Comprehensive Journal of Science
Volume (10), Issue (39), (March, 2026)
ISSN: 3014-6266

مجلة العلوم الشاملة
المجلد (10) العدد 39 مارس 2026
ردمد: 3014-6266

Thermodynamic study of Liquid-Liquid Equilibria in Ternary System of Methanol, Toluene, and Hexane

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تاريخ الاستلام:2026/01/21 –تاريخ المراجعة:2026/02/20– تاريخ القبول: 2026/03/01– تاريخ للنشر :30 /03/ 2026

Abstract:
Liquid- liquid equilibrium (LLE) data are essential for the design and optimization of liquid-liquid extraction processes in chemical and petrochemical industries. In this work, experimental LLE data for the ternary system {Methanol + toluene + hexane} were investigated at 298, 303 ,308 and 313K under atmospheric pressure 101.3 KPa, The equilibrium composition of the coexisting liquid phases were determined and used to construct bimodal curves and tie-line data for the system. Distribution coefficient and separation factors were calculated in order to evaluate the extraction performance of toluene for separating methanol from hexane. The reliability of the experimental tie-line data was examined using Othmer-Tobias and Hand correlations. The experimental data were correlated using the NRTL and UNIQUAC thermodynamic models. Both models successfully represented the phase equilibrium behavior of the system, with the UNIQUAC model showing slightly better agreement with the experimental results. The average root mean square deviation (RMSD) values were approximately 1.013% for UNIQUAC and 1.189%for NRTL.
Keywords: Liquid-liquid equilibrium; Methanol; Toluene; Hexane; Thermodynamic modeling; UNIQUAC; NRTL.

1- Introduction:

In chemical, petrochemical, pharmaceutical and biochemical industries, valuable products are generally made by a combination of processes that include synthesis,

The liquid extraction is one of the main alternatives to consider, which utilizes chemical differences instead of boiling point differences to separate the components. Liquid-liquid extraction is a versatile unit operation which involves two immiscible liquid phases.

The extract is the liquid phase which consists of solvent and extracted solute; while the raffinate is the solute lean phase or liquid phase from which solute has been removed[1]. Liquid-liquid equilibria (LLE) extraction processes have been successfully used in petrochemical, pharmaceutical and food industries[2]. These have been in use since a long time in the oil industry on a large scale for removing aromatic compounds from gasoline or kerosene.

There is an increasing interest for the use oxygenated compounds to produce reformulated gasoline. Among the oxygenated compounds, Methanol (also called methyl alcohol and wood spirit, amongst other names) is an organic chemical compound and the simplest aliphatic alcohol. It is a light, volatile, colorless and flammable liquid with a distinctive alcoholic odour similar to that of ethanol (potable alcohol) [3]. Methanol acquired the name wood alcohol because it was once produced chiefly by the destructive distillation of wood. Today, methanol is mainly produced industrially by hydrogenation of carbon monoxide[4].

2.2- Literatures Review

Fan et al.[11] The separation factor and the partition coefficient . The S value of methyl isobutyl ketone and cyclohexanone past greater than unity , and the S and D values of cyclohexanone past greater than methyl isobutyl ketone , indicating that cyclohexanone is a suitable extractant compared with methyl isobutyl ketone.

Larous et al.[12] , Data for the bimodal curves have been determained by cloud-point titration method and conjugate points on tie-line were obtained by correlating the refractive index of the bimodal curves as a function of composition **.**The distribution coefficient and the selectivity factor of the solvents used were calculated and plotted for the extraction effectiveness of these last. The results obtained show that toluene solvent has a higher selectivity factor than the n-hexane solvent for the extraction of methanol from aqueous solutions.

Gramajo et al[13] , The effect of the temperature on liquid–liquid equilibrium is discussed. Data for the ternary system is available from the literature at 278.15, 283.15, 288.15, 293.15, 298.15 and 303.15 K. All chemicals were quantified by gas chromatography using a thermal conductivity detector. Experimental data for the ternary system are compared with values that calculated using the NRTL and UNIQUAC equations. It is found that the UNIQUAC and NRTL models provide similar good correlations of the solubility curve at these six temperatures.

Liu et al [14] studied the mutual solubility of the esterification process of some free fatty acids Free Fatty Acid (FFA) with methanol. Ternary diagram were plotted in order to determine the tie lines. The results show that the mutual solubility increases with temperature.

Schmitt and Hasse [15] study LLE in the systems water + 1-hexanol, water+ hexyl acetate, water + acetic acid + 1-hexanol, and water + acetic acid + hexyl acetate at temperatures between (280 and 355)K for the scale-up of reactive distillation. The experimental data obtained was then compared with NRTL. The comparison shows that they give reliable predictions for the conditions encountered in reactive distillation.

Naydenov and Bart [16] investigated the effect of the alkyl chain on the alcohol and ester on the phase equilibria for the systems containing reactants and products of esterification reactions. The systems were alcohol (1-propanol or 1-butanol) or acetic acid + ester + the ionic liquid 1-ethyl-3-methylimidazolium hydrogen sulphate [EMIM] [HSO4] were studied at (313.2 ± 0.5) K. The result shows that, increase of the alkyl chain length on alcohol and ester leads to bigger immiscibility regions and better solubility of the alcohol in the ester phase. The distribution of the acetic acid between the two phases is almost independent of the esters for the measured systems and is dependent mainly on the ionic liquid. Letcher and Whitehead, determined the activity coefficient for hydrocarbons such as alkenes, alkynes and cycloalkanes in sulfolane, in order to predict phase separation using the correlation models such as NRTL or UNIQUAC for three component systems involving sulfolane, an aromatic and a hydrocarbon using gas liquid chromatography. They reported that alkynes are completely miscible in sulfolane over the whole concentration range while the alkenes and cycloalkanes are only partially miscible. The activity coefficient for solute in sulfolane increases with increasing carbon number of alkenes or cycloalkanes.

