

Separation of Acetic Acid from Water Using Organic Solvents: Liquid-Liquid Equilibrium Thermodynamic Investigation

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Acetic acid is one of the most important carboxylic acids which is used in many reactions, including the synthesis of acetic esters. Because of the industrial and environmental advantages, the separation of acetic acid from dilute aqueous solutions has recently received much attention. In this study, we investigated the liquid-liquid equilibrium of a ternary system consisting of water + acetic acid + organic solvent at various temperatures. Various thermodynamic models (non-random two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) models) were used to predict the composition of the components in aqueous and organic phases. In these models, intermolecular interactions were considered as a binomial function of reverse temperature. The parameters of two models were determined through the optimization of an objective function. Root mean square deviations of the NRTL and UNIQUAC models, predicting the composition of the components in the ternary mixture of water + acetic acid + organic solvent, were 0.0273 and 0.0422, respectively.

Keywords: Liquid-liquid equilibrium, Ternary system, Organic solvent, NRTL model, UNIQUAC model

INTRODUCTION

Acetic acid is one of the most important carboxylic acids which is used in many reactions, including the synthesis of acetic esters. It can also be used as a solvent for manufacturing various acetate esters and drugs. In addition, this acid can be used as a fungicide. Acetic acid is produced *via* artificial methods or fermentation process. Both methods provide dilute aqueous solutions. Therefore, because of the industrial and environmental advantages, the separation of acetic acid from dilute aqueous solutions has recently received much attention [1]. Although acetic acid and water do not have an azeotrope form, the use of conventional distillation to separate these two molecules is very uneconomical, because this separation method (distillation) requires a column with different steps and a high reflux ratio resulting in a high operation cost. Among the various methods used for the separation of acetic acid

from aqueous solution, the integration of heterogeneous azeotropic extraction and distillation has been considered as a relatively effective method because it has a low energy cost. The key to this method is to find a suitable solvent that can be used both as the extractor and the entrainer [2].

The data on liquid-liquid equilibrium (LLE) is required for the extraction processes. Activity coefficient models such as NRTL (non-random two-liquid) and UNIQUAC (universal quasi chemical) have been successfully applied to liquid-liquid systems to link the LLE data [3]. In each case, the adjustable parameters were obtained by regressing the experimental data to the models and obtaining numerical values for the interaction parameters. The NRTL and UNIQUAC models depend on experimentally optimized interaction parameters of every two molecules in the system [4].

The UNIFAC (universal function group activity coefficient) was applied to predict liquid-liquid equilibrium data. The UNIFAC method is particularly useful for predicting phase equilibrium in the systems that are not

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studied experimentally but contain the same functional groups, whereas the NRTL and UNIQUAC models depend on experimentally optimized interaction parameters [3].

Many studies have been carried out and reported in this field (extraction of dilute acetic acid from water). Several alcohols [3,5], acetate [3,5], ketones [6,7], ethers [2,8] and aromatic hydrocarbons [9-11] have been used as solvents for the recovery of acetic acid. Soares *et al.* [7] used methyl isoamyl ketone for the extraction of acetic acid. Colombo *et al.* [4] examined the liquid-liquid equilibrium of ternary systems of water + acetic acid + ethyl acetate and water + acetic acid + isophorone. Moreover, the ternary system of water + acetic acid + 1-heptanol was evaluated [3,12].

In another study performed by Ghanadzadeh *et al.* [13], the researchers used 2-ethyl-1-hexanol (because of its low cost, high boiling point, very low solubility in water, and high separation factor) as an organic solvent for determining the LLE data in a ternary system (water + acetic acid + 2-ethyl-1-hexanol). In order to examine new solvents for the separation, that could be used as a potential alternative for chlorine or aromatic hydrocarbons, Ince [1] focused on dimethyl glutarate. These esters are environmentally friendly, and have low toxicity and low cost, high stability, and high boiling point, while they are similar to water in terms of viscosity and density [1]. Following this approach, Kirbasülaret *et al.* [14] used diethyl succinate and diethyl glutarate and diethyl adipate as solvents.

Kurumet *et al.* [15] evaluated more than 30 types of solvents for the purification of acetic acid and concluded that methyl tert-butyl ether (MTBE) was a potential entrainer. Zhang *et al.* [2] used diisopropyl ether as a solvent. Compared to MTBE, diisopropylether (DIPE) has lower evaporation point, density, viscosity, and is less soluble. Most importantly, the azeotrope of the DIPE and water with an azeotropic composition contains more water. In other words, the entrainer can carry water to the top of the column, and therefore the azeotropic distillation process requires less entrainer [2]. Two years later, Zhang *et al.* [16] introduced cyclo pentyl methyl ether (CPME) as a new type of hydrophobic ether solvent, which has excellent unique properties and is a likely alternative to tetrahydrofuran (THF), MTBE, dioxane, and other ether solvents [16]. In recent years, various aromatic hydrocarbons such as toluene

[9], *m*-xylene and *o*-xylene [11], 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene [10] have been used as solvents for acetic acid separation.

