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Liquid-liquid equilibrium (LLE) data of ternary mixtures of [water+acetic acid+1-nonanol] and [water+acetic acid+1-decanol] at 298.2-318.2 K and 101.3 kPa

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Abstract−The addition of alcohols to acetic acid and water mixture is effective for extracting acetic acid from the mixture. This work presents the liquid-liquid phase equilibrium (LLE) data of the ternary systems of 1-nonanol/acetic acid/water and 1-decanol/acetic acid/water measured at 298.2, 303.2, 308.2, and 318.2 K at 101.3 kPa. The effectiveness of the extraction process was quantified by the distribution coefficient (D) and selectivity (S). It was found that the extraction capability of 1-nonanol was superior to that of 1-decanol. We also used the Hand plot and the Othmer–Tobias plot to assess the reliability of the experimental LLE data, and the linear coefficient was greater than 0.99. The non-random two-liquid (NRTL) and the universal quasichemical (UNIQUAC) model were also used to correlate the experimental data. The Gibbs energy minimization method was used to evaluate the reliability of the regression parameters of the statistical model. The calculated root mean square deviation (RMSD) values were less than 0.023, indicating that both models were adequate for these systems.

Keywords: LLE, Acetic Acid, 1-Nonanol, 1-Decanol, NRTL, UNIQUAC

INTRODUCTION

Acetic acid is used in the manufacture of coatings, greases, polyesters and sealants, as well as in many industries, including electronics, automobiles, textiles, and packaging. The global market size of acetic acid reached $9.8 billion in 2020. The acetic acid market is projected to continue its growth, reaching $15.1 billion by 2026, with a compound annual growth rate (CAGR) of 6.8% during this period [1]. Acetic acid is also an important raw feed chemical for terephthalic acid (PTA), which is the monomer for thermoplastic polyethylene terephthalate (PET) used for fibers and containers for beverage bottles, medical and other packaging applications. With an increasing societal need for recyclable plastic materials, PET is positioned as one of the most sustainable plastic materials because it can be readily recycled or upcycled to other valuable chemicals. Thus, the supply of high purity acetic acid at low cost is an important part of this circular economy [2]. In biological fermentation processes, acetic acid is produced with many other chemical compounds in dilute solutions. For example, in a C1 gas conversion process, 1-3 wt% of acetic acid is produced as a byproduct [3-5]. Separating acetic acid from a dilute aqueous solution poses some technical challenges in industrial processes because acetic acid tends to dimerize. This phenomenon greatly affects the thermodynamic behavior of the mixture, and the solution exhibits non-ideal activity coefficient behavior.

The efficient separation of acetic acid from dilute aqueous solutions to high purity is industrially very important because it can reduce the corrosion of process equipment and prevent environmental damage caused by acidic wastewater [6]. In general, extractive distillation is effective when the acetic acid concentration is relatively high (e.g., >30%) [7]. However, when the concentration of acetic acid is very low, as in biological processes, conventional distillation is very costly, because the distillation process is energy-intensive [8]. Solvent extraction is an alternative process because the energy requirement is significantly lower and scale-up is relatively straightforward. In solvent extraction, acetates (e.g., isopropyl acetate and ethyl acetate) have been commonly used as solvents to separate acetic acid from aqueous solutions [9]. After solvent extraction, concentrated acetic acid can be obtained by separating acetic acid from the solvent by subsequent distillation stage. However, a solvent having a low boiling point like that of acetic acid requires an excessively large amount of energy in the distillation process. To circumvent this problem, fatty acids with suitable boiling points were used [10]. Unfortunately, the affinity of fatty acids with water is too high and their acidic nature is a source of corrosive damage of process equipment. Other solvents with good extractability such as tributyl phosphate have been proposed, but acetic acid is destroyed during the solvent regeneration process [11,12].

Thus, there is a strong need to find alternative solvent systems to extract acetic acid from an aqueous solution with a proper boiling point and good thermal stability. In addition, such solvent should be non-toxic and inexpensive. Alcohols can be a potentially valu-

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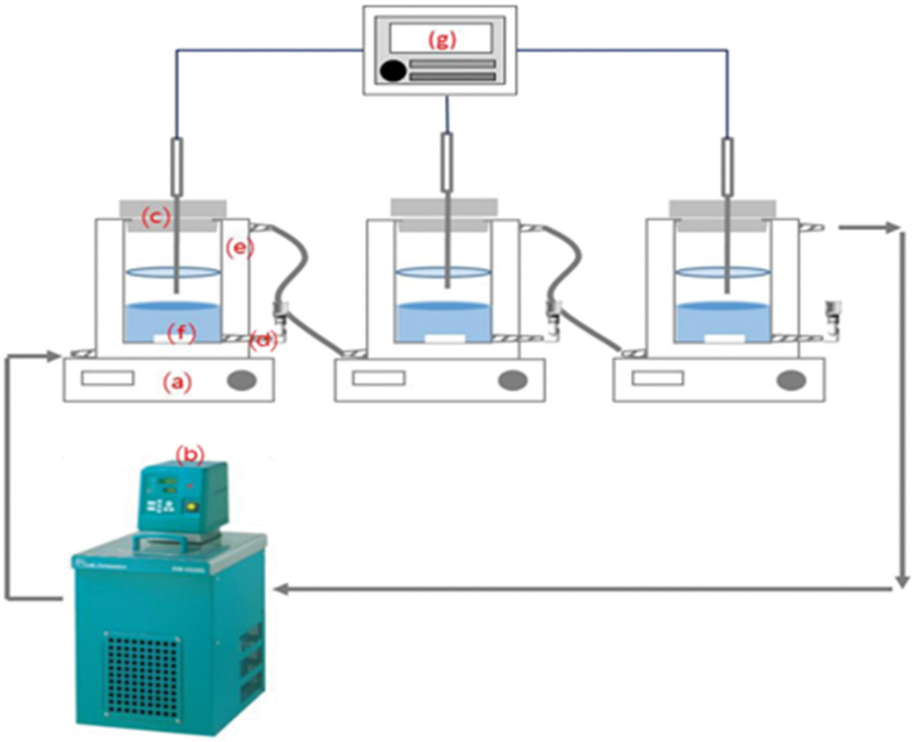

Fig. 1. Schematic of the experimental liquid-liquid equilibrium apparatus: (a) Magnetic stirrer, (b) Liquid circulator, (c) Upper sampling port, (d) Lower sampling port, (e) Water jacket, (f) Magnetic bar, (g) Temperature indicator.

able and effective solvent to meet these requirements. Several studies have been reported on the use of alcohols (e.g., 1-butanol, 2-pentanol and 1-hexanol) having low boiling points as a solvent for extracting acetic acid [13-16]. However, the boiling point of these alcohols is too close to that of acetic acid (b.p. 118 °C), and hence it is difficult to separate the acetic acid-alcohol mixture by distillation. In the past, extractants with a relatively large difference in boiling point from acetic acid, such as 1-heptanol, 2-heptanol, 1-octanol, 2-octanol and iso-octanol, have been studied as well. The distribution coefficient (D) and separation factor (S) of these high boiling point alcohols showed relatively good results compared to other solvents [17-20]. According to their results, alcohols with higher boiling point such as nonanol or decanol might be good candidates as suitable extractants. Therefore, in this work, we investigated 1-nonanol and 1-decanol as new extraction solvents to separate acetic acid from an aqueous mixture since their boiling point differences with acetic acid are much larger than other solvents used in the past. To our best knowledge, there is no report on the use of 1-nonanol and 1-decanol as extraction solvents for this purpose. In our study, we measured the liquid-liquid equilibrium data of the two ternary systems [(i) water/acetic acid/1-nonanol, (ii) water/acetic acid/1-decanol] in the temperature range of 298.2-318.2 K at 101.3 kPa. In addition, solubility data were also obtained, and solubility curves were plotted on the ternary phase diagram. The measured data were fitted using the non-random two-liquid (NRTL) model and the universal quasichemical (UNIQUAC) model, and the binary interaction parameters were estimated.

