0.1842	0.0385	0.7773	0.1979	1.4645	7.4008

^a Standard uncertainties u are $u(T) = 0.1$ K, $u(x_1) = 0.0006$, $u(x_2) = 0.0013$, $u(x_3) = 0.0019$ in aqueous phase, $u(x_1) = 0.0017$, $u(x_2) = 0.0015$, $u(x_3) = 0.0033$ in organic phase.

Thermodynamic modelling

The NRTL model (Non-Random Two Liquid) was used to correlate the liquid-liquid

equilibrium and calculate the activity coefficients. The NRTL model can be applied to ternary systems and superior order,¹⁴ NRTL equations are given by:^{15,16}

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{i=1}^n x_i \tau_{ij} G_{ij}}{\sum_{k=1}^n G_{kj} x_k} \right) \quad (4)$$

$$G_{ji} = \exp(-\alpha_{ij} \tau_{ji}) \quad (\alpha_{ij} = \alpha_{ji}) \quad (5)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{A_{ji}}{T} \quad (\tau_{ij} \neq \tau_{ji}) \quad (6)$$

where: i, j , and k refer to the components, A_{ij} is the binary interaction parameter, α_{ij} represents the non randomness of the NRTL model.

The experimental data for the different studied systems using NRTL model were estimated, calculated, by minimising the objective function which represent the difference between the

experimental and calculated compositions on equilibrium of each component. The consistency of the model predictions was evaluated by the root-mean-square deviation between the experimental and correlated compositions. The objective function (OF) and the root-mean-square deviation ($RMSD$) were given by the following equations:^{17,18}

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

$$RMSD = \left[\frac{\sum_k^m \sum_{j=1}^2 \sum_{i=1}^3 (x_{ijk}^{exp} - x_{ijk}^{cal})^2}{2nm} \right]^{\frac{1}{2}} \quad (8)$$

where i, j and k , respectively, represent the component, the phase and the tie line. x_{ijk}^{exp} and x_{ijk}^{cal} respectively, represent the experimental and the calculated mol fractions.

Figures 1–5 show that the binodal curves of all studied systems are of type (I), as classified by Treybal.¹⁹ With one of the binary mixtures exhibit partial solubility in the investigated temperature. There are the binary mixtures (cyclohexanol/water), (toluene/water) and (mixed solvent/water) which are partially miscible.

For the ternary systems ($M = 0$ and $M = 1$) the heterogeneous region increases in the order cyclohexanol < toluene. This can be explained by the mutual solubilities of alcohols with water which will be affected by the hydrogen bonding between the alcohols and water^{20,21} (water is more

soluble in the mixture cyclohexanol + methanol than in the mixture toluene + methanol).

For the quaternary systems, the heterogeneous region is larger for a mixed solvent ratio ($M = 0.6$) to the region obtained for a mixed solvent ratios ($M = 0.25$, $M = 0.4$). In the case of ratio ($M = 0.6$) the toluene volume is greater than that of cyclohexanol and toluene is insoluble in water which consequently increases the biphasic region. Figures 1–5 show also that the slopes of the tie lines toward the extract phase for all cases of M , indicating that methanol is more soluble in cyclohexanol and toluene and in mixed solvent (cyclohexanol+toluene) than in water. Simulated tie lines, by NRTL model are much closer to the experimentally observed ones, with exception of the ternary system water/methanol/cyclohexanol ($M = 0$) and the pseudo-ternary system ($M = 0.25$)

which exhibit minor deviation from experimentally obtained tie lines. That led us to say that the NRTL model corresponds satisfactorily to the LLE experimental data, which

is confirmed by the values of *RMSD*. The *RMSD* values and binary interaction parameters between methanol, solvents or mixed solvent, and water are presented in Table 4.