The objective of this study is using experimental data obtained from prior studies, UNIQUAC, and NRTL thermodynamic models were used to predict component equilibrium for ternary systems containing water + acetic acid + organic solvents. In order to increase the accuracy of the models as well as the general ones, the interaction terms between different molecules were considered as a binomial function of the reverse temperature.

MATERIALS AND METHODS

LLE Database of Ternary Systems of Water + Acetic Acid + Organic Solvent

The experimental data were collected from 15 previously conducted studies [2-13 and 16-18]. The collected data were related to liquid-liquid equilibrium of ternary systems of water + acetic acid + organic solvents. The solvents included 1,2,4-trimethylbenzene [10], 1,3,5-trimethylbenzene [10], 1-heptanol [3,12], 1-methylpropyl ethanoate [17], 2-ethyl-1-hexanol [13], cyclopentyl methyl ether [16], cyclohexane [18], diisopropyl ether [2], ethyl acetate [4], isobutyl acetate [5], isobutanol [5], isophorone [4], methyl isobutyl ketone [7], methyl tert-butyl ether [8], *m*-xylene [11], *o*-xylene [11], sec-butyl acetate [6] and toluene [9]. The total data for the systems included 689 items and the temperature range was from 278.15-343.15 K.

Thermodynamic Modeling

In this study, we used the NRTL [19] and UNIQUAC [20] thermodynamic models to calculate the activity coefficient of components. As the data are related to different temperatures, so temperature dependence is considered for obtaining the parameters of different models. The models are explained in the following sections.

NRTL model. Equations (1) to (3) are used to calculate the activity coefficients of the NRTL model,

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_l x_l G_{li}} + \sum_j \frac{x_j G_{ij}}{\sum_l x_l G_{li}} \left[\tau_{ij} - \frac{\sum_r x_r \tau_{rj} G_{rj}}{\sum_l x_l G_{li}} \right] \quad (1)$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} = A_{ij} + \frac{B_{ij}}{T} \quad (\tau_{ij} \neq \tau_{ji} \text{ and } \tau_{ii} = 0) \quad (2)$$

$$G_{ij} = \exp(\alpha_{ij} \tau_{ij}) \quad (\alpha_{ij} = \alpha_{ji} \text{ and } \alpha_{ii} = 0) \quad (3)$$

where i, j and k are related to each component, γ_i is the activity coefficient, τ_{ij} and τ_{ji} are the interaction energies between the molecules i and j , x is the molar fraction, A_{ij} and B_{ij} are the binary interaction parameters, and T is the absolute temperature. Moreover, α_{ij} is a non-random parameter that is equal to 0.2, here [19].

UNIQUAC model. Equations (4) to (7) are used to calculate the activity coefficients using the UNIQUAC model,

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j - q_i \left(1 + \ln \left(\sum_j \theta'_j \tau_{ji} \right) - \sum_j \frac{\theta'_j \tau_{ij}}{\sum_k \theta'_k \tau_{kj}} \right) \quad (4)$$

$$\tau_{ij} = e^{-\frac{a_{ij}}{R}} = e^{A_{ij} + \frac{B_{ij}}{T}} \quad (\tau_{ij} \neq \tau_{ji} \text{ and } \tau_{ii} = 0) \quad (5)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (6)$$

$$\phi_i = \frac{\gamma_i x_i}{\sum_j \gamma_j x_j}, \quad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j}, \quad \theta'_i = \frac{q'_i x_i}{\sum_j q'_j x_j} \quad (7)$$

where i, j and k are related to each component, γ_i is the activity coefficient of component i , τ_{ij} and τ_{ji} are the interaction energies between the molecules i and j , x is the molar fraction, A_{ij} and B_{ij} are the binary interaction parameters, and T is the absolute temperature. Moreover, ϕ_i is the volume fraction of component i , θ_i is the surface fraction of the component i , θ'_i is the interaction surface fraction of the component i , r_i is volume of the molecule i , q_i is the surface of molecule i , q'_i is surface interaction of molecule i (for non-water and light non-alcoholic material, $q_i = q'_i$), and z is the coordination number of (equal 8) [20]. Table 1 presents the values of r_i , q_i and q'_i for the materials investigated in this study.

Liquid-liquid Equilibrium Calculations and Parameter Estimation

The binary interaction parameters of the NRTL and UNIQUAC models were obtained by minimizing the deviation between the measured and calculated mass fractions. The objective function is expressed in the following equation:

$$OF = 100 \times \frac{1}{D.M.N} \sum_{k=1}^D \sum_{j=1}^M \sum_{i=1}^N \left((w_{ijk}^{W, \text{exp}} - w_{ijk}^{W, \text{calc}})^2 + (w_{ijk}^{S, \text{exp}} - w_{ijk}^{S, \text{calc}})^2 \right) \quad (8)$$

where D is the total number of references in the database, M is the total number of tie lines in the reference k , N is the total number of components in the data group, i, j and k are the desired components, the tie lines, and the number of groups, and exp. and calc. are the measured and calculated components. In addition, W and S are used for aqueous and organic solvent phases, respectively.

