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Liquid–liquid equilibrium data for water + acetic acid + solvent (dichloromethane + methyl isobutyl ketone) at $T = 301.15$ K

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ABSTRACT

Liquid–liquid equilibrium (LLE) data for water + acetic acid + solvent (dichloromethane + methyl isobutyl ketone) ternary systems are measured experimentally at $T = 301.15$ K and $p = 1$ atm. Different proportions of pure solvents dichloromethane (DCM) and methyl isobutyl ketone (MIBK) are investigated. The cloud-point titration technique is employed in order to determine the equilibrium solubility data. The chemical species' concentrations, in both the light and heavy phases, were estimated using refractive index measurements. For activity coefficients prediction, the non-random two liquids (NRTL) model was used to correlate the measured tie-line data. Two evolutionary optimization methods (i.e., the genetic algorithm and the particle swarm optimization) are used in order to estimate the binary interaction parameters for the NRTL model. In addition to this, both the Othmer–Tobias and the Hand correlations are used to verify the thermodynamic consistency and reliability of the experimental tie-line measured data. Finally, the distribution coefficients and the separation factors are calculated in order to determine the suitability of the mixed solvents for the acetic acid extraction from water. The present results indicate that the mixed solvent (50% DCM + 50% MIBK) is the most suitable solvent for the separation the acetic acid from water.

Keywords: Acetic acid extraction; Liquid–liquid equilibrium; Distribution coefficient and separation factor; Genetic algorithm; Particle swarm optimization

1. Introduction

The determination of accurate phase equilibrium data for multicomponent mixtures has paramount importance to the study of various chemical processes. For example, good design of an extraction equipment requires experimental determination and/or theoretical prediction of liquid–liquid equilibrium (LLE) data. In recent years, several authors [1–6] have investigated LLE of ternary systems. Recently, mixed solvents have been investigated as potential candidates for extraction processes [6,7] including mixtures containing water and acetic acid [8,9].

A water-free acetic acid is called glacial acetic acid, which is a colorless liquid and has a distinctive sour taste and a pungent smell. Concentrated acetic acid is corrosive and can attack skin. On the other hand, when mixed with water it forms vinegar [10]. It is used as a precursor to poly(vinyl acetate) and cellulose acetate.

It is not possible to separate this acid from water by distillation due to a severe tangent pinch. Thus, solvent extraction is a promising alternative for the recovery of the acetic acid diluted in water. Selecting a good extraction solvent has a substantial effect on pure acetic acid retrieval. Several authors [2,11] have studied LLE data for ternary mixtures, which are composed of acetic acid and water. In the present work, we have tried solvents composed of dichloromethane (DCM) and methyl isobutyl ketone (MIBK) mixed in different proportions. These solvents are attractive since they possess low toxicity, are relatively cheap and have less solubility in water.

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We start by describing the experimental setup used in the present study.

After that, the LLE data of the ternary systems (water + acetic acid + mixed solvents) are presented at T = 301.15 K and p = 1 atm. In addition to this, the cloud-point method [12,13] is used to determine the solubility and tie-line data for these ternary systems. This technique allows us to determine the different component concentrations in the two phases at equilibrium [1,13–15]. In agreement with previous works [16–18], the distribution coefficients and the separation factors, which are estimated from our experimental measurements, are reported in the subsequent section. These calculated properties help to estimate the potential of the mixed solvents for the extraction of acetic acid from its diluent (i.e., water). Then, it is shown how the Othmer–Tobias [19] and Hand [20] correlations are used to confirm the quality of our experimental tie-line data. Finally, we make use of the non-random two liquids (NRTL) model [21] to correlate the tie-line data. For this purpose, we have employed two evolutionary optimization techniques: the genetic algorithm (GA) and the particle swarm optimization (PSO) method, in order to estimate the binary interaction parameters of the NTRL model [2].

2. Experimental setup

2.1. Materials

The origin and purity of the chemical components utilized in the present study are as follows: acetic acid (Biochem, p-code: 101132500, France; >99.5%), DCM (Merck, Germany; >99.5%), and MIBK (Sigma-Aldrich, p-code: 101258949, Canada; >98.5%). No further purification was conducted to purify these chemical species. In addition to this, we employed deionized and redistilled water in all experimental runs.