Mohsen-Nia, and Doulabi.[17] The compositions of liquid phases at equilibrium were determined by g.l.c. measurements and the results were correlated with the UNIQUAC and NRTL activity coefficient models. The partition coefficients and the selectivity factor of methanol and ethanol are calculated and compared to suggest which alcohol is more suitable for extracting the aromatic hydrocarbons (toluene or m-xylene) from n-dodecane. The phase diagrams for the ternary mixtures including both the experimental and correlated tie lines are presented. From the phase diagrams and the selectivity factors it is concluded that methanol has a higher efficiency as a solvent in extraction of aromatic hydrocarbon from alkane mixtures.

Veliz et al. [18] , Phase equilibria of methanol + toluene + hexane ternary systems at (278.15, 283.15, 288.15 and 293.15) K at atmospheric pressure were investigated. The influence of temperature on the liquid–liquid equilibrium is discussed. All chemicals were quantified using gas chroma tograph with a thermal conductivity detector coupled to a ChemStation and nitrogen as gas carrier, their mass fractions were higher than 0.999. From literature are found two articles from the same system at different temperatures studied here. Experimental data are com- pared with literature values. Values calculated using the NRTL and UNIQUAC equations are compared with the experimental data and it is found that the UNIQUAC equation fitted the experimental data better than the NRTL model for this ternary system.

2- Materials and Methode:

2.1 Materials

The experimental measurement of liquid-liquid equilibrium must accomplish two things. the composition of the two liquid phases which locate the ends of the tie lines and solubility curve. The ternary system mixtures of three components are allowed to separate into two liquid phases at equilibrium and the equilibrium layers are analyzed for their composition which will give the end points of the tie lines. These endpoints when connected will give the solubility curve.

2-2 Apparatus and Procedures

The used experimental set up Figure(2-1) for the determination of liquid-liquid phase equilibrium data are as follows :

A flask of **250** mL and the temperature of the experimental fluid were controlled by a water jacket around the flask (**Temperature control**). The flask has two opening, one at the top and another at the bottom. Through the top opening the liquids are taken into the flask and during the experimental thermometer is placed into it to record the temperature of the liquids (**T**) The bottom opening is the outlet for the liquids (**sampling ports**). A mixer is provided for the sufficient agitation within the apparatus. The composition of the sample can be analyzed using the *(**Abbe Refractometer***) apparatus equipped with a thermal conductivity detect.

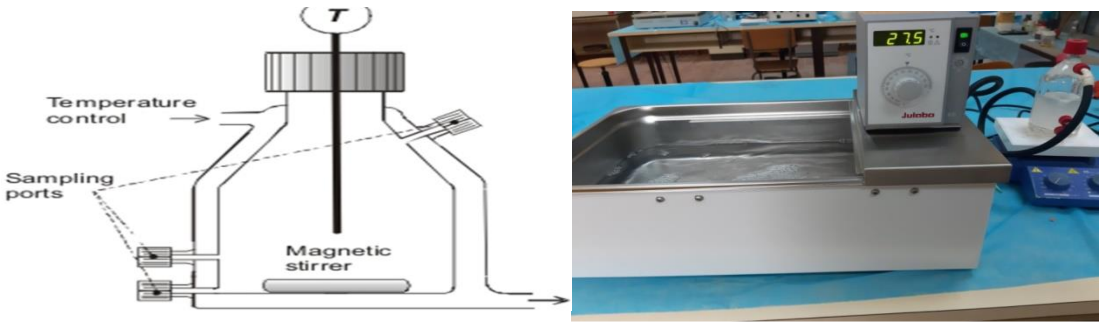
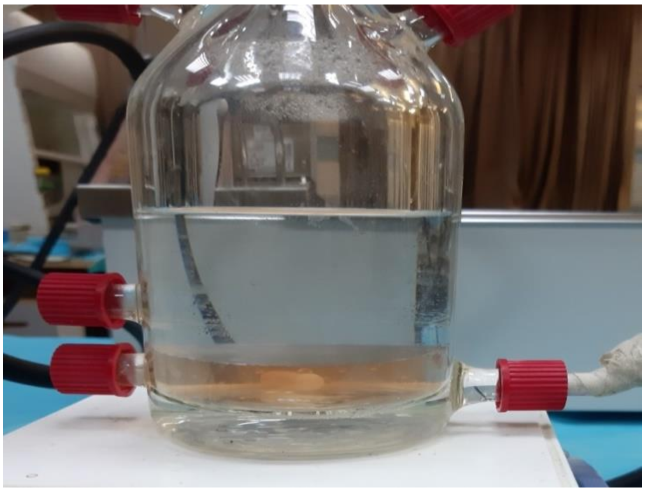


Figure (2-1) The experimental set up used for the determination of liquid-liquid phase.