MATERIALS AND METHODS

1. Materials

Table 1 shows the suppliers and mass fraction of materials used in this study. 1-nonanol (>0.990 mass fraction), 1-decanol (>0.990 mass fraction) and acetic acid (>0.990 mass fraction) were provided by Sejinci Co. (Korea) and HPLC grade water was obtained from Daejung Co. (Korea). Gas chromatography (Young-Lins Instrument CO. model YL6100, Korea) was used to verify the purity of each material. All the chemicals were used as supplied.

Table 1. Suppliers and mass fraction of materials

Component	Source	CAS No.	Mass fraction purity	Analysis
1-Nonanol	Sejinci Co.	143-08-8	>0.980	GC [a]
1-Decanol	Sejinci Co. (Korea)	112-30-1	>0.980	GC [a]
Acetic acid	Sejinci Co. (Korea)	64-19-7	>0.995	GC [a]
Water	Daejung Co. (Korea)	7732-18-5	>0.999	GC [a]

[a]Gas chromatography

2. Experimental Apparatus and Procedure

LLE data were measured in the temperature range of 298.2-318.2 K at a constant pressure of 101.3 kPa. The solubility of acetic acid in water was determined by titration method and the data were used to plot a solubility curve on a ternary diagram. The LLE experimental apparatus (Fig. 1) and titration method were presented in detail in our previous paper [21,22].

To analyze the sample by GC, propanol was used as an internal standard. For samples with 1-nonanol, the initial temperature of the oven was set to 393.2 K; the temperature was raised by 60K/min and maintained at 573.2 K for 3 minutes. For the 1-decanol system, the initial temperature of the oven and the heating mode were the same as the 1-nonanol samples, but the final oven temperature was maintained at 583.2 K for 3 minutes. For both materials, the temperature of the injector and the detector was maintained at 543.2 K. The flow rate of helium (carrier gas) was controlled at 30 ml/min. To test the integrity of the data, the standard uncertainty was calculated using the following equations [23]:

$$x_i = \frac{1}{n}\sum_{k=1}^{n} X_{i,k} \quad (1)$$

$$u_i = \left[\frac{1}{n(n-1)}\sum_{k=1}^{n}(X_{i,k} - x_i)^2\right]^{1/2} \quad (2)$$

where, n represents the number of experiments and $X_{i,k}$ is the independent observation of X_i (input quantity) obtained under the same measurement conditions. u_i is the standard uncertainty associated with the input estimate x_i.

RESULTS AND DISCUSSION

1. Experimental Data

Table 2 and Table 3 show the solubility data of the 1-nonanol

Table 2. Experimental solubility curve data (in mass fraction) of [water (1)/acetic acid (2)/1-nonanol (3)] system at different temperatures

T/K[a]	w_1[b]	w_2[b]	w_3[b]	w_1[b]	w_2[b]	w_3[b]	w_1[b]	w_2[b]	w_3[b]
298.2	0.0529	0.0000	0.9471	0.1453	0.4694	0.3853	0.2446	0.6010	0.1543
	0.0609	0.1007	0.8384	0.1521	0.4966	0.3513	0.2988	0.5980	0.1031
	0.0709	0.1352	0.7938	0.1574	0.5131	0.3295	0.3452	0.5767	0.0781
	0.0828	0.1760	0.7412	0.1664	0.5282	0.3054	0.3978	0.5477	0.0545
	0.0868	0.2071	0.7061	0.1768	0.5419	0.2813	0.4577	0.5123	0.0300
	0.0876	0.2593	0.6532	0.1855	0.5541	0.2604	0.5637	0.4195	0.0168
	0.1100	0.3350	0.5549	0.1935	0.5651	0.2414	0.6857	0.3062	0.0082
	0.1221	0.3974	0.4805	0.2048	0.5904	0.2048	0.9941	0.0000	0.0059
303.2	0.0354	0.0000	0.9646	0.1232	0.4306	0.4462	0.4518	0.5186	0.0296
	0.0512	0.1120	0.8368	0.1397	0.4696	0.3907	0.4921	0.4843	0.0236
	0.0576	0.1649	0.7775	0.1760	0.4942	0.3298	0.5369	0.4501	0.0130
	0.0710	0.1840	0.7450	0.2152	0.5430	0.2418	0.6353	0.3548	0.0090
	0.0792	0.2122	0.7086	0.2550	0.5651	0.1799	0.7454	0.2447	0.0089
	0.0817	0.2888	0.6295	0.2997	0.5773	0.1230	0.8571	0.1396	0.0030
	0.0876	0.3278	0.5846	0.3544	0.5651	0.0805	0.9792	0.0100	0.0108
	0.1002	0.3792	0.5206	0.4067	0.5454	0.0479	0.9917	0.0000	0.0083
308.2	0.0376	0.0000	0.9624	0.1308	0.4395	0.4297	0.2582	0.5774	0.1644
	0.0565	0.1012	0.8424	0.1434	0.4704	0.3862	0.3452	0.5767	0.0781
	0.0709	0.1352	0.7938	0.1504	0.4976	0.3520	0.3978	0.5477	0.0545
	0.0790	0.1767	0.7443	0.1666	0.5075	0.3259	0.4577	0.5123	0.0300
	0.0832	0.2079	0.7089	0.1858	0.5159	0.2983	0.4989	0.4832	0.0178
	0.0842	0.2602	0.6556	0.2006	0.5262	0.2732	0.5656	0.4209	0.0135
	0.1073	0.3361	0.5567	0.2130	0.5354	0.2516	0.6857	0.3062	0.0082
	0.1198	0.3985	0.4818	0.2228	0.5445	0.2326	0.9941	0.0000	0.0059
318.2	0.0272	0.0000	0.9728	0.1266	0.4416	0.4318	0.2936	0.5876	0.1188
	0.0475	0.1021	0.8504	0.1397	0.4724	0.3878	0.3452	0.5767	0.0781
	0.0626	0.1365	0.8009	0.1471	0.1996	0.3534	0.3978	0.5477	0.0545
	0.0713	0.1782	0.7505	0.1635	0.5094	0.3271	0.4577	0.5123	0.0300
	0.0758	0.2096	0.7146	0.1831	0.5176	0.2993	0.4989	0.4832	0.0178
	0.0775	0.2621	0.6604	0.1982	0.5278	0.2740	0.5656	0.4209	0.0135
	0.1017	0.3382	0.5601	0.2107	0.5369	0.2524	0.6857	0.3062	0.0082
	0.1150	0.4006	0.4844	0.2208	0.5460	0.2332	0.9941	0.0000	0.0059

[a]The standard uncertainty for temperature, u(T)=0.05 K.