2.2. Apparatus and procedure

We used a thermostated cell, which was equipped with a magnetic stirrer and an isothermal fluid jacket, in order to measure the solubility curves for the quaternary systems (water + acetic acid + mixed solvents [DCM + MIBK]) using the cloud-point method [6,11,15,17]. The various mixed solvents, investigated in the present study, are listed in Table 1. They contain different proportions of DCM and MIBK. The cell temperature was set at 301.15 ± 0.1 K and monitored by a mercury-in-glass thermometer. The shift from a homogeneous to a heterogeneous mixture allows us to determine the titration end point. Indeed, (1) binary mixtures of water + acetic acid are titrated with solvent, and (2) binary mixtures of solvent + acetic acid are titrated with water, up to the point where we detect the transition from homogeneity to cloudiness. For this purpose, we carried refractive index measurements using the Nahita Model 690/1 refractometer. The turbidity observations allowed the determination of the end point as described in reference [22].

Concerning the experimental equipment, an experimental setup including a 250-mL glass cell is used to determine the tie-lines. For a detailed experimental procedure, we

Table 1
Solubility data for the (water (1) + acetic acid (2) + mixed solvent [DCM + MIBK] (3)) quaternary systems at T = 301.15 K

0% MIBK + 100% DCM		25% MIBK + 75% DCM		50% MIBK + 50% DCM		75% MIBK + 25% DCM		100% MIBK + 0% DCM	
x_1	x_3	x_1	x_3	x_1	x_3	x_1	x_3	x_1	x_3
0.9616	0.0182	0.9614	0.0214	0.9625	0.0144	0.9604	0.0162	0.9472	0.0236
0.9203	0.0226	0.9311	0.0223	0.9348	0.0195	0.9300	0.0223	0.9242	0.0249
0.8872	0.0295	0.8838	0.0272	0.8845	0.0293	0.8096	0.0313	0.8789	0.0319
0.8111	0.0312	0.8078	0.0316	0.8054	0.0328	0.7463	0.0333	0.8041	0.0356
0.7324	0.0467	0.7374	0.0421	0.7444	0.0334	0.6884	0.0361	0.7382	0.0413
0.6792	0.0532	0.6773	0.0538	0.6844	0.0402	0.5835	0.0608	0.6812	0.0478
0.6127	0.0801	0.5765	0.0794	0.5790	0.0663	0.5101	0.0833	0.5827	0.0668
0.5828	0.0984	0.4830	0.1321	0.5106	0.0890	0.4706	0.1046	0.5042	0.0949
0.5522	0.1166	0.4449	0.1631	0.4689	0.1121	0.2016	0.4205	0.4716	0.1077
0.4350	0.2158	0.2436	0.3974	0.2433	0.3977	0.1828	0.4539	0.1521	0.4473
0.2606	0.4109	0.2168	0.4354	0.2045	0.4421	0.1223	0.5479	0.1373	0.4785
0.1971	0.5036	0.1623	0.5226	0.1558	0.5275	0.0499	0.6799	0.0924	0.5677
0.1787	0.5299	0.1068	0.6386	0.0973	0.6434	0.0143	0.8188	0.0430	0.6831
0.1596	0.5590	0.0806	0.7077	0.0652	0.7188	0.0094	0.9424	0.0281	0.7403
0.1360	0.6136	0.0664	0.7797	0.0379	0.8015	0.0077	0.9699	0.0126	0.8210
0.1105	0.6847	0.0501	0.8635	0.0195	0.8915			0.0123	0.9004
0.0800	0.7651	0.0365	0.9191	0.0168	0.9367			0.0056	0.9461
0.0630	0.8512	0.0294	0.9487	0.0144	0.9643			0.0048	0.9757
								0.0606	0.8942
								0.0421	0.9400

Note: Uncertainty $\mu(x)$ = ±0.0001 and $\mu(T)$ = ±0.1 K and atmospheric pressure.

refer the reader to our previous work [6]. For this purpose, we prepared mixtures of known weight of water, acetic acid and mixed solvent. An analytical balance (model Nahita 5034/200, accurate to ±0.0001 g) was used to weight all mixtures. In order to achieve phase separation, we have agitated the mixture during 3 h with a magnetic stirrer and then left this mixture to settle down for 24 h. With the help of a syringe, we removed samples from the solvent-rich phase (i.e., the upper layer) and the water-rich phase (i.e., the lower layer). Then, we carried out the measurement of the refractive indices of these samples [11].