Ternary mixtures of known composition (**Methanol** + **Toluene**+ **Hexane**) were precisely prepared in closed vials and mixed during at least **1h** at **298, 303, 308,** and **313** K. The accuracy of the temperature is 1 K. The total weight of each sample was approximately **100 g.** When the thermodynamic equilibrium was achieved, the system separated into two liquid phases (Figure 2-2) that became transparent with a well-defined interface. After this decantation, the lower phase containing mainly (**Methanol**), and the remaining (**Hexane**)-rich upper phase were successively collected and weighted. After separation, samples of both hases were still transparent and were carefully analyzed to determine their compositions in order to build the LLE tie-lines. The top phase is taken out with the help of a syringe and the bottom phase is taken out through the bottom outlet. Then the samples are taken separately and analyzed using (***Abbe Refractometer***). This procedure was repeated for the different compositions of the liquids[5].



Figure(2-2) The separation of the two liquid phases liquid-liquid equilibrium.

3 -Analysis Methods

- **Refractive Index Method:**

In this the three components were agitated in a constant temperature bath over a period of 2 hours. At the end of this period the flasks were allowed to remain in the bath until the phases had completely separated. Then the samples of the separated layers were withdrawn and their refractive indexes were measured. The composition of the equilibrium layers were determined by references to alarge scale plot of refractive index against solute concentration for saturated solution. In case of dissolved salts each layer was boiled separately and condensed to make it salt free and then refractive index of each layer was measured

- **Specific Gravity Method :**

  Here similar procedure is followed as in other case. The separated layers were withdrawn and their specific gravities were measured. The compositions of the equilibrium layers were determined by references to a large-scale plot of specific gravity against solute concentration for saturated solutions. In case of dissolved salts each layer is boiled separately and condensed to make it salt free and then specific gravity of each layer was measured

- **Gas chromatograph method [42]:**

  is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, column length and the temperature.

4 – Result and Descation:

4-1: Liquid – Liquid equilibrium experimental data:

3-1.1-Distribution coefficients, Di, Separation factor S , Othmer-Tobias :

The experimental binodal curve and tie-line data on the ternary system (Methanol $_{(A)}$ + Toluene $_{(B)}$ + Hexane $_{(C)}$) at 298k , 303k. and 308k. 313k , The distribution coefficients and separation factors for each temperature are given in.

Table 3.1: Distribution coefficients, Di , Separation factors, **S,** of Methanol $_{(A)}$ - Hexane $_{(C)}$ at each temperature.

298k	D S	5.736 140	5.788 100	5.602 75	5.581 45	5.484 25
303k	D S	5.881 130	5.891 90	5.900 72	5.945 39	5.971 20
308k	D S	6.023 128	6.012 87	6.032 69	6.034 35	6.061 19
313k	D S	6.112 125	6.188 83	6.134 65	6.191 30	6.199 15

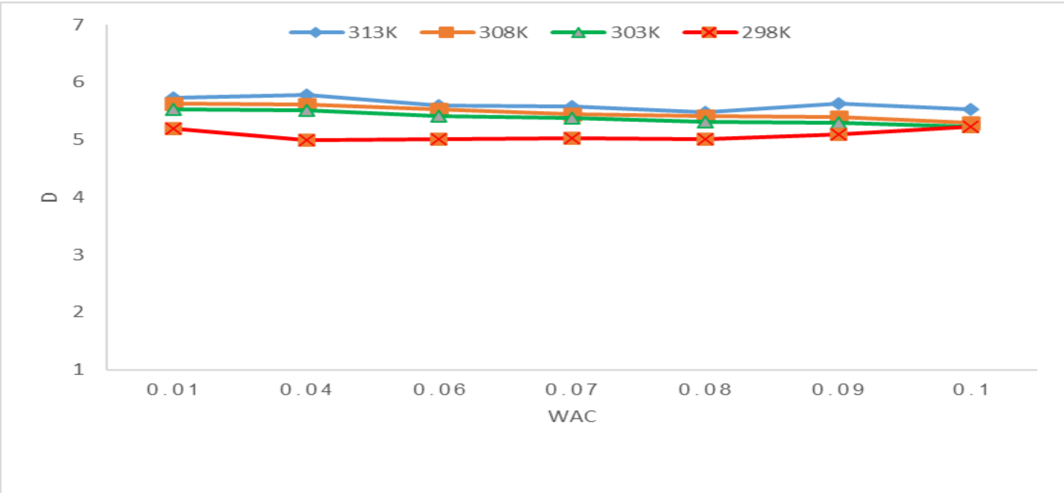


Figure 3.1 : Distribution coefficient, D, for Methanol $_{(A)}$ - Hexane $_{(C)}$ at each temperature.