[b]The standard uncertainty for mass fraction, u(w)=0.0008.

Table 3. Experimental solubility curve data (in mass fraction) of [water (1)/acetic acid (2)/1-decanol (3)] system at different temperatures

T/K[a]	w_1[b]	w_2[b]	w_3[b]	w_1[b]	w_2[b]	w_3[b]	w_1[b]	w_2[b]	w_3[b]
298.2	0.0234	0.0000	0.9766	0.1017	0.4645	0.4338	0.3011	0.6027	0.0962
	0.0345	0.0646	0.9009	0.1122	0.5035	0.3844	0.3459	0.5779	0.0762
	0.0439	0.1228	0.8333	0.1166	0.5401	0.3433	0.3988	0.5490	0.0522
	0.0515	0.1795	0.7690	0.1258	0.5686	0.3057	0.4589	0.5137	0.0273
	0.0567	0.2461	0.6972	0.1404	0.5827	0.2769	0.5004	0.4847	0.0149
	0.0657	0.3100	0.6243	0.1526	0.5943	0.2531	0.5656	0.4209	0.0135
	0.0770	0.3683	0.5547	0.1819	0.5970	0.2211	0.6857	0.3062	0.0082
	0.0914	0.4189	0.4897	0.2113	0.6019	0.1868	0.9941	0.0000	0.0059
303.2	0.0354	0.0000	0.9646	0.1232	0.4306	0.4462	0.4518	0.6027	0.0296
	0.0512	0.1120	0.8368	0.1397	0.4696	0.3907	0.4921	0.5779	0.0236
	0.0576	0.1649	0.7775	0.1760	0.4942	0.3298	0.5369	0.4501	0.0130
	0.0710	0.1840	0.7450	0.2152	0.5430	0.2418	0.6353	0.3548	0.0099
	0.0792	0.2122	0.7086	0.2550	0.5651	0.1799	0.7454	0.2447	0.0099
	0.0817	0.2888	0.6295	0.2997	0.5773	0.1230	0.8571	0.1396	0.0033
	0.0876	0.3278	0.5846	0.3544	0.5652	0.0805	0.9792	0.0100	0.0108
	0.1002	0.3792	0.5206	0.4067	0.5454	0.0479	0.9917	0.0000	0.0083
308.2	0.0141	0.0000	0.9859	0.1170	0.5007	0.3822	0.3028	0.6059	0.0913
	0.0345	0.0646	0.9009	0.1224	0.5365	0.3411	0.3481	0.5815	0.0704
	0.0400	0.1233	0.8367	0.1296	0.5661	0.3043	0.3988	0.5490	0.0522
	0.0480	0.1802	0.7718	0.1427	0.5811	0.2762	0.4540	0.5082	0.0378
	0.0598	0.2453	0.6948	0.1556	0.5922	0.2522	0.4916	0.4762	0.0322
	0.0657	0.3100	0.6243	0.2040	0.5972	0.1987	0.5599	0.4167	0.0233
	0.0770	0.3683	0.5547	0.2220	0.6041	0.1739	0.6774	0.3025	0.0202
	0.0914	0.4189	0.4897	0.2435	0.6091	0.1474	0.9882	0.0000	0.0118
318.2	0.0137	0.0000	0.9863	0.0836	0.4738	0.4425	0.3502	0.5851	0.0646
	0.0240	0.0654	0.9107	0.0964	0.5124	0.3912	0.4036	0.5556	0.0408
	0.0342	0.1240	0.8417	0.1056	0.5468	0.3476	0.4602	0.5151	0.0247
	0.0445	0.1809	0.7747	0.1174	0.5740	0.3086	0.4989	0.4832	0.0178
	0.0488	0.2482	0.7030	0.2237	0.6050	0.1713	0.5656	0.4209	0.0135
	0.0558	0.3133	0.6309	0.2456	0.6101	0.1442	0.6829	0.3049	0.0122
	0.0633	0.3738	0.5629	0.2719	0.6130	0.1151	0.9882	0.0000	0.0118
	0.0751	0.4264	0.4985	0.3044	0.6092	0.0864			

[a]The standard uncertainty for temperature, u(T)=0.05 K.
[b]The standard uncertainty for mass fraction, u(w)=0.0008.

system and the 1-decanol system, respectively. Tables 4 and 5, respectively, show the measured LLE data for both systems, where w_i denotes the mass fraction of the component *i*. Figs. 2-5 show the binodal solubility curves, the LLE data obtained from the experiments, and the values correlated with the NRTL and UNIQUAC models over the temperature range employed in our study for water/acetic acid/1-nonanol system. Figs. 6-9 show a similar graph for the water/acetic acid/1-decanol system.

We also used the Othmer-Tobias [24] and Hand [25] equations to validate the reliability and consistency of the experimental LLE data.

$$\ln\left[\frac{1-w_1^I}{w_1^I}\right] = a + b\ln\left[\frac{1-w_3^{II}}{w_3^{II}}\right] \tag{3}$$

$$\ln\left[\frac{w_2^I}{w_1^I}\right] = c + d\ln\left[\frac{w_2^{II}}{w_3^{II}}\right] \tag{4}$$

where constants a, b, c and d are the parameters of the Othmer-Tobias correlations and the Hand equations. w_2^I and w_1^I denote the mass fractions of acetic acid and water in the aqueous phase, while w_2^{II} and w_3^{II} are mass fractions of acetic acid and extractant in the organic phase. Each R^2 value and parameter are listed in Table 6, and the corresponding linear regression graphs are shown in Figs. 10 and 11. Since all R^2 values are greater than 0.98 and converge to 1, both the reliability and consistency of our experimental data are satisfactory.