3. Results and discussion

3.1. Thermodynamic equilibrium solubility data

In this section, we report the experimental thermodynamic equilibrium data including the solubility curves for the water + acetic acid + mixed solvents quaternary systems at a temperature of 301.15 K and a pressure of 1 atm. The experimental data are shown in Table 1 where x_i denotes the mass fraction of the ith chemical component. The experimental tie-line data for the ternary systems at T = 301.15 K and p = 1 atm are given in Table 2. Figs. 1–5 show both the binodal

Table 2
Experimental and NRTL tie-line data for the water (1) + acetic acid (2) + mixed solvent (DCM + MIBK) (3) quaternary systems at T = 301.15 K

Aqueous phase				Organic phase			
Experimental		NRTL		Experimental		NRTL	
x_1	x_3	x_1	x_3	x_1	x_3	x_1	x_3
Water (1) + acetic acid (2) + mixed solvent (0% DCM + 100% MIBK) (3)							
0.9676	0.0191	0.9685	0.0249	0.0447	0.9329	0.0610	0.9104
0.8708	0.0298	0.8644	0.0378	0.0687	0.8238	0.0989	0.7923
0.8439	0.0303	0.8382	0.0386	0.0743	0.7941	0.0969	0.7691
0.8215	0.0311	0.8101	0.0394	0.0869	0.7496	0.0949	0.7446
0.7833	0.0363	0.7800	0.0404	0.1007	0.7118	0.0929	0.7187
0.7277	0.0470	0.7463	0.0415	0.1080	0.6870	0.0908	0.6911
0.6888	0.0520	0.6979	0.0433	0.1383	0.6055	0.0883	0.6553
Water (1) + acetic acid (2) + mixed solvent (25% DCM + 75% MIBK) (3)							
0.9617	0.0219	0.9389	0.0291	0.0255	0.9540	0.0770	0.9174
0.9147	0.0238	0.9045	0.0301	0.0434	0.8909	0.0738	0.8644
0.8625	0.0282	0.8621	0.0314	0.0541	0.8418	0.0717	0.8214
0.7762	0.0363	0.7729	0.0347	0.0750	0.7365	0.0686	0.7479
0.7241	0.0447	0.7385	0.0363	0.0779	0.7225	0.0679	0.7264
0.6769	0.0543	0.7034	0.0381	0.0823	0.7043	0.0676	0.7081
0.6182	0.0689	0.6356	0.0426	0.1147	0.6220	0.0677	0.6817
Water (1) + acetic acid (2) + mixed solvent (50% DCM + 50% MIBK) (3)							
0.9486	0.0179	0.9260	0.0327	0.0171	0.9304	0.0551	0.9003
0.8859	0.0275	0.8749	0.0331	0.0225	0.8765	0.0524	0.8521
0.7983	0.0323	0.8095	0.0336	0.0346	0.8211	0.0494	0.7938
0.7488	0.0338	0.7575	0.0341	0.0526	0.7569	0.0474	0.7530
0.6966	0.0388	0.7068	0.0347	0.0741	0.6976	0.0460	0.7202
0.6454	0.0499	0.6573	0.0356	0.1048	0.6297	0.0451	0.6954
Water (1) + acetic acid (2) + mixed solvent (75% DCM + 25% MIBK) (3)							
0.8512	0.0282	0.8589	0.0086	0.0102	0.9229	0.0201	0.9233
0.7860	0.0322	0.7933	0.0144	0.0127	0.8608	0.0258	0.8563
0.7139	0.0348	0.7175	0.0242	0.0194	0.8017	0.0328	0.7932
0.6581	0.0432	0.6632	0.0338	0.0332	0.7538	0.0385	0.7512
0.6285	0.0503	0.6301	0.0409	0.0417	0.7195	0.0423	0.7264
Water (1) + acetic acid (2) + mixed solvent (100% DCM + 0% MIBK) (3)							
0.7801	0.0375	0.7882	0.0206	0.0068	0.9394	0.0005	0.9541
0.7463	0.0403	0.7568	0.0201	0.0103	0.9163	0.0008	0.9293
0.6730	0.0484	0.6876	0.0412	0.0125	0.8880	0.0015	0.8907
0.6485	0.0539	0.6552	0.0499	0.0125	0.8663	0.0019	0.8752
0.5914	0.0647	0.5919	0.0702	0.0125	0.8407	0.0028	0.8474
0.5307	0.0857	0.5278	0.0951	0.0142	0.8124	0.0039	0.8213

Note: Uncertainty $\mu(x)$ = ±0.0001 and $\mu(T)$ = ±0.1 K and atmospheric pressure.