In this study, to compare the accuracy of the proposed models, we used root mean square deviation (RMSD). RMSD is defined as:

$$RMSD = \left(\frac{1}{D.M.N} \sum_{k=1}^D \sum_{j=1}^M \sum_{i=1}^N \left((w_{ijk}^{W, \text{exp}} - w_{ijk}^{W, \text{calc}})^2 + (w_{ijk}^{S, \text{exp}} - w_{ijk}^{S, \text{calc}})^2 \right) \right)^{\frac{1}{2}} \quad (9)$$

Calculation Algorithm

Using the equilibrium equations for various components in the aqueous and organic solvent phases, the following equations were obtained:

$$w_i^W \gamma_i^W (w_1^W \cdot w_2^W \cdot w_3^W) = w_i^S \gamma_i^S (w_1^S \cdot w_2^S \cdot w_3^S); \quad i = 1, 2, 3 \quad (10)$$

$$K_i = \frac{\gamma_i^W}{\gamma_i^S} = \frac{w_i^S}{w_i^W}; \quad i = 1, 2, 3 \quad (11)$$

where K_i is the equilibrium constant between the two phases for the i component. The mass balance for the system is as follows:

$$F = W + S = 1 \quad (12)$$

Table 1. Values of r_i , q_i and q'_i Parameters in the Studied Systems

Component	r_i	q_i	q'_i
Water	0.9200	1.400	1.000
Acetic acid	2.2024	2.072	2.072
1,2,4-Trimethylbenzene	5.3928	4.104	4.104
1,3,5-Trimethylbenzene	5.3928	4.104	4.104
1-Heptanol	5.4770	4.672	4.672
1-Methyl propyl ethanoate	4.8266	4.192	4.192
2-Ethyl-1-hexanol	6.1500	5.020	5.020
Cyclopentyl methyl ether	4.2142	3.248	3.248
Cyclohexane	4.0464	3.240	3.240
Diisopropyl ether	4.7423	4.088	4.088
Ethyl acetate	3.4786	3.116	3.116
Isobutyl acetate	4.8266	4.192	4.192
Isobutanol	3.4535	3.048	3.048
Isophorone	5.9315	4.940	4.940
Methyl isobutyl ketone	4.7300	5.500	5.500
Methyl tert-butyl ether	4.0678	3.632	3.632
<i>m</i> -xylene	4.6578	3.536	3.536
<i>o</i> -xylene	4.6578	3.536	3.536
Sec-butyl acetate	4.8266	4.192	4.192
Toluene	3.9200	2.970	2.970

$$Z_i F = w_i^W W + w_i^S S \quad i = 1, 2, 3 \quad (13)$$

$$w_i^S = \frac{K_i Z_i}{1 + (K_i - 1)s}; \quad i = 1, 2, 3 \quad (15)$$

where F, W and S are mass of feed, mass of water-rich phase, and mass of organic solvent-rich phase. Furthermore, Z_i is the mass fraction of component i in the feed. By integrating Eqs. (11), (12) and (13), the following equations were obtained:

$$w_i^W = \frac{Z_i}{1 + (K_i - 1)s}; \quad i = 1, 2, 3 \quad (14)$$

Considering that the sum of the mass fractions in two phases of water-rich and solvent-rich are equal to 1, $\sum w_i^W - \sum w_i^S = 0$, we have:

$$\sum_{i=1}^3 \frac{Z_i (K_i - 1)}{1 + (K_i - 1)s} = 0 \quad (16)$$

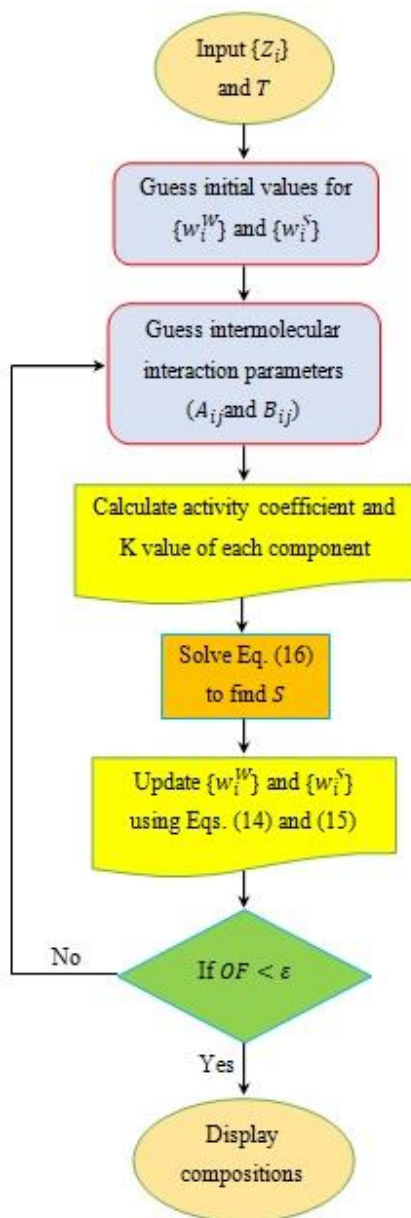


Fig. 1. Procedure of liquid-liquid equilibrium calculation for the thermodynamic models.