To check the performance of 1-nonanol and 1-decanol as extractants, selectivity (S) and distribution coefficient (D) values as defined in Eqs. (5) and (6) were calculated from each tie line data and are

Table 4. LLE data (in mass fraction) for [water (1)/acetic acid (2)/1-nonanol (3)] system with distribution coefficient (D) and selectivity (S) at different temperatures

Water-rich phase (I)		Solvent-rich phase (II)		D[a]	S[b]
w_1[d]	w_2[d]	w_1[d]	w_2[d]		
T=298.2 K[c]					
0.9433	0.0420	0.0495	0.0307	0.73	13.92
0.8867	0.1086	0.0556	0.0780	0.72	11.45
0.8320	0.1642	0.0611	0.1108	0.67	9.18
0.7802	0.2130	0.0640	0.1422	0.66	8.13
0.7108	0.2839	0.0738	0.1863	0.65	6.32
0.6507	0.3452	0.0800	0.2203	0.63	5.19
0.5883	0.4062	0.0789	0.2522	0.62	4.62
				0.67[e]	8.41[f]
T=303.2 K[c]					
0.9499	0.0430	0.0461	0.0349	0.81	16.72
0.8792	0.1010	0.0511	0.0779	0.77	13.27
0.8171	0.1711	0.0501	0.1291	0.75	12.31
0.7647	0.2324	0.0599	0.1617	0.70	8.88
0.7100	0.2799	0.0612	0.1937	0.69	8.02
0.6546	0.3294	0.0676	0.2350	0.71	6.91
0.6057	0.3841	0.0701	0.2610	0.67	5.87
				0.73[e]	10.28[f]
T=308.2 K[c]					
0.9568	0.0420	0.0476	0.0323	0.71	18.88
0.8882	0.1030	0.0507	0.0772	0.68	15.30
0.8223	0.1715	0.0494	0.1173	0.66	12.43
0.7486	0.2424	0.0607	0.1585	0.63	9.13
0.7087	0.2839	0.0609	0.1838	0.60	5.97
0.6546	0.3377	0.0676	0.2130	0.59	4.58
0.6157	0.3769	0.0701	0.2306	0.57	3.43
				0.68[e]	9.58[f]
T=318.2 K[c]					
0.9423	0.0542	0.0359	0.0390	0.71	18.88
0.8858	0.1079	0.0398	0.0742	0.68	15.30
0.8348	0.1593	0.0447	0.1061	0.66	12.43
0.7646	0.2276	0.0532	0.1446	0.63	9.13
0.7018	0.2938	0.0712	0.1781	0.60	5.97
0.6257	0.3696	0.0806	0.2182	0.59	4.58
0.5364	0.4550	0.0906	0.2637	0.57	3.43
				0.64[e]	9.96[f]

[a] $D = w_2^{II}/w_2^{I}$

[b] $S = \dfrac{w_2^{II}/w_2^{I}}{w_1^{II}/w_1^{I}}$

[c] The standard uncertainty for temperature, u(T)=0.05 K.

[d] The standard uncertainty for mass fraction, u(w)=0.0011.

[e] Average value of distribution coefficient (D).

[f] Average value of selectivity (S).

Table 5. LLE data (in mass fraction) for [water (1)/acetic acid (2)/1-decanol (3)] system with distribution coefficient (D) and selectivity (S) at different temperatures

Water-rich phase (I)		Solvent-rich phase (II)		D[a]	S[b]
w_1[d]	w_2[d]	w_1[d]	w_2[d]		
T=298.2 K[c]					
0.9513	0.0443	0.0425	0.0265	0.59	13.38
0.8723	0.1178	0.0499	0.0668	0.56	9.91
0.8200	0.1715	0.0463	0.0915	0.53	9.44
0.7385	0.2497	0.0540	0.1290	0.51	7.06
0.6680	0.3231	0.0534	0.1593	0.49	6.16
0.6236	0.3696	0.0696	0.1800	0.48	4.36
0.5394	0.4555	0.0773	0.2198	0.48	3.36
				0.53[e]	7.67[f]
T=303.2 K[c]					
0.9335	0.0539	0.0319	0.0351	0.65	19.06
0.8724	0.1097	0.0345	0.0690	0.63	15.90
0.8010	0.1814	0.0407	0.1118	0.62	12.13
0.7384	0.2359	0.0450	0.1412	0.60	8.15
0.6969	0.2859	0.0512	0.1712	0.60	9.82
0.6247	0.3587	0.0490	0.2171	0.61	7.72
0.5099	0.4647	0.0617	0.2560	0.55	4.55
				0.61[e]	11.05[f]
T=308.2 K[c]					
0.9448	0.0542	0.0451	0.0343	0.63	13.25
0.8626	0.1201	0.0391	0.0736	0.61	13.51
0.8116	0.1716	0.0412	0.1032	0.60	11.84
0.7069	0.2792	0.0460	0.1274	0.59	9.81
0.7684	0.2154	0.0540	0.1666	0.59	7.87
0.6247	0.3548	0.0560	0.2008	0.56	6.31
0.5286	0.4454	0.0636	0.2450	0.55	4.57
				0.59[e]	9.60[f]
T=318.2 K[c]					
0.9253	0.0734	0.0343	0.0462	0.62	17.97
0.8821	0.1152	0.0318	0.0713	0.61	16.16
0.8487	0.1492	0.0475	0.0903	0.60	10.94
0.7748	0.2156	0.0427	0.1300	0.60	10.81
0.7112	0.2790	0.0426	0.1644	0.58	9.83
0.6231	0.3621	0.0511	0.1936	0.53	6.51
0.5427	0.4511	0.0515	0.2351	0.52	5.49
				0.58[e]	11.10[f]

[a] $D = w_2^{II}/w_2^{I}$

[b] $S = \dfrac{w_2^{II}/w_2^{I}}{w_1^{II}/w_1^{I}}$

[c] The standard uncertainty for temperature, u(T)=0.05 K.

[d] The standard uncertainty for mass fraction, u(w)=0.0011.

[e] Average value of distribution coefficient (D).

[f] Average value of selectivity (S).

shown in Tables 4 and 5. Fig. 12 graphically presents D and S over the mass fraction of acetic acid in the organic phase, w_2^{II}.

$$D = \frac{w_2^{II}}{w_2^{I}}, \tag{5}$$

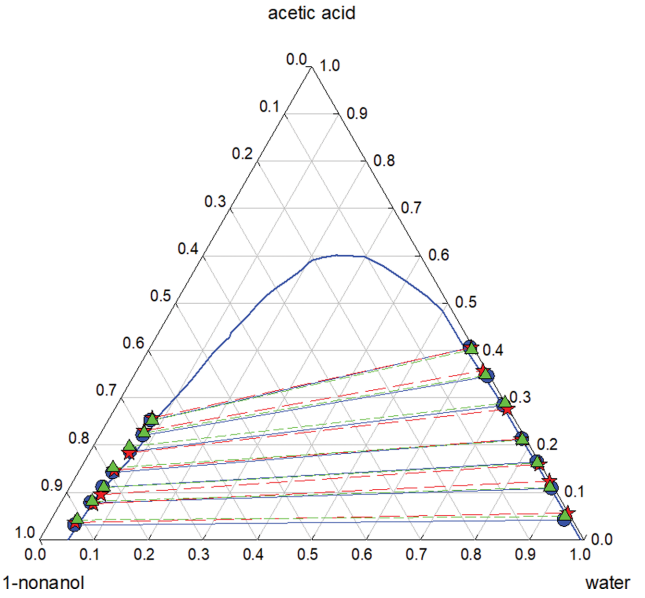

Fig. 2. LLE data (in mass fraction) for water/acetic acid/1-nonanol system at T=298.2 K; —, experimental solubility data; ●—●, experimental tie-line data; ★—★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