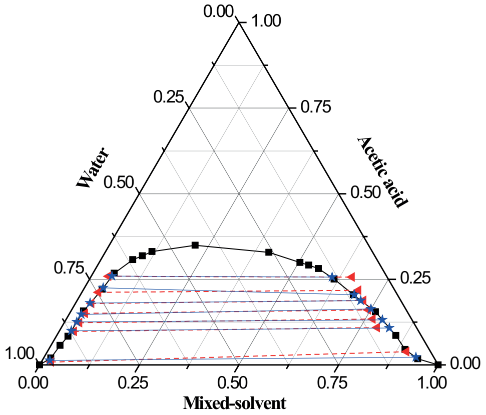

Fig. 1. Phase diagram for the experimental LLE of (water + acetic acid + mixed solvent [0% DCM + 100% MIBK]) quaternary systems at $T = 301.15$ K: (-★-) experimental tie-line data and (-◄-) NRTL calculated tie-line data.

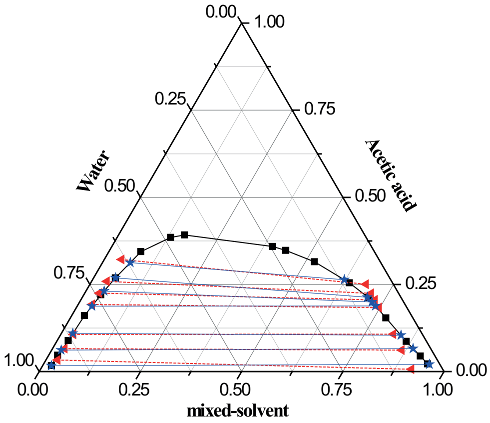

Fig. 2. Phase diagram for the experimental LLE of (water + acetic acid + mixed solvent [25% DCM + 75% MIBK]) quaternary systems at $T = 301.15$ K: (-★-) experimental tie-line data and (-◄-) NRTL calculated tie-line data.

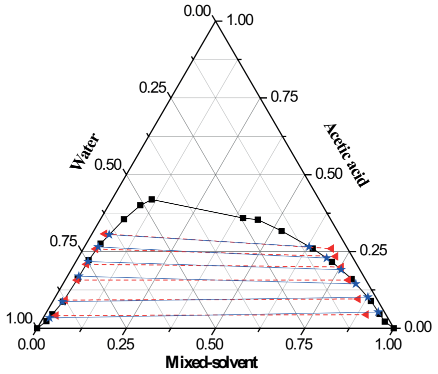

Fig. 3. Phase diagram for the experimental LLE of (water + acetic acid + mixed solvent [50% DCM + 50% MIBK]) quaternary systems at $T = 301.15$ K: (-★-) experimental tie-line data and (-◄-) NRTL calculated tie-line data.

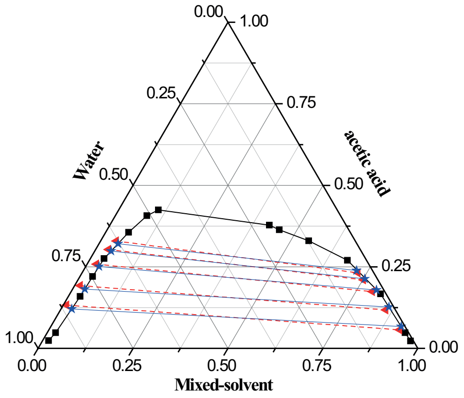

Fig. 4. Phase diagram for the experimental LLE of (water + acetic acid + mixed solvent [75% DCM + 25% MIBK]) quaternary systems at $T = 301.15$ K: (-★-) experimental tie-line data and (-◄-) NRTL calculated tie-line data.