Table 4

The NRTL binary interaction parameters and *RMSD* values for ternary and quaternary systems

Component			<i>RMSD</i>
<i>i-j</i>	<i>A_{ij}</i>	<i>A_{ji}</i>	
water/methanol/cyclohexanol (<i>M</i> = 0)			
1-2	9.191	2.810	3.879.10 ⁻²
1-3	-1.576	-3.346	
2-3	5.153	11.555	
water/methanol/cyclohexanol+toluene (<i>M</i> = 0.25)			
1-2	1.346	0.908	4.668.10 ⁻²
1-3	9.235	1.095	
2-3	2.604	4.412	
water/methanol/cyclohexanol+toluene (<i>M</i> = 0.4)			
1-2	2.471	1.385	4.137.10 ⁻²
1-3	11.113	1.014	
2-3	2.268	5.210	
water/methanol/cyclohexanol+toluene (<i>M</i> = 0.6)			
1-2	9.513	1.495	2.896.10 ⁻²
1-3	1.616	-0.018	
2-3	5.502	7.401	
water/methanol/toluene (<i>M</i> = 1)			
1-2	0.591	2.935	3.441.10 ⁻²
1-3	5.392	-1.422	
2-3	1.918	4.676	

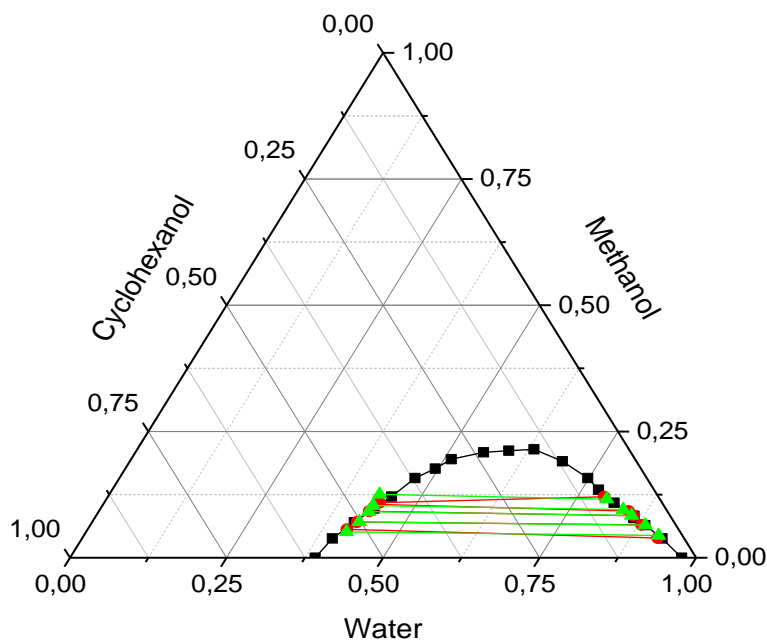


Fig. 1 – The LLE phase diagram of water–methanol–cyclohexanol system for *M* = 0 at 291.15 K (■) solubility curve, (●) experimental tie lines, (▲) NRTL Model.

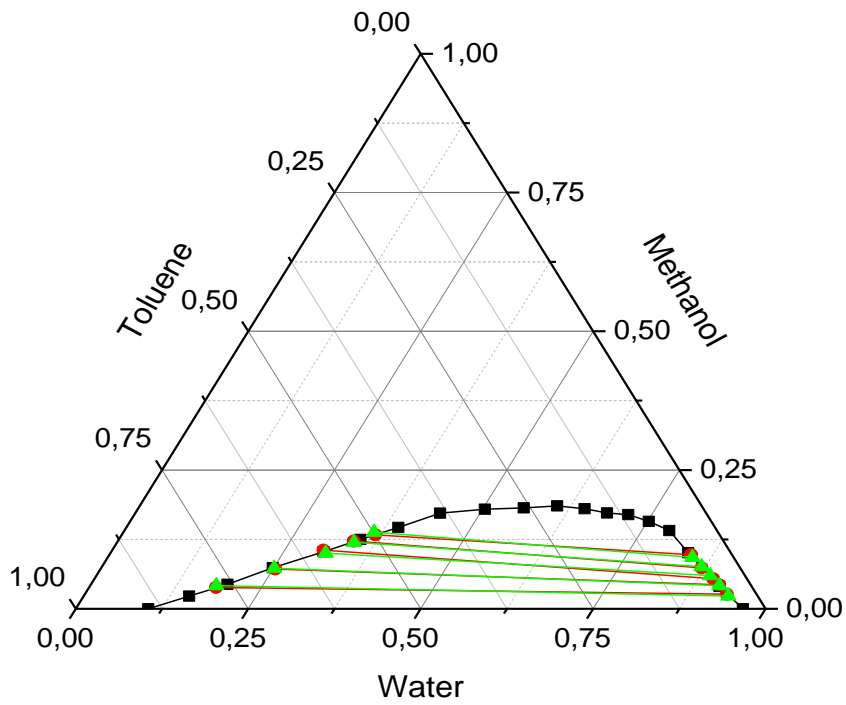


Fig. 2 – The LLE phase diagram of water–methanol–toluene system for $M = 1$ at 291.15 K (■) solubility curve, (●) experimental tie lines, (▲) NRTL Model.