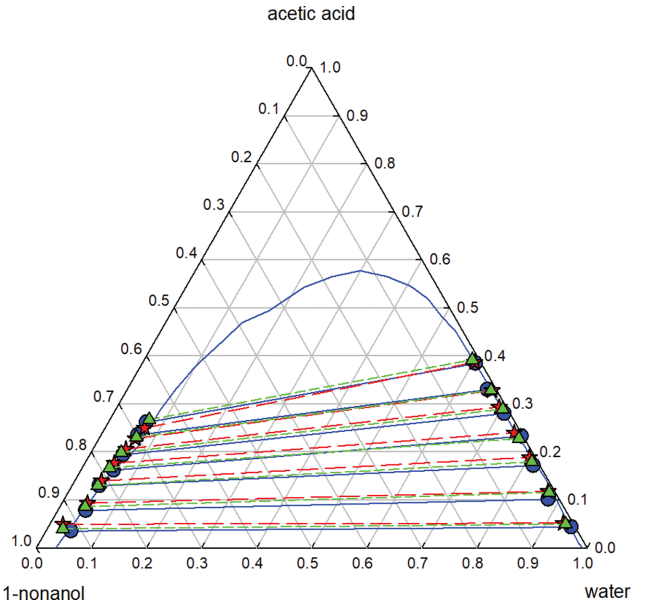

Fig. 3. LLE data (in mass fraction) for water/acetic acid/1-nonanol system at T=303.2 K; —, experimental solubility data; ●—●, experimental tie-line data; ★—★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

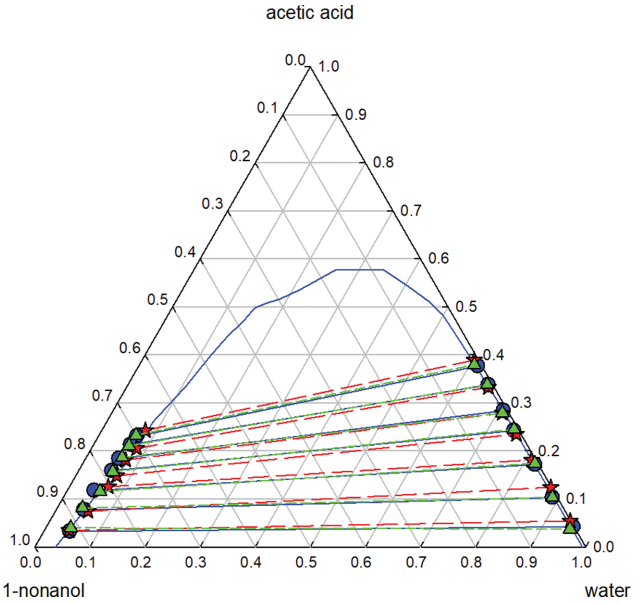

Fig. 4. LLE data (in mass fraction) for water/acetic acid/1-nonanol system at T=308.2 K; —, experimental solubility data; ●—●, experimental tie-line data; ★—★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

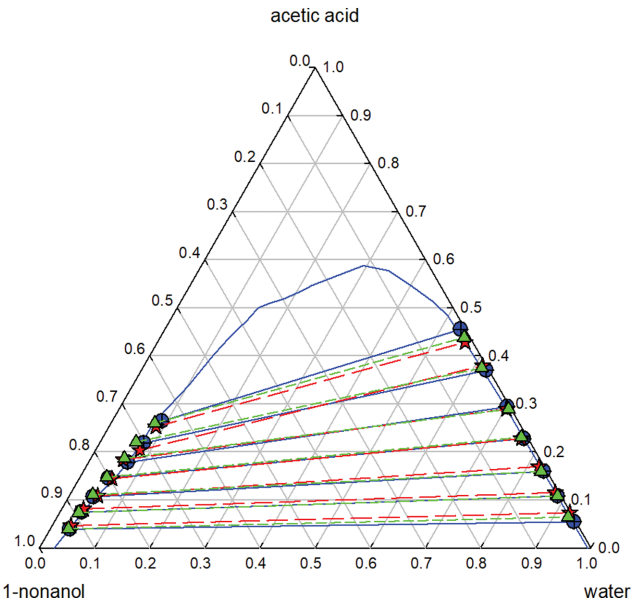

Fig. 5. LLE data (in mass fraction) for water/acetic acid/1-nonanol system at T=318.2 K; —, experimental solubility data; ●—●, experimental tie-line data; ★—★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

$$S = \frac{w_2^{II}/w_2^{I}}{w_1^{II}/w_1^{I}} \quad (6)$$

In the above equations, w_i denotes the mass fraction of the *i*-th component, and the superscripts I and II represent the water-rich phase and the solvent-rich phase, respectively. To ascertain the potential of 1-nonanol and 1-decanol as solvents to extract acetic acid from an aqueous mixture, the selectivity (S) vs. distribution coefficient (D) data are presented in Fig. 13 for 1-nonanol and 1-decanol at 303.2 K. Also shown in Fig. 13 are the data for other solvents (1-heptanol, 2-heptanol, 1-octanol, 2-octanol and iso-octanol) reported in the literature [17-20]. As can be seen in Fig. 13 and Table 7, 2-heptanol shows the best performance among the solvents. For the distribution coefficients (D), the order of performance was 2-heptanol>1-hepatanol>2-octanol≈1-nonanol>1-de-

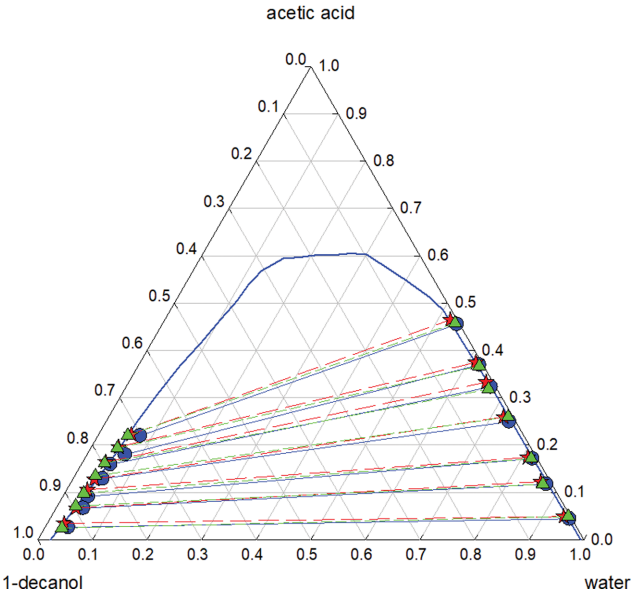

Fig. 6. LLE data (in mass fraction) for water/acetic acid/1-decanol system at T=298.2 K; —, experimental solubility data; ●—●, experimental tie-line data; ★--★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