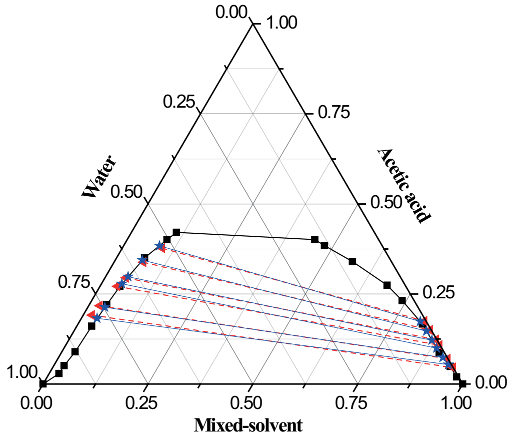

Fig. 5. Phase diagram for the experimental LLE of (water + acetic acid + mixed solvent [100% DCM + 0% MIBK]) quaternary systems at $T = 301.15$ K: (-★-) experimental tie-line data and (-◄-) NRTL calculated tie-line data.

curves and the tie-line data. According to the classification of Treybal [23], all the considered ternary systems are of type I LLE data. In fact, among the three liquid pairs (i.e., (1) acetic acid + water, (2) acetic acid + solvent and (3) water + solvent), only the third is a heterogeneous system.

3.2. Correlation of the liquid–liquid equilibrium data

Two recent methods of constrained and unconstrained solution optimization methods [24,25] are used in the present study. These are the GA and the PSO methods. Both methods are commonly characterized by their ability to find a global optimal solution.

In the GA technique [1,7], we start by randomly selecting a population of individuals. In this iterative method, the population in each step is a named generation. At each iteration, each individual fitness is calculated for the entire population [4]. To construct a new generation, the individuals of the current population with the best fitness are chosen where individual's genome is recombined and/or mutated. This procedure is repeated until the global optimum solution is found or the user-defined maximum number of iterations is exceeded.

On the other hand, Kennedy and Eberhart [24,26] developed an optimization algorithm that mimics the living behavior and social patters of interacting organisms in large groups (e.g., bird flock). In this method, named PSO, an initial random position distribution of swarm population is assigned to a priory specified search space. Then, swarm population individuals are allowed to move around where the population best position is found. The optimal criterion is based on the minimization of the so-called fitness function. Using the same procedure as that was used by the GA algorithm, the search is terminated either when a global solution is found or when the maximum number of iterations is exceeded.

The NRTL model [21] was chosen to correlate the experimental data of the tie-lines. The non-randomness parameters in the NRTL model (α) is usually set equal to 0.2 in order to reduce the dimensions of the optimization search domain. The correlated tie-line data for all ternary systems, at T = 301.15 K and p = 1 atm, are presented in Table 2. In addition to this, Figs. 1–5 compare the results between the calculated and experimental tie-lines. It is evident that the NRTL model can predict well the experimental behavior of the tie-lines. In Table 3, the interaction binary parameters of the NRTL model, using the two proposed optimization algorithms (GA and PSO), are presented along with the model prediction error. This error is computed based on the root-mean square deviation (rmsd).

The above optimization problem is formulated so that we take the advantage of the closure equation that relates the six binary interaction parameters as follows [3,5]:

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{1}$$

Table 3
NRTL (α = 0.2) binary interaction parameters (A_{ij} and A_{ji}) and root-mean square deviation (rmsd) values for the (water (1) + acetic acid (2) + mixed solvent [DCM + MIBK] (3)) quaternary systems

Systems	*i–j*	GA	PSO	rmsd	
		$A_{ij} \times 10^3$	$A_{ij} \times 10^3$	GA	PSO
Water (1) + acetic acid (2) + mixed solvent (100% DCM + 0% MIBK) (3)	1–2	–0.3988	–0.3967	0.6054	0.5464
	1–3	1.3473	1.0219		
	2–3	–0.3000	0.3985		
	2–1	–0.0214	0.6858		
	3–1	0.7189	0.5170		
	3–2	–0.7486	–0.6142		
Water (1) + acetic acid (2) + mixed solvent (25% DCM + 75% MIBK) (3)	1–2	–0.8927	0.6266	1.0379	1.3511
	1–3	1.9767	1.1189		
	2–3	–0.6297	–0.2492		
	2–1	–0.0194	–0.0380		
	3–1	0.2105	0.1892		
	3–2	–2.0485	–0.0920		
Water (1) + Acetic acid (2) + (50% DCM + 50% MIBK) (3)	1–2	0.8277	0.8484	0.7455	2.0942
	1–3	1.2952	1.1697		
	2–3	–0.5617	–0.2310		
	2–1	–0.4854	0.0472		
	3–1	0.5321	0.2734		
	3–2	0.1408	0.2302		
Water (1) + acetic acid (2) + mixed solvent (75% DCM + 25% MIBK) (3)	1–2	–0.8079	–152.8230	3.4318	0.5948
	1–3	1.5449	938.2297		
	2–3	0.9271	–385.6870		
	2–1	–0.6377	–620.3305		
	3–1	–0.9003	481.7381		
	3–2	–4.8178	–843.9582		
Water (1) + acetic acid (2) + mixed solvent (0% DCM + 100% MIBK) (3)	1–2	0.6852	–0.0639	0.4034	1.1149
	1–3	1.5655	1.1458		
	2–3	–0.4782	–0.3903		
	2–1	–0.0216	–0.3541		
	3–1	0.0513	0.1221		
	3–2	–0.3723	–1.0514		