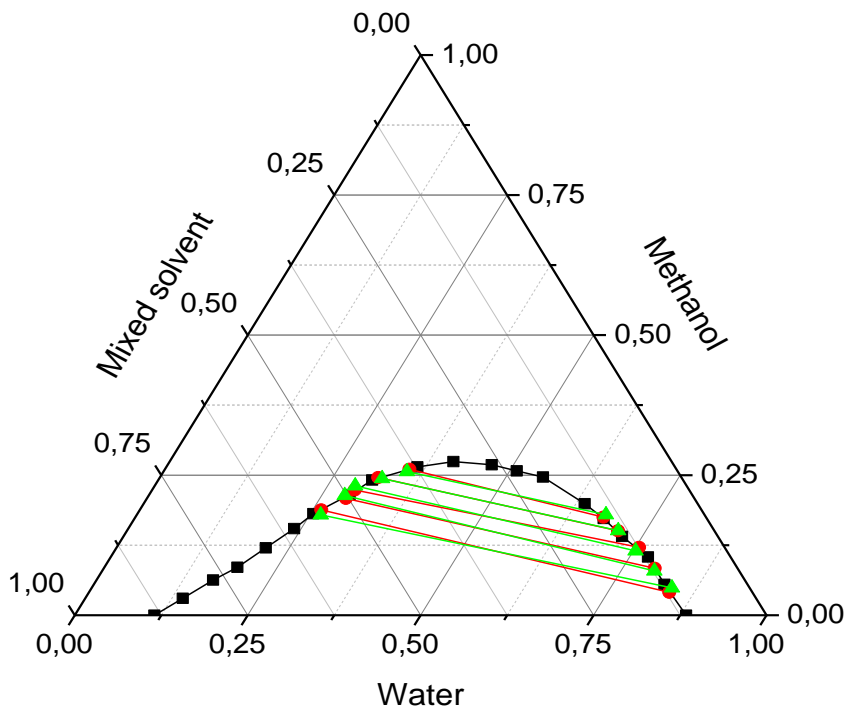


Fig. 3 – The LLE phase diagram of water–methanol–mixed solvent system for $M = 0.25$ at 291.15 K (■) solubility curve, (●) experimental tie lines, (▲) NRTL Model.

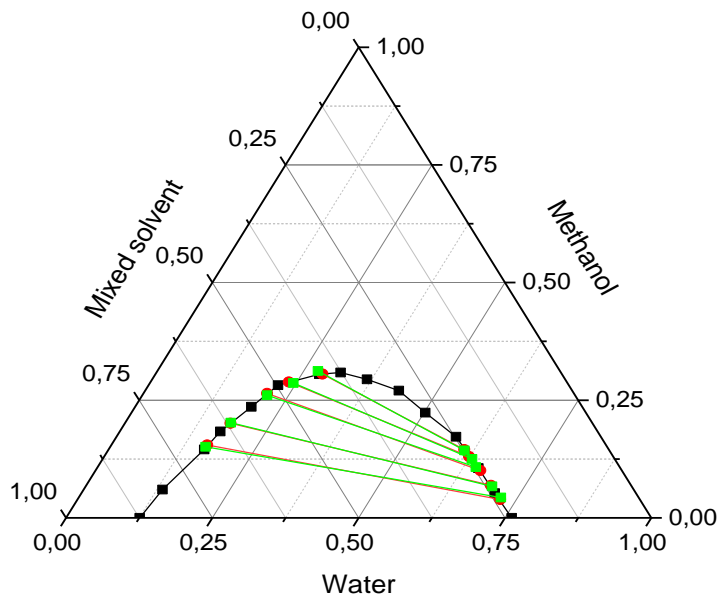


Fig. 4 – The LLE phase diagram of water–methanol–mixed solvent system for $M = 0.4$ at 291.15 K (■) solubility curve, (●) experimental tie lines, (▲) NRTL Model.