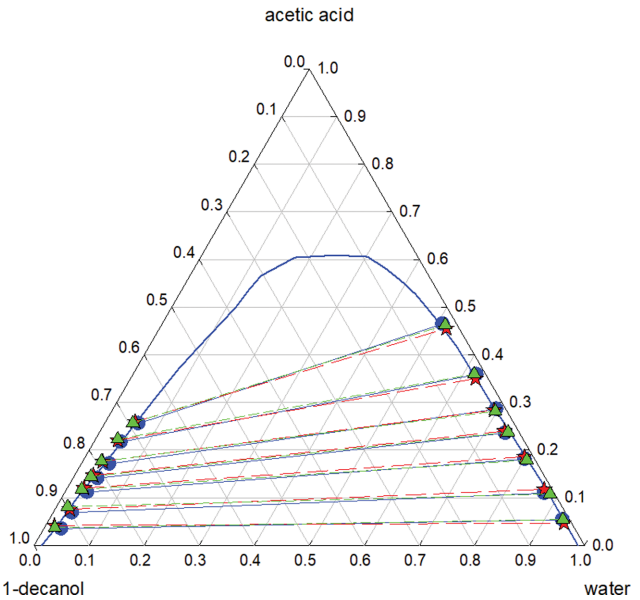

Fig. 7. LLE data (in mass fraction) for water/acetic acid/1-decanol system at T=303.2 K; —, experimental solubility data; ●—●, experimental tie-line data; ★--★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

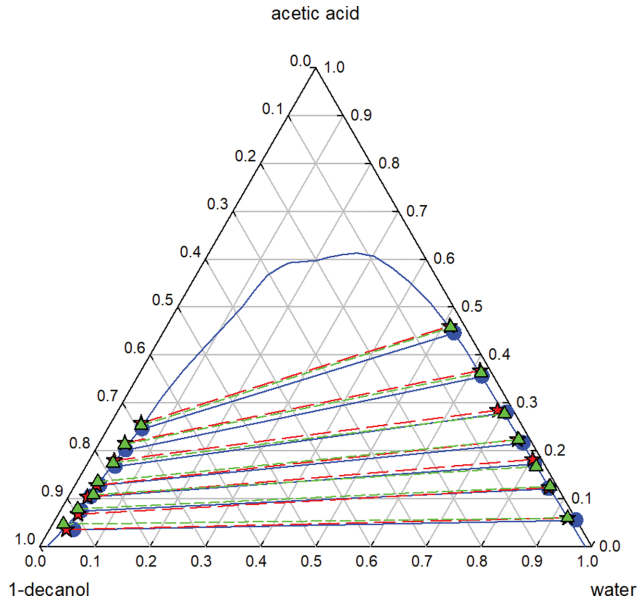

Fig. 8. LLE data (in mass fraction) for water/acetic acid/1-decanol system at T=308.2 K; —, experimental solubility data; ●—●, experimental tie-line data; ★--★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

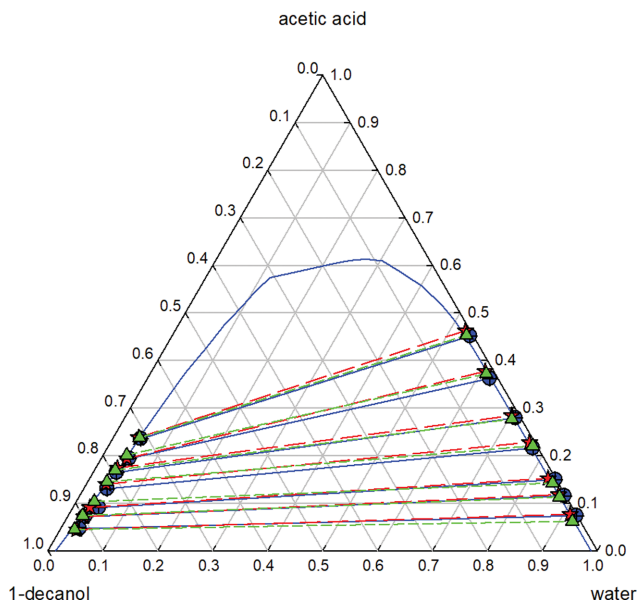

Fig. 9. LLE data (in mass fraction) for water/acetic acid/1-decanol system at T=318.2K; —, experimental solubility data; ●—●, experimental tie-line data; ★--★, calculated NRTL data; ▲---▲, calculated UNIQUAC data.

canol≈1-octanol≈iso-octanol. When selectivity (S) is compared, the performance is in the order of iso-octanol>2-octanol≈2-heptanol> 1-nonanol≈1-decanol≈1-octanol≈1-heptanol. When considering both factors, 2-heptanol shows the best performance and 2-octanol and 1-hepatanol shows the second and 1-nonanol shows the third best. However, there is another very important factor to consider in selecting the extracting solvent: after the extraction step, acetic acid should be separated from the solvent by distillation, and hence the boiling point difference between the solvent and acetic acid is an important factor that affects the economy of the final separation process. The boiling point of 2-heptanol, 2-octanol and 1-hepatanol is 159, 178 and 175 °C, respectively, and that of acetic acid is 118 °C. The boiling point of 1-nonanol is 214 °C and the boiling point difference from that of acetic acid is 96 °C

Table 6. Constants of the Othmer-Tobias plot and Hand plot for the [water/acetic acid/1-nonanol] and [water/acetic acid/1-decanol] systems

T/K	Othmer-Tobias correlation			Hand correlation		
	a	b	$^{a}R^2$	c	d	$^{a}R^2$
Water/Acetic acid /1-nonanol						
298.2	0.7132	−0.4238	0.9989	0.8875	−0.5893	0.9978
303.2	0.7032	−0.4286	0.9963	0.8867	−0.5055	0.9995
308.2	0.6203	−0.5830	0.9926	0.8493	−0.6485	0.9980
318.2	0.7394	−0.4970	0.9989	0.8432	−0.7176	0.9986
Water/Acetic acid/1-decanol						
298.2	0.7132	−0.4238	0.9989	0.8875	−0.5893	0.9978
303.2	0.7438	−0.6833	0.9980	0.8539	−0.7960	0.9974
308.2	0.6316	−0.7717	0.9886	0.8482	−0.8210	0.9963
318.2	0.6551	−0.7779	0.9935	0.8014	−0.8945	0.9924