Thus, we reduced the dimension of the search domain by one leaving the search space with only five independent binary interaction parameters.

In order to compare the results obtained by the GA and PSO, the error was measured based on the rmsd between the computed (using the NRTL model) and experimental mass fractions using the following expression:

$$\text{rmsd} = \sqrt{\frac{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}\left(x_{ijk}^{\text{exp}} - x_{ijk}^{cal}\right)^2}{6n}} \tag{2}$$

where x_{ijk}^{exp} is the mass fraction of the experimental tie-line; x_{ijk}^{cal} is the computed one; $k = 1, 2, \ldots, n$ (tie-line); j is the index of the aqueous or organic phase ($j = 1$ or 2); and i is the chemical species index ($i = 1$, 2 or 3).

A close look at the values of the rmsd (reported in Table 3) allows one to conclude that the PSO and GA algorithms perform well for all studied cases as indicated by the small values of the rmsd. Actually, the rmsd values for all the studied quaternary mixtures were less than 3.43%. Such small values of the rmsd confirm the reliability of the calculated results. In Figs. 1–5, both the experimental and calculated data of the quaternary systems are presented. It is clear from these plots that the NRTL model can be considered as an accurate model for the prediction of the experimental LLE data.

3.3. Distribution coefficients and separation factors

In order to access the extraction efficiency of the acetic acid from water by the mixed solvents, the distribution (partition) coefficients and the separation factors were calculated. By definition, the distribution coefficients (d_i) ($i = 1$ for water and 2 for acetic acid) and the separation factors (S) of the mixed solvent were calculated from the measured experimental data as follows [22]:

$$d_i = \frac{x_{i3}}{x_{i1}} \tag{3}$$

$$S = \frac{d_2}{d_1} = \frac{x_{23} / x_{21}}{x_{13} / x_{11}} \tag{4}$$

In the above Eqs. (3) and (4), x_{13} and x_{23} denote the mass fractions of water and acetic acid in organic phase (3 is the index of the organic phase), respectively, while x_{11} and x_{21} represent the mass fractions of water and acetic acid in the aqueous phase (1 is the index of the aqueous phase), respectively.

In this study, the values of the distribution coefficients as well as the separation factors are presented in Table 4. On the other hand, the distribution coefficients and the separation factors are shown in Figs. 6 and 7 as function of the acetic acid composition in the aqueous phase. It is obvious that the mixed solvent (50% DCM + 50% MIBK) has the highest separation factor with $S = 86.94$. This high value indicates the efficiency of this mixed solvent to extract acetic acid from water. Moreover, the values of all the separation factors were found to be greater than unity and vary from 4.54 to 86.94 for the present reported systems. This indicates that extraction of acetic acid by these mixed solvents is feasible. It should also be noted that the separation factors are not constant over the whole two-phase region.

Table 4
Distribution coefficients of water (d_1) and acetic acid (d_2) and separation factors (S) at $T = 301.15$ K