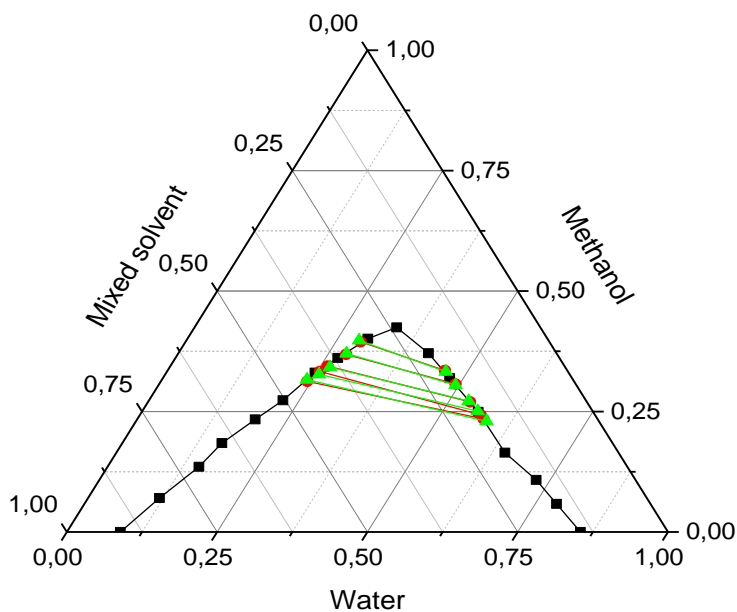


Fig. 5 – The LLE phase diagram of water–methanol–mixed solvent system for $M = 0.6$ at 291.15 K (■) solubility curve, (●) experimental tie lines, (▲) NRTL Model.

Consistency of experimental tie-line data

The consistency of experimental tie-line data of the ternary and quaternary systems was verified by applying the Othmer-Tobias,²² and Hand correlations,⁹ which are expressed as follows:

$$\ln\left(\frac{1-x_1^I}{x_3^I}\right) = a + b \ln\left(\frac{1-x_3^{II}}{x_3^{II}}\right) \quad (9)$$

$$\ln\left(\frac{x_2^{II}}{x_3^{II}}\right) = a_1 \ln\left(\frac{x_2^I}{x_1^I}\right) + b_1 \quad (10)$$

where: x_1^I is the molar fraction of water in the aqueous phase, x_3^{II} is the molar fraction of solvent or mixed solvent in the organic phase, x_2^I is the molar fraction of methanol in the aqueous phase, x_2^{II} is the molar fraction of methanol in the organic phase,

a , b , a_1 and b_1 are the parameters of the Othmer-Tobias and Hand equations, respectively (are adjusted on experimental data).

The values of the parameters and the determination coefficients R^2 of each correlation

are given in Table 5. A determination coefficient R^2 close to 1 suggests a high degree of consistency

in the associated data. The plots of these equations were shown in Figs. 6–9.

Table 5

Results of empirical equations for ternary and quaternary systems

Othmer-Tobias			Hand		
a	b	R^2	a_1	b_1	R^2
water/methanol/cyclohexanol ($M = 0$)					
-2.0349	2.8821	0.9123	0.7067	-0.0254	0.9362
water/methanol/cyclohexanol+toluene ($M = 0.25$)					
-1.3140	1.4024	0.9547	0.3799	0.0207	0.9112
water/methanol/cyclohexanol+toluene ($M = 0.4$)					
-0.5902	0.4691	0.9870	0.7939	0.7871	0.9847
water/methanol/cyclohexanol+toluene ($M = 0.6$)					
-0.5237	0.8727	0.9874	0.5117	0.9432	0.9889
water/methanol/toluene ($M = 1$)					
-1.7966	0.6845	0.9370	1.2300	1.5027	0.9461

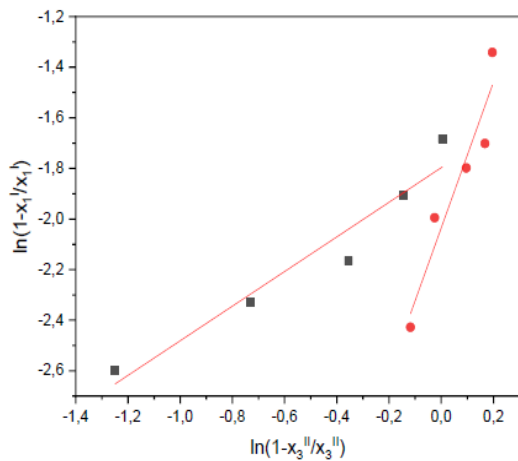


Fig. 6 – Othmer Tobias plots of ternary systems at $T = 291.15$ K: (■) toluene, (●) cyclohexanol.