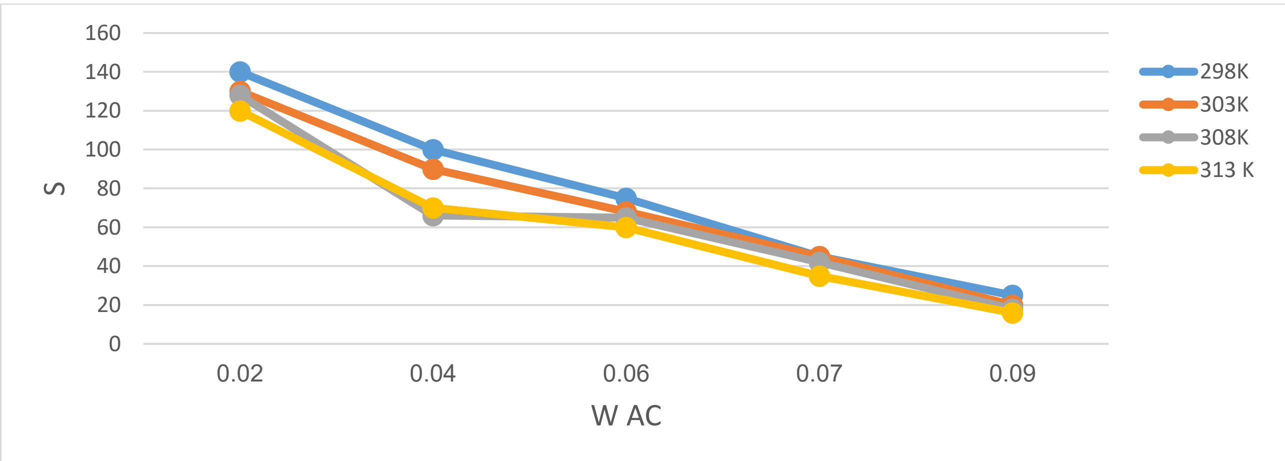
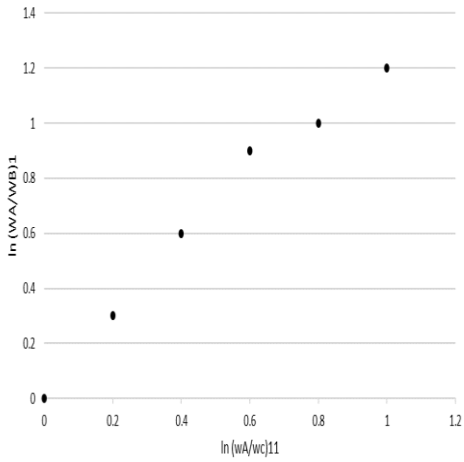


Figure 3.2 Separation factor, s, as a function of the mass fraction.

Othmer-Tobias : $\ln((1- w11) / w11) = a + b \ln((1- w 33) / w 33)$



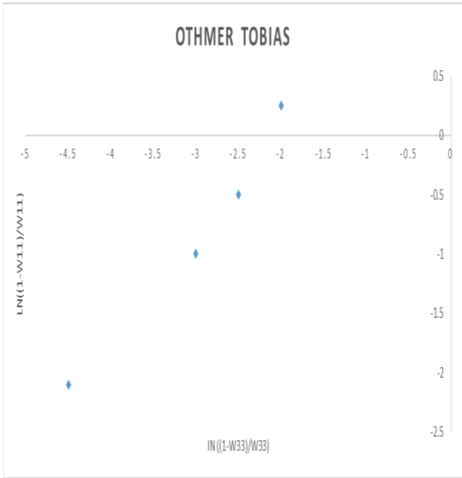


Figure 3.3: Othmer-Tobias plot of the system & Figure 3.4: Hand plots of the system

Table 3-2: Experimental data of (W_A Methanol, W_B Toluene, W_C Hexane) ternary system at 298,303,308,and 313K; Wi denotes mass fraction.

		Methanol rich phase			Hexane rich phase	
T	W_A	W_B	W_C	W_A	W_B	W_C
298						
	0.6007	0.0914	0.3079	0.2032	0.3155	0.4813
	0.4975	0.1009	0.4016	0.1395	0.4320	0.4285
	0.4018	0.1381	0.4601	0.0642	0.4812	0.4546
	0.4855	0.1984	0.3161	0.0256	0.2072	0.7672
303						
	0.5953	0.1044	0.3003	0.1528	0.4323	0.4149
	0.4021	0.1514	0.4465	0.0780	0. 3794	0.5426
	0.4193	0.2070	0.3737	0.0421	0.2028	0.7551
	0.5147	0.3191	0.1662	0.0256	0.2079	0.7665
308						
	0.5922	0.1195	0.2883	0.1643	0.3359	0.4998
	0.4033	0. 1682	0.4285	0.0934	0.3791	0.5275
	0.4285	0.2189	0.3526	0.0593	0.2992	0.6415
	0.4018	0.3231	0.2751	00.278	0.1347	0.5873
313						
	0.5891	0.1347	0.2762	0.1812	0.3371	0.4817
	0.4130	0.1863	0.4007	0.1140	0.3122	0.5738
	0.4363	0.2292	0.3345	0.0760	0.2263	0.6977
	0.5455	0.3291	0.1254	0.0661	0.3487	0.5852

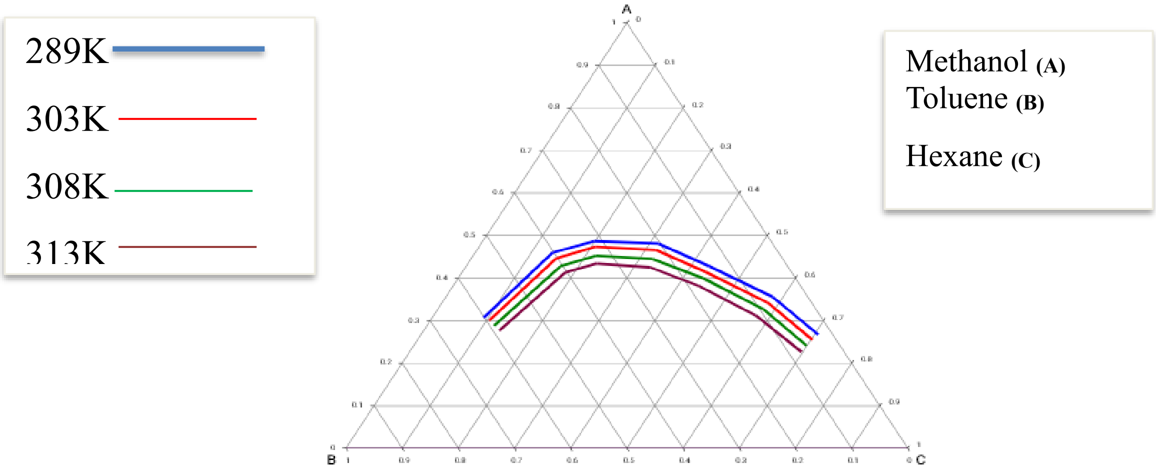


Figure 3-4 Experimental LLE data at 298,303,308 and 313K

3-3 liquid-liquid equilibrium experimental data applied for Models:

The composition of liquid – liquid phase equilibrium which have been calculated for models NRTL , UNIQUAC at different isothermal and isobaric are given in the following tables .

Table (3-3): Calculated of models LLE data for the (Methanol $_{(A)}$ + Toluene $_{(B)}$ + Hexane $_{(C)}$) ternary system at 298K .

	Methanol $_{(A)}$ rich phase			Hexane $_{(C)}$ rich phase		
	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$
NRTL	0.5817	0.0812	0.3371	0.1221	0.3199	0.5580
	0.4413	0.1911	0.3676	0.1455	0.5300	0.3245
	0.3911	0.1291	0.4798	0.0941	0.5121	0.3938
	0.4911	0.1819	0.3270	0.0481	0.3017	0.6502
UNIQUAC	0.5622	0.1331	0.3047	0.1822	0.3981	0.4197
	0.6111	0.1918	0.1971	0.0923	0.3961	0.7123
	0.5441	0.2415	0.2144	0.0891	0.3221	0.5888
	0.5231	0.3498	0.1271	0.2991	0.1490	0.5519

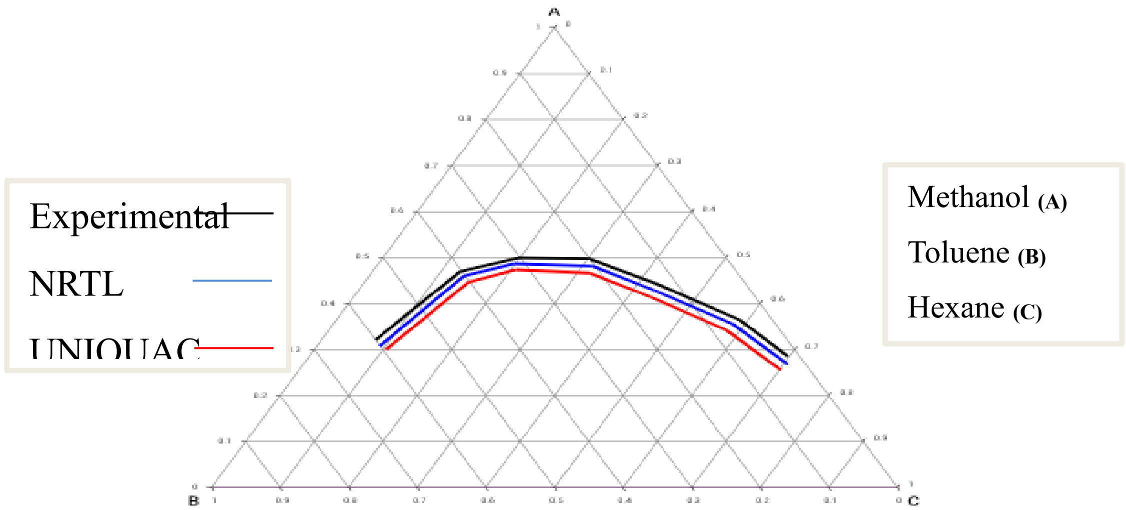


Figure (3- 5) Comparison between NRTL , UNIQUAC from the experimental data LLE at 298K.

Table (3-4): Calculated of models LLE data for the (Methanol (A + Toluene (B) + Hexane (C)) ternary system at 303K .

	Methanol (A) rich phase			Hexane (C) r.ich phase		
	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$
NRTL	0.6911	0.1191	0.1898	0.1911	0.4391	0.3698
	0.4311	0.1729	0.3960	0.0891	0.3994	0.5115
	0.4431	0.2217	0.3352	0.0431	0.2028	0.7541
	0.5911	0.3411	0.0678	0.0391	0.2079	0.7530
UNIQUAC	0.5823	0.1331	0.2846	0.1881	0.3671	0.4448
	0.4456	0.1933	0.3611	0.1981	0.3891	0.4128
	0.4521	0.2411	0.3068	0.0991	0.3671	0.5338
	0.4300	0.2311	0.3400	0.0893	0.3678	0.5429