The equilibrium computation algorithm is summarized in Fig. 1.

Distribution Coefficient and Selectivity

In liquid-liquid extraction studies, the most important factors for a solvent are the distribution coefficient and selectivity, which are defined by the following equations:

$$K_2 = \frac{w_2^S}{w_2^W} \quad (17)$$

$$\beta = \frac{K_2}{K_1} = \frac{w_2^S/w_2^W}{w_1^S/w_1^W} \quad (18)$$

where K_2 is the distribution coefficient and β is the

Table 2. NRTL Interaction Parameters in “Water + Acetic Acid + Organic Solvent” for Different Organic Solvents Obtained From Global Temperature Fit

Component j	Component i							
	Water				Acetic acid			
	A _{ij}	B _{ij} (K)	A _{ji}	B _{ji} (K)	A _{ij}	B _{ij} (K)	A _{ji}	B _{ji} (K)
Water	-	-	-	-	-0.1360	1.3714	-0.7732	2.8176
1,2,4-Trimethylbenzene	0.0934	4.5588	-4.1184	5.7759	2.4225	-3.5636	-2.5660	7.7788
1,3,5-Trimethylbenzene	-1.3651	-1.7778	-3.6782	4.3123	-1.7060	-0.2998	-0.8675	2.6683
1-Heptanol	1.0352	5.6150	-2.7517	-1.8979	0.7189	3.5272	-1.2130	2.9625
1-Methyl propyl ethanoate	-1.0845	-0.3200	-1.8024	-0.9078	-1.5313	-3.0972	1.5514	-0.5651
2-Ethyl-1-hexanol	-0.9969	2.7333	-1.9072	3.7411	-1.1614	1.1554	1.9344	2.6772
Cyclopentyl methyl ether	0.5096	-0.2709	-3.5819	5.1887	4.4547	0.7146	-0.6178	5.1059
Cyclohexane	-0.4264	-1.5853	-5.5561	-4.0232	2.9666	-11.4126	-2.7110	5.0723
Diisopropyl ether	-2.2407	-0.0763	-7.1699	-1.1177	-3.2166	0.1578	2.4630	3.7692
Ethyl acetate	-0.5128	-0.2447	-1.9644	-0.8349	-1.3895	5.1311	-0.3563	1.1277
Isobutyl acetate	-0.5328	0.2991	-2.3853	-0.2700	-1.4547	3.8483	-0.3308	1.5645
Isobutanol	0.3003	3.0834	-2.0610	2.1196	2.8299	-1.0728	-0.3607	2.2976
Isophorone	0.1550	0.6215	-1.7747	1.4149	7.0213	-4.2580	1.9734	0.2549
Methyl isobutyl ketone	3.0142	-5.3671	-4.5007	0.0558	0.6182	-0.3234	-3.6962	4.5306
Methyl tert-butyl ether	-0.3544	-0.3907	-2.5618	-0.1614	-0.1051	-3.7265	-0.4097	-1.4860
<i>m</i> -xylene	-0.8299	2.2551	-4.1541	2.8241	-0.9109	3.1952	-1.4997	0.0812
<i>o</i> -xylene	-2.0127	-0.7300	-2.4814	-0.2360	-2.3076	-2.5178	-0.0626	0.0615
Sec-butyl acetate	-3.0670	-3.1871	-1.0480	-0.6084	-3.9811	-1.4417	2.5263	2.2369
Toluene	-1.8198	-0.0774	-2.3838	-0.7490	-0.1463	-1.2372	-0.9758	2.6415

selectivity. The value of β must always be higher than one. Moreover, when the distribution coefficient is larger than a defined amount, less solvent is needed.

RESULTS AND DISCUSSION

Parameters of Intermolecular Interaction

Among all of the experimental data described in the

Materials and Methods section, 70% were used to determine the interaction parameters of the mentioned models. Using the algorithm mentioned above, the intermolecular interaction parameters were obtained for the NRTL and UNIQUAC models. In this study, genetic algorithm (GA) method was used to calculate the intermolecular interaction parameters. Using the algorithm shown in Fig. 1 and the Genetic Algorithm toolbox in MATLAB 2019a software, the model interaction parameters were calculated. These parameters were calculated to minimize the target function (Eq. (1)).

To ensure the consistency of the binary interaction parameters obtained in this work, we use the topological analysis of LLE correlations, recently designed by Marcilla *et al.* [21]. According to this test, the parameters presented in Tables 2 and 3 are very consistent and satisfy the Gibbs sustainability criteria while providing a very good agreement with the tie lines. Tables 2 and 3 show the values of interaction parameters between different molecules for the NRTL and UNIQUAC models, respectively. As indicated in these tables, the interaction parameters between water and acetic acid molecules for all the systems are considered the same. These values are determined regardless of the organic solvent type in the mixture. In other words, there is only one value for the interaction between water and acetic acid molecules.