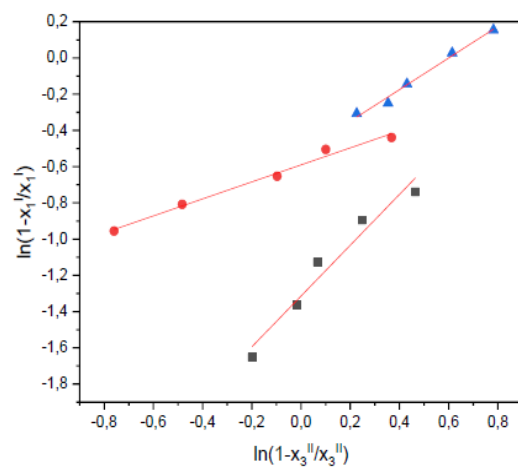


Fig. 7 – Othmer Tobias plots of quaternary systems at $T = 291.15$ K: (■) $M = 0.25$, (●) $M = 0.4$, (▲) $M = 0.6$.

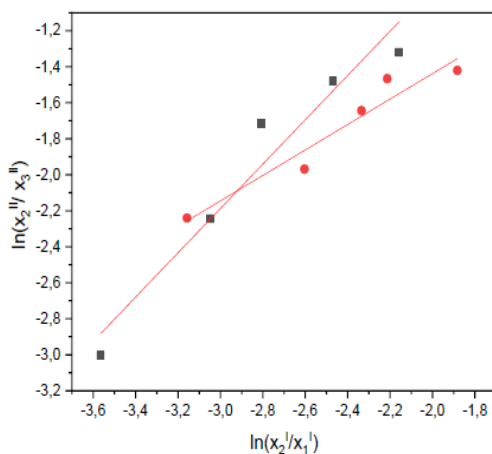


Fig. 8 – Hand plots of ternary systems at $T = 291.15$ K: (■) toluene, (●) cyclohexanol.

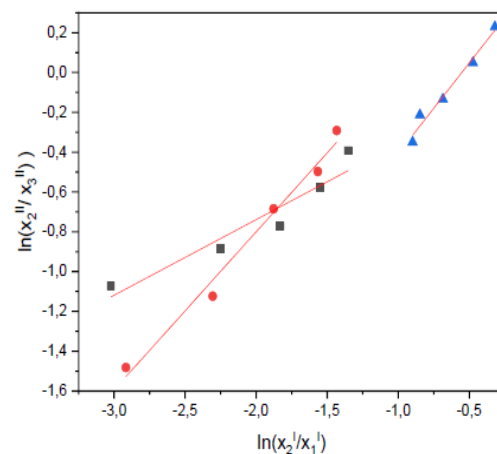


Fig. 9 – Hand plots of quaternary systems at $T = 291.15$ K: (■) $M = 0.25$, (●) $M = 0.4$, (▲) $M = 0.6$.

The determination coefficients R^2 of the studied systems are close to 1, indicates the good agree and consistence of the tie lines data, with exception of

the ternary system water/methanol/cyclohexanol ($M = 0$) and the pseudo ternary system ($M = 0.25$), where the determination coefficients R^2 of Othmer-

Tobias and Hand correlations are slightly greater than 0.9 (0.9123 and 0.9123 respectively), which are considered reasonable and acceptable and indicate that the experimental related data are reliable.

Distribution Coefficient and Separation Factor

The extraction efficiency of cyclohexanol, toluene and mixed solvent (toluene + cyclohexanol in different ratios) was determined by calculating the separation factors (S), which represent the ability of a solvent to selectively extract the solute (methanol) from its solution (water). The separation factor formula was given as follows:^{9,23}

$$S = \frac{D_2}{D_1} = \frac{\frac{x_2^{II}}{x_2^I}}{\frac{x_1^{II}}{x_1^I}} \quad (11)$$

where D_2 and D_1 are the distribution coefficients of methanol and water respectively, x_1^I , x_2^I and x_1^{II} , x_2^{II} represent the molar fraction of water and methanol respectively in the aqueous (the raffinate) and the organic (the extract) phases.