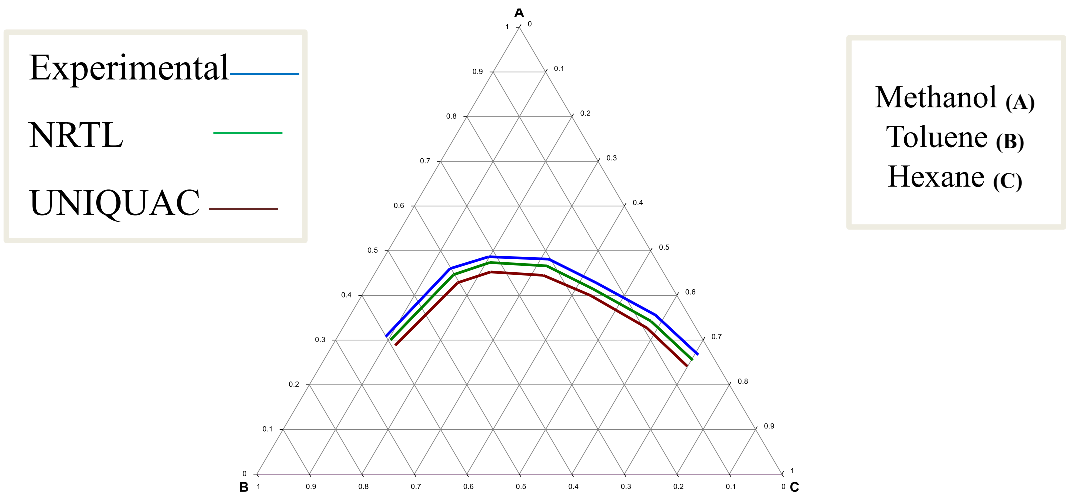


Figure (3-6) Comparison between NRTL , UNIQUAC from the experimental data LLE at 303 K.

Table (3-5) : Calculated of models LLE data for the **(** Methanol $_{(A)}$ + Toluene $_{(B)}$ + Hexane $_{(C)}$ **)** ternary system at 308K.

	Methanol $_{(A)}$ rich phase			Hexane $_{(C)}$ rich phase		
	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$
NRTL	0.5711	0.1213	0.3076	0.1711	0.3711	0.4578
	0.6321	0.1811	0.1868	0.0991	0.3551	0.5458
	0.5111	0.2219	0.2670	0.0611	0.3001	0.6388
	0.4512	0.3319	0.2169	0.2921	0.1447	0.5632
UNIQUAC	0.5561	0.0912	0.3527	0.1231	0.3215	0.5554
	0.4231	0.1991	0.3778	0.1455	0.5311	0.3234
	0.3781	0.1287	0.4932	0.0932	0.5123	0.3945
	0.3900	0.1832	0.4268	0.0561	0.3091	0.6348

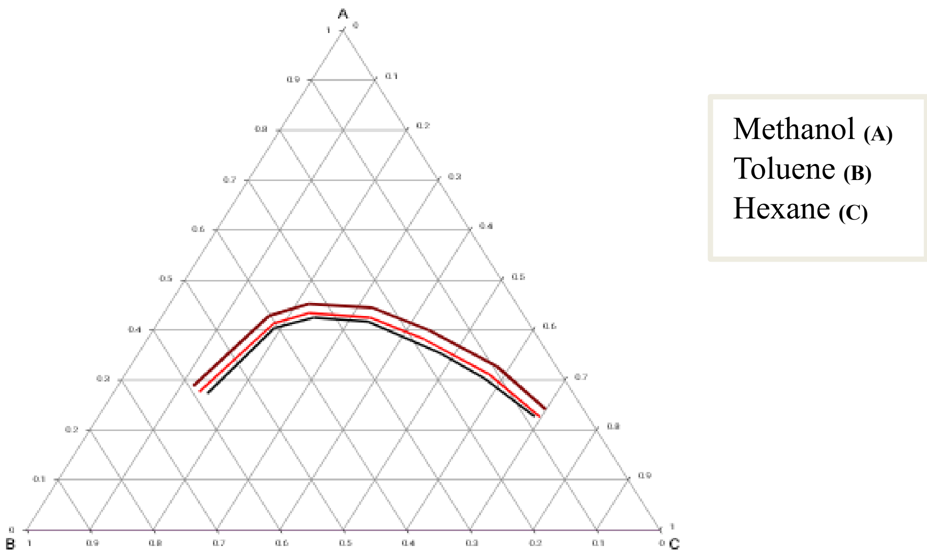


Figure (3-7) Comparison between NRTL **,** UNIQUAC from the experimental data LLE at 308 K.

Table (3-6): Calculated of models LLE data for the (Methanol $_{(A)}$ + Toluene$_{(B)}$ + Hexane $_{(C)}$) ternary system at 313K .

	Methanol $_{(A)}$ rich phase			Hexane $_{(C)}$ rich phase		
NRTL	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$	$X_{(A)}$	$X_{(B)}$	$X_{(C)}$
	0.5911	0.1391	0.2698	0.1921	0.3571	0.4508
	0.4332	0.1931	0.3737	0.1991	0.3311	0.4698
	0.4411	0.2311	0.3278	0.0861	0.2511	0.6628
	0.5511	0.3391	0.1098	0.0771	0.3911	0.5318
UNIQUAC	0.6812	0.1145	0.2043	0.1823	0.4451	0.3726
	0.4451	0.1891	0.3658	0.0712	0.3768	0.5520
	0.4561	0.2215	0.3224	0.0334	0.2012	0.7654
	0.5891	0.3412	0.0697	0.0399	0.3212	0.6389