$^{a}R^2$: Regression coefficient

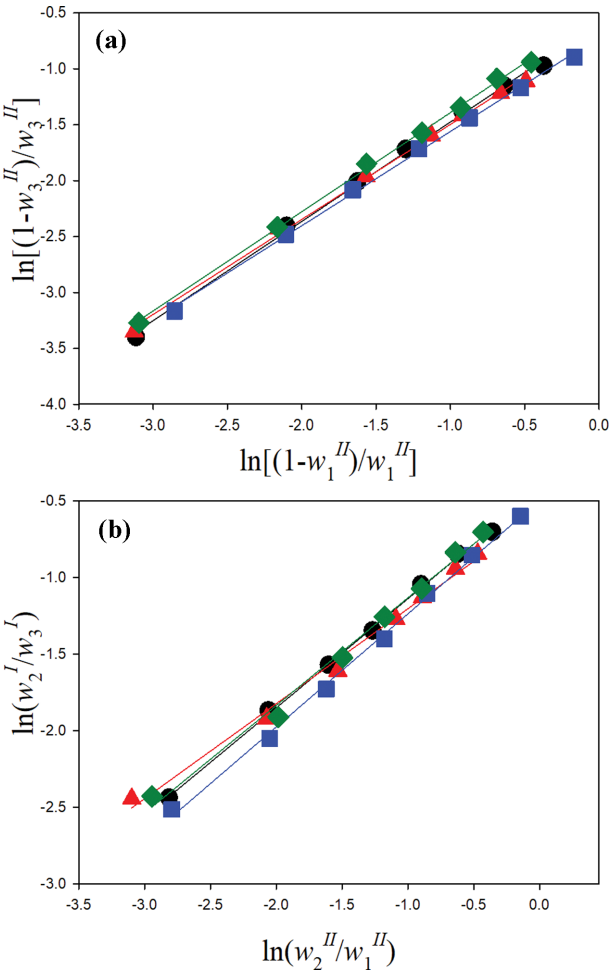

Fig. 10. (a) Othmer-Tobias plot and (b) Hand plot for water/acetic acid/1-nonanol system; ●, T=298.2 K; ◆, T=303.2 K; ▲, T=308.2 K; ■, T=318.2 K.

and, therefore, 1-nonanol is a much better solvent than those three solvents for distillation. Considering the distribution coefficient,

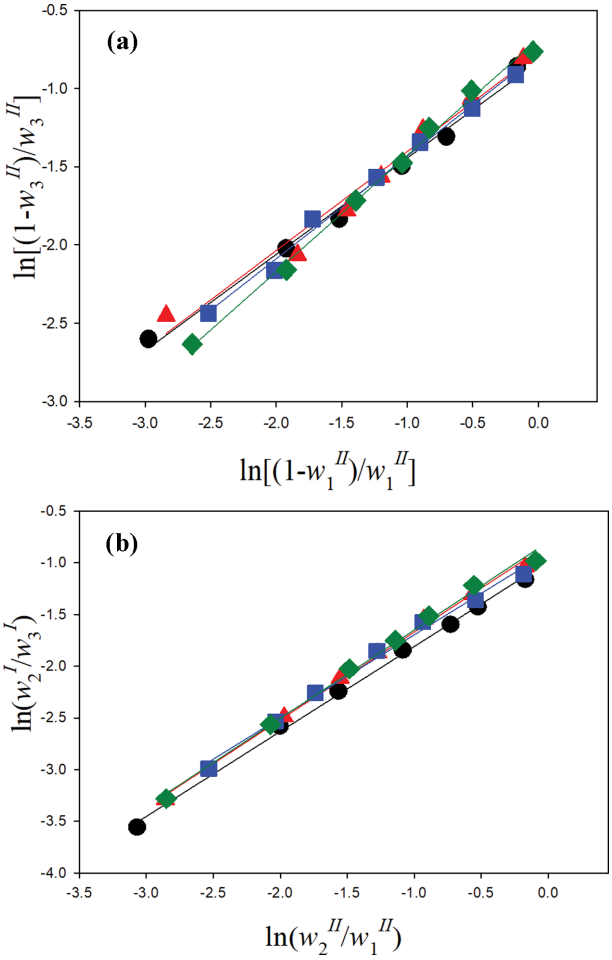

Fig. 11. (a) Othmer-Tobias plot and (b) Hand plot for water/acetic acid/1-nonanol system; ●, T=298.2 K; ◆, T=303.2 K; ▲, T=308.2 K; ■, T=318.2 K.

Table 7. Distribution coefficient (D) and selectivity (S) of acetic acid for different solvents at 303.2 K

Solvent	T/K	D^a	S^b
1-Heptanol	303.2	0.8227	10.2500
2-Heptanol	303.2	0.8884	15.7700
1-Octanol	303.2	0.6038	10.7000
2-Octanol	303.2	0.7463	16.0700
Iso-octanol	303.2	0.5942	19.1400
1-Nonanol (this work)	303.2	0.7311	10.2840
1-Decanol (this work)	303.2	0.6071	11.0470

$^{a}D = w_2^{II}/w_2^{I}$

$^{b}S = \dfrac{w_2^{II}/w_2^{I}}{w_1^{II}/w_1^{I}}$

selectivity, and post-extraction distillation process, we conclude that 1-nonanol has a stronger potential to be the most effective solvent than other solvents for extracting acetic acid from water.

2. Data Correlation

Experimental data was correlated with the NRTL and UNIQUAC

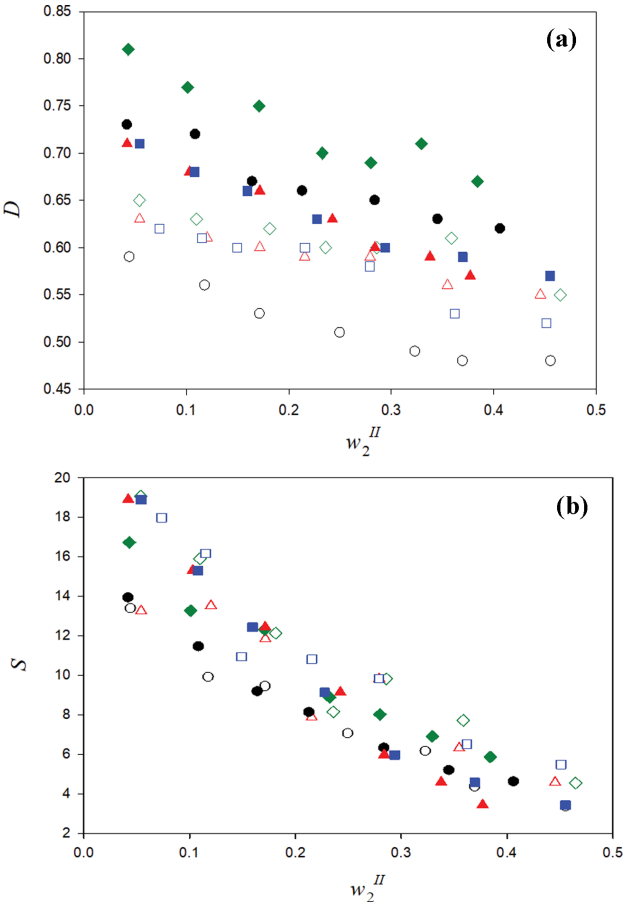

Fig. 12. (a) Distribution coefficients (D) vs. mass fraction of acetic acid in water-rich phase (w_2^{II}), and (b) Selectivity (S) vs. mass fraction of acetic acid in water-rich phase (w_2^{II}) for [water/acetic acid/1-nonanol] and [water/acetic acid/1-decanol] systems at different temperatures; ●, 1-nonanol (298.2 K); ◆, 1-nonanol (303.2 K); ▲, 1-nonanol (308.2 K); ■, 1-nonanol (318.2 K); ○, 1-decanol (298.2 K); ◇, 1-decanol (303.2 K); △, 1-decanol (308.2 K); □, 1-decanol (318.2 K).