The experimental values of distribution coefficients and separation factors are given in Table 3. According to this table, the distribution coefficient of methanol almost in all cases is greater than 1 which means that the both solvents (cyclohexanol, toluene) and the mixed solvent (cyclohexanol + toluene) could be used to extract methanol from water (extraction feasible). It is also seen from Table 3 that the values of separation factors are high and greater than 1. The mixed solvent at ratio $M = 0.4$ has a higher separation factors, comparing with cyclohexanol, toluene and mixed solvent at the ratios (0.25, 0.6). Consequently, the mixed solvent (toluene+cyclohexanol) for $M=0.4$ was found to be the best solvent.

To confirm this, we use the selectivity diagram on a solvent-free basis which is established by plotting X_{MetOH}^{II} vs X_{MetOH}^I ²⁴ as shown in Fig. 10,

$$\text{with } X_{MetOH}^{II} = \frac{x_2^{II}}{x_2^{II} + x_1^{II}} \quad (\text{in the organic phase}) \quad (12)$$

$$X_{MetOH}^I = \frac{x_2^I}{x_2^I + x_1^I} \quad (\text{in the aqueous phase}) \quad (13)$$

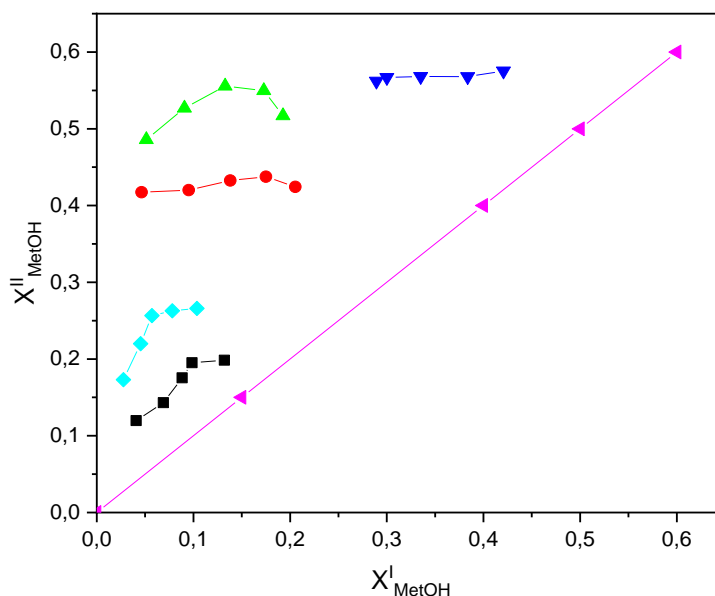


Fig. 10 – Selectivity diagram of (water + methanol+ solvents) at 291.15 K:
 (■) $M = 0$, (◆) $M = 1$, (●) $M = 0.25$, (▲) $M = 0.4$, (▼) $M = 0.6$, (▲) First bisector.

Figure 10. shows that mixed solvent at $M = 0.4$ ratio present a better selectivity towards methanol compared with the other ratios, as its curve is the furthest from the first bisector. An additional result is that mixed solvent (toluene + cyclohexanol) may be used as an alternative of these pure solvents.

CONCLUSIONS

As a conclusion from the study of Liquid-liquid equilibria (LLE) data for water/methanol/ mixed solvent (cyclohexanol+toluene) at different ratios

(0, 0.25, 0.4, 0.6, 1) and at 291.15 K and atmospheric pressure.

The solubility curves for all studied systems have the typical type I shape, where one of the binary mixtures has a miscibility gap. The NRTL model gives a good prediction of the liquid-liquid equilibrium with a minor deviation from experimentally obtained tie-lines for the ternary system water/methanol/cyclohexanol ($M = 0$) and the pseudo-ternary system water/methanol/cyclohexanol + toluene ($M = 0.25$). The Othmer-Tobias equation seems to be the most appropriate for correlate the consistence of experimental tie line data. The distribution coefficients and the separation factors of all ratios of mixed solvent were calculated and compared, the selectivity diagram was also made. The results showed that the distribution coefficients of methanol were greater than 1 in all studied systems indicating that extraction is feasible. The mixed solvent (toluene + cyclohexanol) with a ratio $M = 0.4$ had a higher separation factor indicating that this mixed solvent is the appropriate solvent to extract methanol from its aqueous mixture in this study. This is clearly confirmed by the selectivity diagram which is the furthest, most distant, from the first bisector (for this mixed solvent ratio 0.4).

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