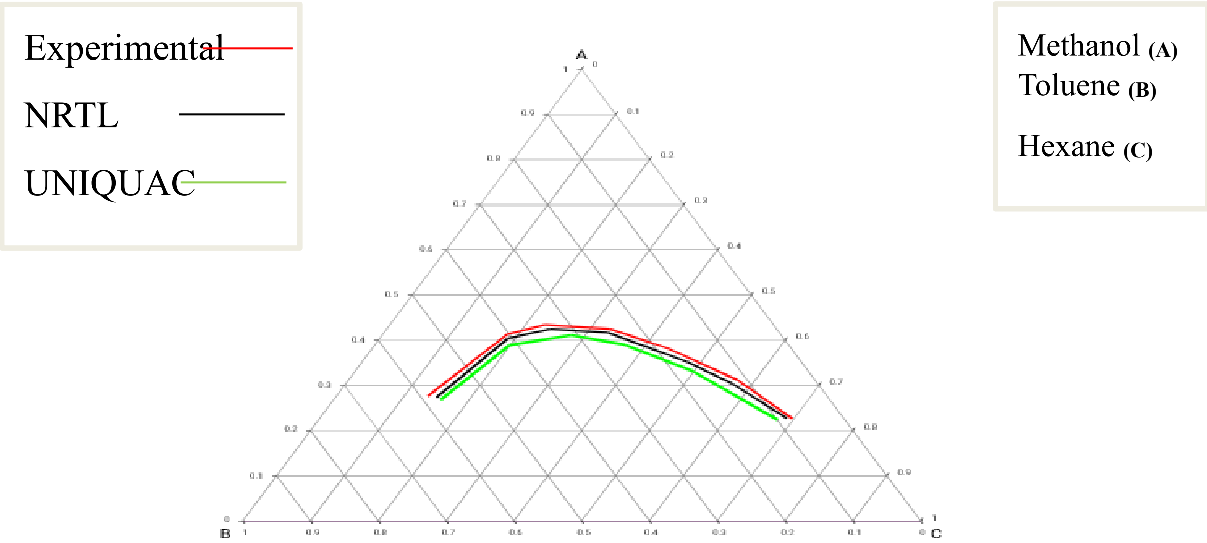


Figure (3-8) Comparison between NRTL , UNIQUAC from the experimental data LLE at 313 K.

Table (3-8) Optimum NRTL interaction parameters for system (Methanol $_{(A)}$ + Toluene $_{(B)}$ + Hexane $_{(C)}$) according to the equation, where

$G_{ij}=\exp(-\alpha_{ij}\,\tau_{ij})$; $\alpha_{ij}=\alpha_{ji}$; $\tau_{ij}=(a_{ij}+b_{ij})/T$

T(K)	i-j	*Aij*	*Aji*	*Bij*	*Bji*
298	**1-2**	120.11	-130.51	200.12	-123.40
	1-3	200	-312.11	40.10	40.11-
	2-3	-14.10	1137.10	167.32-	231
303	**1-2**	158	-4131.21	610	-612
	1-3	230.22	-91.67	1632	432
	2-3	32.230	53.90	23.97	-216
308	**1-2**	324	-18.21	356.70	2421
	1-3	986	42.3	1512	-231
	2-3	453	-673.11	654	864
313	**1-2**	654	322	950	-953
	1-3	247	342.81	542	2317
	2-3	753	-431.03	2195	-876

Table (3-9) Optimum UNIQUAC interaction parameters for the system(Methanol $_{(A)}$ + Toluene $_{(B)}$ + Hexane $_{(C)}$) According to the Equation:

τij=exp (Aij ⁄ T) aij=AijT^2+Aji$T$

T(K)	i-j	Aij	Aji
298	**1-2**	321	411
	1-3	230	-765
	2-3	894	-328
303	**1-2**	901	543
	1-3	108	-2315
	2-3	-532	-532
308	**1-2**	231	711
	1-3	-321	-123
	2-3	-863	-411
313	**1-2**	8765	391
	1-3	-3221	-531
	2-3	321	-346

Table (3-10) RMSD % , FObj% values for the studied models:

T(K)	UNIQUAC		NRTL	
	FObj %	RMSD	FObj%	RMSD
298	0.901	3.991	4.123	1.310
303	1.040	2.321	3.342	1.211
308	0.601	1.112	2.945	1.231
313	1.510	1.333	2.451	1.007
Average	2.188	1.013	3.215	1.189

6-1 Discussion:

1-The experimental binodal curve and tie-line data on the ternary system (Methanol + Toluene + Hexane) were measured at (298, 303, 308 and 313) are given in Tables (3-1). The experimental LLE data and predicted tie lines at each temperature were plotted and shown in Figures (3.1) ,(3.2) , (3.3) , (3.4) and. As can be seen in Figures (3.1) ,(3.2) , (3.3) , and (3.4), it was found that the ability of Toluene to separate the Methanol from Hexane and, but miscible , From the provided figures, it can be observed that Toluene has the ability to separate Methanol from Hexane due to the differences in their solubilities. However, you did not specify the nature of the miscibility between the components Methanol and Hexane, The separation factor is not constant over the whole heterogeneous region. The extraction power of the solvent at each temperature, plots of D vs. W_{AD} and S vs. W_{AC}, are shown in Figures (3.3) and (3.4), respectively. The reliability of experimentally measured tie lines can be ascertained by applying the OthmerTobias and: Hand correlation at each temperature (Othmer and Tobias, 1942) the linearity of the plot indicates the degree of consistency of the related data. Similar results were observed for the rest of the data.

2- To determine which model, UNIQUAC or NRTL, is more suitable for the LLE calculations in the ternary system comprising Methanol, Toluene, and Hexane at the given temperatures (298K, 303K, 308K, and 313K), it is necessary to compare the predicted results of both models with the available experimental data. Experimental LLE data is crucial for model validation and selection. These data provide information about the phase behavior and composition of the liquid phases at equilibrium for the given system and temperatures. By comparing the experimental data with the predictions of UNIQUAC and NRTL, you can assess the accuracy and reliability of each model. Ideally, the model that better matches the experimental LLE data and provides more accurate predictions should be considered the better choice. It is important to evaluate both the overall agreement between the model predictions and the experimental data and the accuracy in predicting key features such as tie-line lengths, binodal curves, and critical points.