The value of the target function (Eq. (8)) for ternary systems, consisting of water + acetic acid + organic solvents, using the NRTL and UNIQUAC models are 0.074 and 0.180, respectively. It was observed that the accuracy of the models was as follows: NRTL > UNIQUAC.

Comparison of the Accuracy of Models

The accuracy of each thermodynamic model was calculated through applying the presented thermodynamic models on the database. Table 4 shows the root mean square deviation of different models for each of the references, independently. Table 5 shows the values of the RMSD for each ternary mixture, regardless of temperature.

Tables 4 and 5 show the distribution coefficient and selectivity values for different solvents. As shown in Table 5, toluene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene had the highest selectivity values; 46.46, 31.89 and 29.91, respectively. Moreover, the lowest

selectivity values among the investigated solvents in this study were related to o-xylene, m-xylene and 1-heptanol; 4.81, 5.55 and 5.58 values, respectively.

The average distribution coefficients for cyclohexane and isophorone solvents are the lowest (0.057) and highest (4.589), respectively (see Table 5). As shown in Table 4, with increasing the temperature, the selectivity and distribution coefficients reduced and increased, respectively. For example, the selectivity values of toluene at 288.15, 298.15 and 313.15 K were 66.26, 37.91 and 31.66, respectively, that could be attributed to the lower boiling point of water compared to that of acetic acid. In addition, with increasing the temperature, the water/acetic acid ratio in organic phase was increased; the selectivity reduced. At these temperatures (288.15, 298.15 and 313.15 K), the acetic acid distribution coefficients in toluene solvent were 0.096, 0.116 and 0.122, respectively.

Figure 2 shows the mass fraction of the acetic acid predicted by various models in the water-rich phase (aqueous phase) and compares them with the experimental values.

Figure 3 shows these values for the organic solvent-rich phase (organic phase). As shown in these two figures (Figs. 2 and 3), two models were more accurate in predicting the amount of acetic acid in the water-rich phase than in the organic solvent-rich phase.

Furthermore, Fig. 4 presents the accuracy of the NRTL and UNIQUAC thermodynamic models in predicting the composition. In addition, this figure shows the total accuracy of each model. The RMSD values of the NRTL and UNIQUAC models for “water + acetic acid + organic solvents” were 0.0273 and 0.0422, respectively. The accuracy of the models was as follows: NRTL > UNIQUAC.

CONCLUSIONS

Acetic acid is one of the most important carboxylic acids used in various reactions. Although the mixture of acetic acid and water does not form an azeotrope, the distillation operation for their separation is uneconomical. Therefore, different organic solvents are used to isolate acetic acid in an aqueous solution. In this study, using the experimental data collected from previously

Table 3. UNIQUAC Interaction Parameters in “Water + Acetic Acid + Organic Solvents” Obtained from Global Temperature Fit

Component j	Component i							
	Water				Acetic acid			
	A _{ij}	B _{ij} (K)	A _{ji}	B _{ji} (K)	A _{ij}	B _{ij} (K)	A _{ji}	B _{ji} (K)
Water	-	-	-	-	1.43247	-9.59636	1.21937	11.6571
1,2,4-Trimethylbenzene	1.3447	1.0686	11.8053	2.7897	-0.1423	2.7043	1.1055	-10.3867
1,3,5-Trimethylbenzene	1.2433	-3.1368	13.2723	-5.8991	0.3266	-2.0421	0.6288	-13.5243
1-Heptanol	-13.5441	-9.1310	2.1471	-6.7588	-12.0230	16.7332	1.9216	4.7495
1-Methyl propyl ethanoate	-9.9019	1.7698	2.4433	3.6863	-10.9940	-2.3912	1.5195	0.3764
2-Ethyl-1-hexanol	4.4902	-0.5717	1.5112	5.8639	1.1548	-3.3022	1.4040	-7.6062
Cyclopentyl methyl ether	2.1364	-1.6194	0.5340	-2.6216	0.7421	0.4839	0.3674	-3.8334
Cyclohexane	0.9156	5.4619	9.8117	1.8261	-11.0104	-2.4365	2.1199	-3.4754
Diisopropyl ether	7.4080	5.3984	-2.7605	-6.3393	3.3017	-10.5033	0.4814	-7.7675
Ethyl acetate	1.6350	-4.0756	1.0287	6.3814	4.0839	10.8680	1.7063	9.0460
Isobutyl acetate	-10.5601	2.6062	2.4949	4.5699	-8.1819	-11.6660	1.5273	-1.1869
Isobutanol	0.3081	5.6186	1.2314	11.1669	4.4760	-0.1766	2.6484	8.5651
Isophorone	-13.1515	-5.0923	2.1498	6.0777	-8.2432	3.7732	1.9112	-3.4495
Methyl isobutyl ketone	4.3869	0.9507	12.2929	-0.7422	-1.4858	0.4555	-1.4801	5.7695
Methyl tert-butyl ether	-4.5675	1.5240	14.0873	5.7285	-19.4076	-4.6529	0.5152	9.5694
<i>m</i> -xylene	3.0016	-3.3051	6.5266	-2.0599	1.3824	-4.0630	-1.3188	-6.7834
<i>o</i> -xylene	2.4359	2.4239	13.0113	16.9656	-10.2940	2.9023	2.0597	4.3225
Sec-butyl acetate	-13.4705	-6.4177	2.3256	9.4942	-9.8443	-5.4910	1.6171	8.9294
Toluene	3.8782	-1.5160	-3.8726	7.6437	1.7918	-2.7091	-1.9945	-1.2499

conducted studies, the NRTL and UNIQUAC thermodynamic models were investigated. The results showed that the accuracy of the NRTL model was more than that of the UNIQUAC model. Moreover, comparison

of different organic solvents showed that toluene had a higher selectivity than other solvents. In addition, the solvents used in this liquid-liquid extraction acted better at lower temperatures.