d_1	d_2	S
Water (1) + acetic acid (2) + mixed solvent (0% DCM + 100% MIBK) (3)		
0.0462	1.6842	36.46
0.0789	1.0815	13.71
0.0880	1.0461	11.88
0.1058	1.1092	10.49
0.1286	1.0394	8.08
0.1484	0.9099	6.13
0.9884	0.2008	4.92
Water (1) + acetic acid (2) + mixed solvent (25% DCM + 75% MIBK) (3)		
0.0265	1.2488	47.11
0.0474	1.0683	22.52
0.0627	0.9524	15.18
0.0966	1.0053	10.40
0.1076	0.8633	8.02
0.1216	0.7939	6.53
0.8415	0.1855	4.54
Water (1) + acetic acid (2) + mixed solvent (50% DCM + 50% MIBK) (3)		
0.0180	1.5672	86.94
0.0254	1.1663	45.92
0.0433	0.8518	19.65
0.0702	0.8763	12.47
0.1064	0.8628	8.11
0.1624	0.8713	5.37
Water (1) + acetic acid (2) + mixed solvent (75% DCM + 25% MIBK) (3)		
0.0120	0.5547	46.29
0.0162	0.6959	43.07
0.0272	0.7119	26.20
0.0505	0.7130	14.13
0.0663	0.7436	11.21
Water (1) + acetic acid (2) + mixed solvent (100% DCM + 0% MIBK) (3)		
0.0087	0.2949	33.84
0.0138	0.3439	24.89
0.0185	0.3571	19.23
0.0192	0.4073	21.13
0.0211	0.4269	20.20
0.0267	0.4520	16.89

3.4. Othmer–Tobias and Hand correlations

The thermodynamic consistency of the measured tie-line data can be validated using Othmer–Tobias [16] and Hand [20] correlations for the quaternary systems with the expressions defined by Eqs.(5) and (6), respectively:

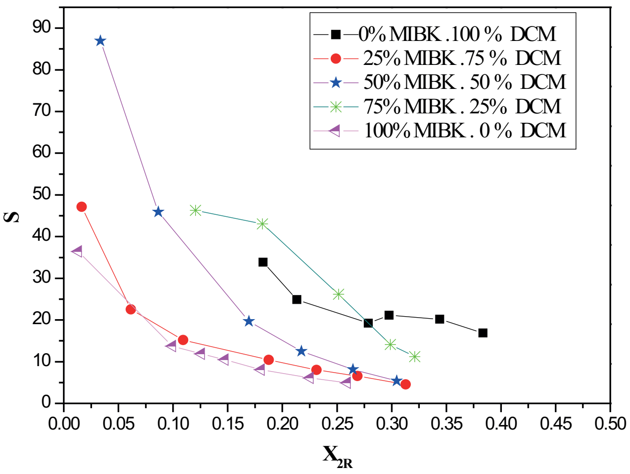

Fig. 6. Separation factors (S) of (water + acetic acid + mixed solvent [DCM + MIBK]) as a function of mass fraction of acetic acid in the aqueous phase X_{2R} at $T = 301.15$ K.

$$\ln\left[\frac{1-x_{33}}{x_{33}}\right] = a_1 + b_1 \ln\left[\frac{1-x_{11}}{x_{11}}\right] \tag{5}$$

$$\ln\left[\frac{x_{21}}{x_{11}}\right] = a_2 + b_2 \ln\left[\frac{x_{23}}{x_{33}}\right] \tag{6}$$

where x_{11} and x_{21} are the water and acetic acid compositions (mass fractions) in the aqueous phase, respectively, and x_{23} and x_{33} are the compositions (mass fractions) of acetic acid and solvents in the organic phase, respectively. The constants a_1 and b_1, and a_2 and b_2 are the parameters of the Othmer–Tobias and the Hand correlations, respectively. The estimated values of these parameters are listed in Table 5 and are graphically shown in Figs. 8 and 9 for the studied systems in this work. The goodness of fitting and the reliability of the estimated parameters are indicated by the high values of the correlation factor (R^2), which were greater than 0.97.

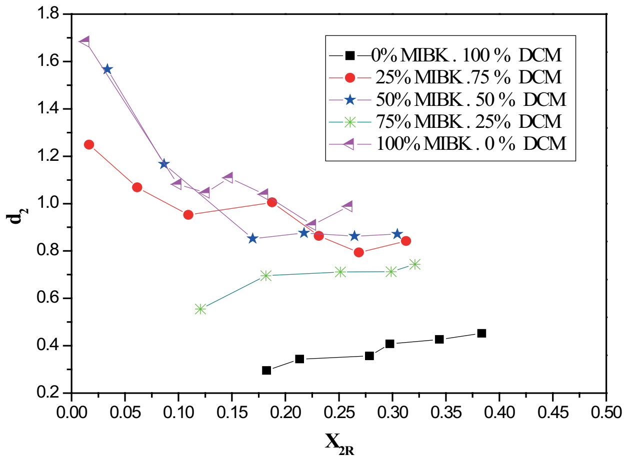

Fig. 7. Distribution coefficients (d_2) of (water + acetic acid + mixed solvent [DCM + MIBK]) as a function of mass fraction of acetic acid in the aqueous phase X_{2R} at $T = 301.15$ K.