Without access to the specific experimental data and the corresponding predictions from UNIQUAC and NRTL, it is not possible to definitively determine which model is more suitable for the given system and temperatures. Therefore, it is recommended to compare the model predictions with the experimental data and select the model that demonstrates better agreement and accuracy.

3-The composition of liquid-liquid equilibrium (LLE) data for systems (Methanol + Toluene + Hexane) were measured at (**298, 303, 308** and **313** are shown in tables(3-1,3-2) ,The experimental liquid-liquid equilibrium data are shown in tables (3-3, to 3-6) For ternary system (Methanol + Toluene + Hexane) These values used to plot the solubility curves and that are shown in figures (3-1 to 3-5),The effect of temperature on the separation of Methanol from Hexane using Toluene can depend on the specific properties of the components and their interactions. Generally, temperature can influence the phase behavior and solubility of the components in a liquid-liquid equilibrium (LLE) system. In the (Methanol + Toluene + Hexane) system, increasing the temperature can potentially enhance the separation of Methanol from Hexane using Toluene. This is because Toluene is typically more soluble in Methanol than in Hexane, and as temperature increases, the solubility of Toluene in Methanol tends to increase more significantly compared to its solubility in Hexane. As a result, at higher temperatures, the relative solubilities of the components can change, leading to a shift in the LLE phase behavior. This shift can cause Toluene to preferentially dissolve in the Methanol-rich phase, facilitating the separation of Methanol from Hexane. However, it's important to note that the specific effect of temperature on the separation process can also depend on other factors such as the composition ratios, the relative volatility of the components, and the presence of any azeotropic behavior in the system. To gain a more comprehensive understanding of the temperature effect, it would be helpful to analyze the specific composition values at the given temperatures (298K, 303K, 308K, and 313K), as mentioned earlier. With that information, a more detailed analysis of the LLE data and the temperature's impact on the separation process can be provided.

4- The experimental liquid-liquid equilibrium data were used to calculate the optimum NRTL, and UNIQUAC interaction parameters between, (Methanol + Toluene + Hexane) , The NRTL and UNIQUAC equation were fitted to experimental data using an iterative computer program EXCEL with the objective function.

$$F_{obj} = \sum_{i=1}^{i=3} \sum_{k=1}^{3} \left[\left(X_{i,K}^{I,exp} - X_{i,k}^{I,Cal} \right)^2 + \left(X_{i,k}^{II,exp} - X_{i,k}^{II,cal} \right)^2 \right] \quad .(4.1)$$

The Objective function (F_{obj}) at each temperature are shown in table (3-10). The UNIQUAC equation gave the lowest average F_{obj} value of 2.188%, and better prediction of the equilibrium behavior of the system The NRTL model has satisfactorily correlated to the

experimental data with F_{obj} values of 3.215%. For ternary system (Methanol + Toluene +Hexane).

5- The optimization results were judged by calculating the corresponding RMSD values. The root mean square deviations (RMSD) are calculated from the difference between the experimental data and the prediction of each model at each temperature according to the following formula

$$RMSD = \sqrt{\frac{\sum_{i=1}^{3} \sum_{k=1}^{N} \left(X_{i,k}^{I,exp} - X_{i.k}^{I,cal}\right)^2 + \left(X_{i.k}^{II,exp} - X_{i,k}^{II,cal}\right)^2}{4N}} \quad (4.2)$$

The root mean square deviations (RMSD) at each temperature are shown in table (3-10). The UNIQUAC equation gave the lowest average RMSD value of 1.013%, and better prediction of the equilibrium behavior of the system. The NRTL model has satisfactorily correlated to the experimental data with RMSD values of 1.189%. For ternary system (Methanol +Toluene + Hexane).

7.1- Conclusions:

Liquid-liquid equilibrium data for the ternary system methanol+ toluene+ hexane were experimentally determined at 298-313K. the results indicate that temperature significantly influences the phase behavior of the system . toluene was found to be an effective solvent for facilitating the separation of methanol from hexane. Both NRTL and UNIQUAC models successfully correlated the experimental LLE data, with UNIQAC providing slightly better predictions.

Recommendations:

1-Validate the measurements: Before drawing any firm conclusions or making extensive use of the data, it is essential to ensure the accuracy and reliability of the measurements. Cross-check the experimental results with established literature data or conduct replicate experiments to verify the consistency and reproducibility of the measurements.

2-Analyze phase diagrams: Plot the measured data on ternary phase diagrams at each temperature. This will provide a visual representation of the system's phase behavior and help identify the regions of immiscibility, tie-lines, and binodal curves. By examining the diagrams, you can gain a better understanding of the system's liquid-liquid equilibrium.

3-Compare with thermodynamic models: Utilize thermodynamic models such as UNIQUAC, NRTL, or UNIFAC to compare their predictions with the measured data. This will help assess the accuracy and reliability of the models in representing the system's phase behavior. Select

the model that best matches the experimental results and provides the most accurate predictions.

4-Consider further experiments: If the measured data and thermodynamic models do not provide a complete understanding of the system, consider conducting additional experiments at different temperatures or varying composition ratios. These additional measurements can help fill any gaps in the data and provide a more comprehensive understanding of the system's liquid-liquid equilibrium.

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