Table 4. Liquid-liquid Equilibrium Data of “Water + Acetic Acid + Organic Solvent” for Different Organic Solvents, and the Accuracy of the UNIQUAC and NRTL Models at Different Temperatures

No.	System	T (K)	NDP	K_2	$\beta = k_2/k_1$	RSMD		Ref.
						NRTL	UNIQUAC	
1	Water + acetic acid + 1,2,4-trimethylbenzene	303.15	10	0.125	44.50	0.0301	0.0254	[10]
2		313.15	10	0.130	33.04	0.0302	0.0261	[10]
3		323.15	10	0.133	28.36	0.0305	0.0269	[10]
4		333.15	10	0.138	23.67	0.0307	0.0274	[10]
5		343.15	10	0.144	19.97	0.0314	0.0278	[10]
6	Water + acetic acid + 1,3,5-trimethylbenzene	303.15	10	0.133	43.87	0.0120	0.0232	[10]
7		313.15	10	0.138	39.67	0.0131	0.0231	[10]
8		323.15	10	0.146	29.71	0.0135	0.0234	[10]
9		333.15	10	0.156	25.71	0.0140	0.0229	[10]
10		343.15	10	0.161	20.51	0.0144	0.0222	[10]
11	Water + acetic acid + 1-heptanol	288.15	8	2.215	5.26	0.0200	0.0141	[3]
12		298.15	8	2.308	5.61	0.0205	0.0164	[3]
13		303.15	8	2.203	5.19	0.0206	0.0166	[3]
14		308.15	8	2.238	5.50	0.0201	0.0169	[3]
15		318.15	8	2.337	6.38	0.0200	0.0156	[3]
16		278.15	6	2.162	5.24	0.0223	0.0238	[12]
17		293.15	6	2.135	5.00	0.0194	0.0202	[12]
18		303.15	6	2.306	5.72	0.0202	0.0180	[12]
19		313.15	7	2.399	6.17	0.0188	0.0154	[12]
20	Water + acetic acid + 1-methyl propyl ethanoate	283.15	18	2.297	11.30	0.0206	0.0389	[17]
21		323.15	16	2.353	10.45	0.0242	0.0324	[17]
22	Water + acetic acid + 2-ethyl-1-hexanol	298.15	9	2.590	13.25	0.0191	0.1023	[13]
23		303.15	9	2.884	15.26	0.0197	0.0999	[13]
24		308.15	9	2.811	14.36	0.0198	0.0964	[13]
25		313.15	9	2.712	15.22	0.0187	0.1042	[13]
26	Water + acetic acid + cyclopentyl methyl ether	293.15	9	0.948	20.72	0.0322	0.0353	[16]
27		298.15	8	0.923	12.76	0.0420	0.0387	[16]
28		303.15	9	0.826	11.73	0.0350	0.0344	[16]

Table 4. Continued

29		308.15	8	0.842	9.21	0.0465	0.0392	[16]
30		313.15	9	0.841	8.54	0.0376	0.0402	[16]
31		318.15	8	0.866	4.94	0.0445	0.0488	[16]
32	Water + acetic acid + cyclohexane	303.15	12	0.046	3.46	0.0137	0.0130	[18]
33		313.15	12	0.050	11.81	0.0133	0.0130	[18]
34		323.15	12	0.065	10.00	0.0187	0.0186	[18]
35		333.15	12	0.065	8.69	0.0181	0.0193	[18]
36	Water + acetic acid + diisopropyl ether	293.15	10	0.531	13.26	0.0360	0.0404	[2]
37		303.15	10	0.424	10.31	0.0499	0.0519	[2]
38		313.15	10	0.518	7.60	0.0603	0.0645	[2]
39	Water + acetic acid + ethyl acetate	283.15	6	2.806	8.87	0.0166	0.0782	[4]
40		298.15	6	2.705	7.92	0.0179	0.0752	[4]
41		313.15	6	2.583	7.07	0.0185	0.0730	[4]
42	Water + acetic acid + isobutyl acetate	283.15	17	2.089	10.48	0.0158	0.0368	[5]
43		323.15	16	2.206	9.90	0.0169	0.0356	[5]
44	Water + acetic acid + isobutanol	283.15	11	2.990	5.46	0.0368	0.0362	[5]
45		323.15	13	2.811	4.61	0.0355	0.0508	[5]
46	Water + acetic acid + isophorone	283.15	6	4.880	11.51	0.0537	0.0443	[4]
47		298.15	6	4.565	10.65	0.0537	0.0454	[4]
48		313.15	6	4.323	10.00	0.0530	0.0466	[4]
49	Water + acetic acid + methyl isobutyl ketone	288.15	11	0.658	7.53	0.0266	0.0677	[7]
50		298.15	9	0.664	6.73	0.0287	0.0767	[7]
51		313.15	11	0.648	7.10	0.0282	0.0671	[7]
52	Water + acetic acid + methyl tert-butyl ether	293.15	9	1.049	10.41	0.0191	0.0446	[8]
53		298.15	9	1.065	10.76	0.0188	0.0436	[8]
54		303.15	9	0.977	8.58	0.0185	0.0439	[8]
55		308.15	9	1.065	12.10	0.0181	0.0387	[8]
56		313.15	8	1.037	11.76	0.0189	0.0368	[8]
57		318.15	8	1.029	12.42	0.0177	0.0328	[8]
58	Water + acetic acid + <i>m</i> -xylene	303.15	10	0.167	8.05	0.0207	0.0147	[11]