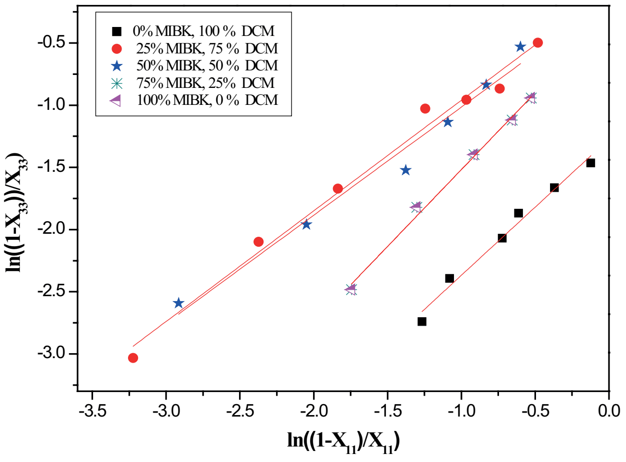

Fig. 8. Othmer–Tobias plots of the (water + acetic acid + mixed solvent [DCM + MIBK]) quaternary systems at $T = 301.15$ K.

Table 5
Constants of Othmer–Tobias and Hand correlations for the water (1) + acetic acid (2) + mixed solvent (DCM + MIBK) (3) quaternary systems at $T = 301.15$ K

Solvent mixtures	Othmer–Tobias correlation			Hand correlation		
	a_1	b_1	R^2	a_2	b_2	R^2
0% DCM + 100% MIBK	0.05974	1.17378	0.99296	0.11068	0.82152	0.98428
25% DCM + 75% MIBK	0.13269	1.14354	0.99325	–0.07026	0.88963	0.98474
50% DCM + 50% MIBK	0.22419	1.30954	0.98026	–0.14621	0.86899	0.97280
75% DCM + 25% MIBK	0.11370	0.86015	0.98881	–0.28208	1.23571	0.99319
100% DCM + 0% MIBK	0.41796	0.85794	0.98704	–1.27168	1.09589	0.97803

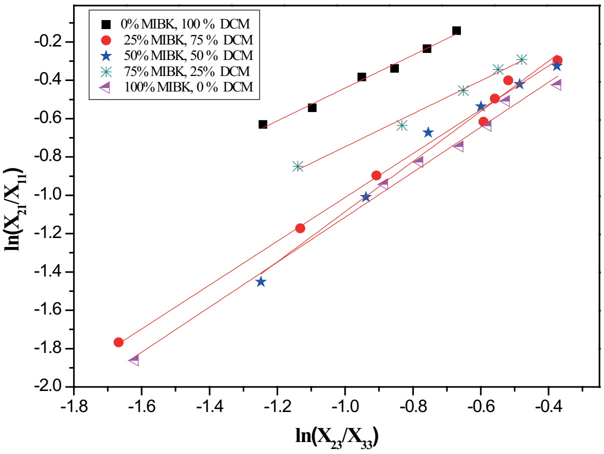

Fig. 9. Hand plots of the (water + acetic acid + mixed solvent [DCM + MIBK]) quaternary systems at $T = 301.15$ K.

4. Conclusions

In this work, the measured LLE data for the various quaternary systems (water + acetic acid + mixed solvents) were presented at $T = 301.15$ K and $p = 1$ atm. The selected solvents were composed of mixed pure DCM and MIBK in different proportions. It was found that all systems exhibit a type I liquid–liquid thermodynamics equilibrium behavior. With the help of the Othmer–Tobias and Hand correlations, the consistency and reliability of the measured data were guaranteed. It is found that the acetic acid is more soluble in the mixed solvents indicating the efficiency of the mixed solvent to extract acetic acid from water. The NRTL model was used to correlate the measured tie-line data of the studied systems. By applying both the GA and PSO optimization algorithms, the binary interaction parameters of the NRTL model were successfully estimated. The separation factors, which give an indication of the potential of the solvents to extract acetic acid from water, were all greater than unity. These factors were found to vary from 4.54 to 86.94. It is found that that the mixed solvent with 50% DCM and 50% MIBK has the highest separation factor and hence is the best for the separation of acetic acid from water.

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