Table 4. Continued

59		313.15	10	0.171	3.29	0.0172	0.0160	[11]
60		323.15	9	0.101	4.98	0.0155	0.0135	[11]
61		333.15	9	0.115	6.02	0.0169	0.0145	[11]
62		343.15	9	0.120	5.38	0.0177	0.0154	[11]
63	Water + acetic acid + o-xylene	303.15	10	0.179	4.51	0.0149	0.0335	[11]
64		313.15	9	0.107	5.23	0.0102	0.0195	[11]
65		323.15	9	0.106	4.63	0.0101	0.0205	[11]
66		333.15	9	0.106	4.46	0.0103	0.0221	[11]
67		343.15	9	0.115	5.26	0.0100	0.0228	[11]
68	Water + acetic acid + sec-butyl acetate	298.15	8	2.014	7.23	0.0446	0.0385	[6]
69		303.15	8	2.076	7.72	0.0471	0.0325	[6]
70		308.15	8	1.987	6.72	0.0460	0.0365	[6]
71		313.15	8	2.028	6.72	0.0454	0.0329	[6]
72	Water + acetic acid + toluene	288.15	9	0.096	66.26	0.0145	0.0104	[9]
73		298.15	7	0.116	37.91	0.0163	0.0090	[9]
74		313.15	8	0.122	31.66	0.0171	0.0085	[9]

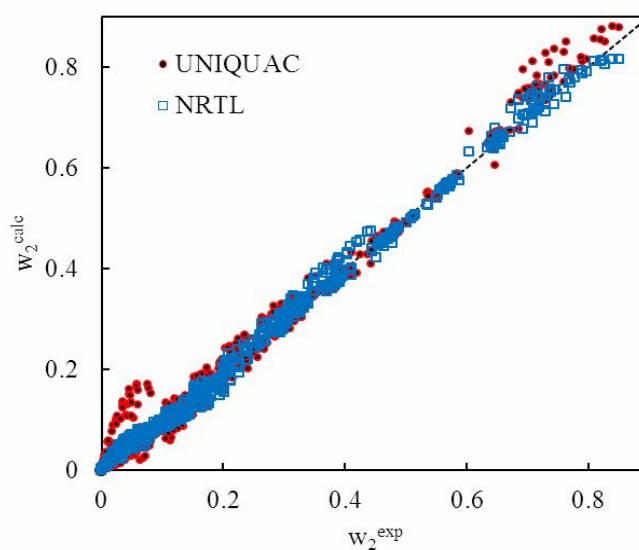
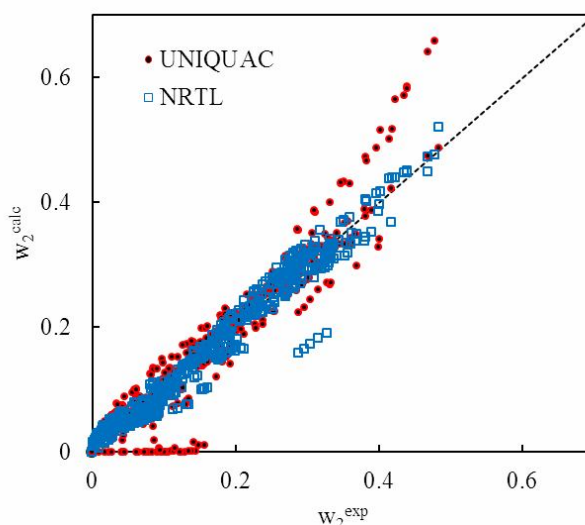
**Fig. 2.** Comparison between the calculated and experimental acetic acid mass fraction (w_2) for the liquid-liquid equilibrium (aqueous phase).

Table 5. Liquid-liquid Equilibrium Data of “Water + Acetic Acid + Organic Solvents” and the Accuracy of Different Models

System	T (K)	NDP	K ₂	$\beta = k_2/k_1$	RSMD	
					NRTL	UNIQUAC
Water + acetic acid + 1, 2, 4-trimethylbenzene	303.15-343.15	50	0.134	29.91	0.0306	0.0267
Water + acetic acid + 1, 3, 5-trimethylbenzene	303.15-343.15	50	0.147	31.89	0.0134	0.0230
Water + acetic acid + 1-heptanol	278.15-318.15	65	2.259	5.58	0.0202	0.0174
Water + acetic acid + 1-methyl propyl ethanoate	283.15-323.15	34	2.323	12.40	0.0224	0.0360
Water + acetic acid + 2-ethyl-1-hexanol	298.15-313.15	36	2.749	15.76	0.0193	0.1010
Water + acetic acid + cyclopentyl methyl ether	293.15-318.15	51	0.874	12.67	0.0397	0.0396
Water + acetic acid + cyclohexane	303.15-333.15	48	0.057	9.31	0.0161	0.0162
Water + acetic acid + diisopropyl ether	293.15-313.15	30	0.491	9.82	0.0498	0.0288
Water + acetic acid + ethyl acetate	283.15-313.15	18	2.698	9.41	0.0177	0.0755
Water + acetic acid + isobutyl acetate	283.15-323.15	33	2.146	8.34	0.0163	0.0362
Water + acetic acid + isobutanol	283.15-323.15	24	2.893	7.45	0.0361	0.0540
Water + acetic acid + isophorone	283.15-313.15	18	4.589	8.85	0.0535	0.0455
Water + acetic acid + methyl isobutyl ketone	288.15-313.15	31	0.656	8.41	0.0278	0.0702
Water + acetic acid + methyl tert-butyl ether	293.15-318.15	52	1.037	10.70	0.0185	0.0404
Water + acetic acid + <i>m</i> -xylene	303.15-343.15	47	0.136	5.55	0.0177	0.0149
Water + acetic acid + <i>o</i> -xylene	303.15-343.15	46	0.124	4.81	0.0114	0.0245
Water + acetic acid + sec-butyl acetate	298.15-313.15	32	2.026	20.08	0.0458	0.0352
Water + acetic acid + toluene	288.15-313.15	24	0.111	46.46	0.0159	0.0094
Total	278.15-343.15	689	1.199	13.15	0.0273	0.0424

**Fig. 3.** Comparison between the calculated and experimental acetic acid mass fraction (w_2) for the liquid-liquid equilibrium (organic phase).

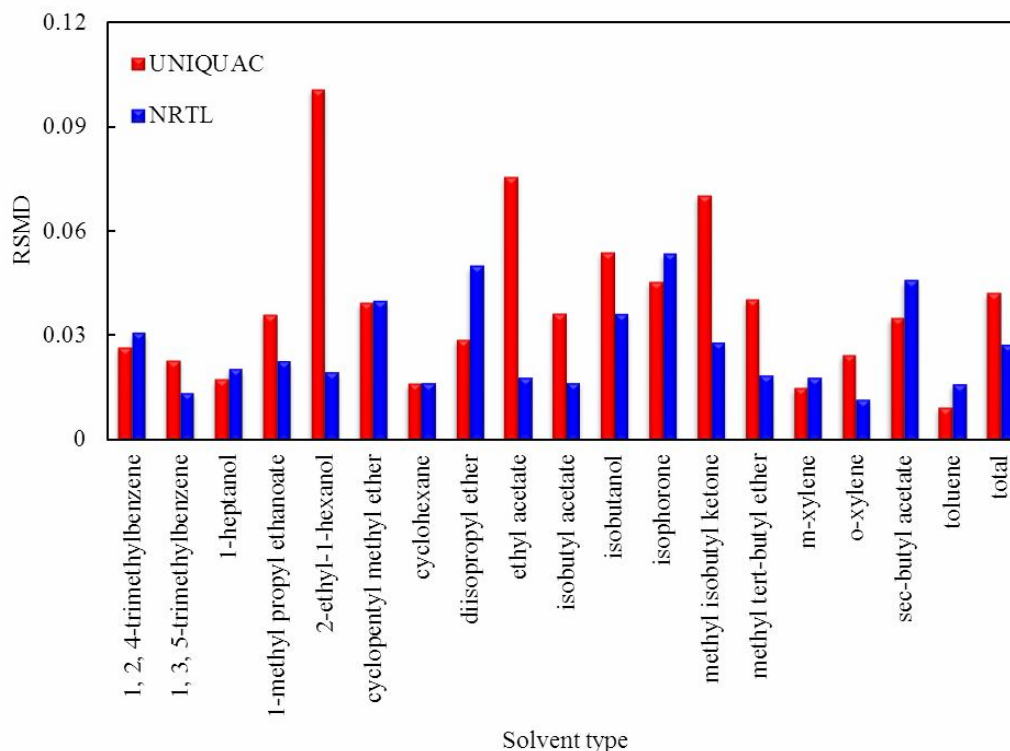


Fig. 4. Comparison of the accuracy of the thermodynamic models to calculate the composition of components of “water + acetic acid + organic solvent” ternary systems.

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