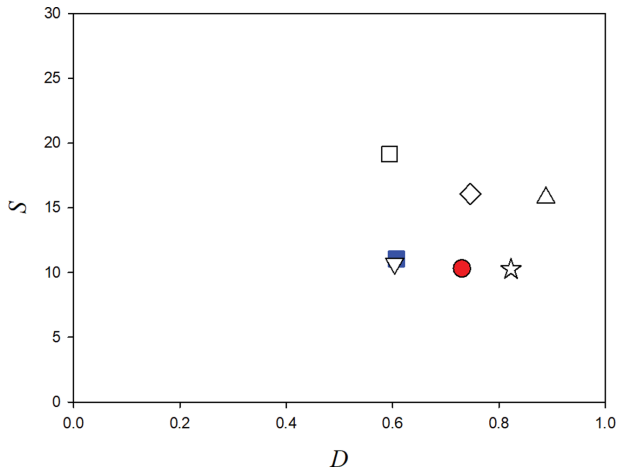

Fig. 13. Selectivity (S) vs. distribution coefficient (D) of acetic acid for different solvents at 303.2 K: ●, 1-nonanol (this work); ■, 1-decanol (this work); ☆, 1-heptanol [17]; △, 2-heptanol [18]; ▽, 1-octanol [19]; ◇, 2-octanol [19]; □, iso-octanol [19].

Table 8. UNIQUAC Structural parameters (r and q) for pure components

Component	r	q
Water	0.9200	1.4000
Acetic acid	2.2024	2.0720
1-Nonanol	6.9227	7.6183
1-Decanol	7.5552	8.3264

models [26,27]. The data were fitted by Gibbs Energy minimization method [28]. A detailed explanation of the NRTL and UNIQUAC equations can be found in our previous work [21]. The UNIQUAC structural parameters r (molecular geometric volume) and q (molecular geometric surface) are listed Table 8. Table 9 shows the calculated binary parameters for water/acetic acid/1-nonanol system and the root-mean-square deviation (RMSD) values. The RMSD values represent how accurately the model predicts the tie-lines in ternary phase diagrams. Table 10 shows the binary parameters and RMSD values for water/acetic acid/1-decanol system. RMSD values were calculated using the following equation:

$$\mathrm{RMSD}=\left[\frac{\Sigma_{i=1}^{3}\Sigma_{j=1}^{2}\Sigma_{k=1}^{n}(x_{ijk}^{exp}-x_{ijk}^{cal})^{2}}{6n}\right]^{1/2} \quad (7)$$

The small RMSD values for the two ternary systems studied in our experimental work (less than 0.023) indicate that both models are quite adequate. From using a Graphical User Interface in MATLAB software code, the consistency of binary subsystems and interaction parameters was confirmed [29]. The calculated G^M/RT surfaces, including all the experimental tie lines at 303.2 K, are shown in the Figs. 14 and 15. Also, the calculated NRTL miscibility boundary at 303.2 K is shown in Fig. 16.

CONCLUSIONS

We have presented the liquid-liquid equilibrium (LLE) data measured at 298.2-318.2 K for two ternary systems, water/acetic acid/1-nonanol and water/acetic acid/1-decanol, at atmospheric pressure. In addition, binodal solubility data were used to construct ternary phase diagrams for the two mixtures. Since the linear regression factor R^2 of both solubility curves was larger than 0.9800, the consistency of our experimental data has been confirmed. In order to evaluate the performance of 1-nonanol and 1-decanol as a solvent for extracting acetic acid, their selectivity (S) and distribution coefficient (D) values were calculated and compared with other solvents. For the distribution coefficients (D), the order of performance was 2-heptanol>1-hepatanol>2-octanol≈1-nonanol>1-decanol≈1-octanol≈iso-octanol. For the selectivity (S), the order of performance was iso-octanol>2-octanol≈2-heptanol>1-nonanol≈1-decanol≈1-octanol≈1-heptanol. When both factors are considered together, 2-heptanol, 2-octanol and 1-hepatanol show the better performance than 1-nonanol, but the boiling point differences between 2-heptanol, 2-octanol and 1-hepatanol and acetic acid (41, 60 and 57 °C, respectively) are much smaller than that of 1-nonanol and acetic acid (96 °C). This indicates that the 1-nonanol is more advantageous than 2-heptanol, 2-octanol and 1-hepatanol in

Table 9. Parameters of the NRTL and UNIQUAC models for [water (1)/acetic acid (2)/1-nonanol (3)] system and their RMSD values at different temperatures

	T/K	τ_{ij}			RMSD
NRTL[a]	298.2	τ_{12}=−0.2935	τ_{13}=5.4644	τ_{23}=0.4240	0.0113
		τ_{21}=−0.2720	τ_{31}=1.6204	τ_{32}=0.2812	
	303.2	τ_{12}=0.8354	τ_{13}=3.6354	τ_{23}=0.7831	0.0103
		τ_{21}=−0.9753	τ_{31}=2.7484	τ_{32}=0.3524	
	308.2	τ_{12}=1.2810	τ_{13}=4.5103	τ_{23}=0.7380	0.0122
		τ_{21}=−1.3819	τ_{31}=2.8240	τ_{32}=0.3850	
	318.2	τ_{12}=0.4389	τ_{13}=3.9754	τ_{23}=0.3724	0.0082
		τ_{21}=−0.8413	τ_{31}=1.8450	τ_{32}=0.2759	
UNIQUAC[b]	298.2	τ_{12}=4.1651	τ_{13}=0.1221	τ_{23}=1.4010	0.0131
		τ_{21}=1.4384	τ_{31}=0.3949	τ_{32}=1.1030	
	303.2	τ_{12}=5.1812	τ_{13}=1.1387	τ_{23}=4.5412	0.0068
		τ_{21}=0.9721	τ_{31}=0.1172	τ_{32}=2.7731	
	308.2	τ_{12}=4.2053	τ_{13}=1.1423	τ_{23}=3.0018	0.0047
		τ_{21}=1.3630	τ_{31}=0.0442	τ_{32}=1.2883	
	318.2	τ_{12}=5.9722	τ_{13}=0.0972	τ_{23}=1.7241	0.0071
		τ_{21}=1.1236	τ_{31}=0.1782	τ_{32}=1.9750	

[a] $\tau_{ij}=(g_{ij}-g_{jj})/RT$. τ_{ij} is a NRTL model binary interaction parameter (dimensionless).
[b] $\tau_{ij}=\exp(-\varepsilon_{ij})/RT$. τ_{ij} is a UNIQUAC model binary interaction parameter (dimensionless).

Table 10. Parameters of the NRTL and UNIQUAC models for [water (1)/acetic acid (2)/1-nonanol (3)] system and their RMSD values at different temperatures

	T/K	τ_{ij}			RMSD
NRTL[a]	298.2	τ_{12}=0.2513	τ_{13}=4.4644	τ_{23}=0.2712	0.0121
		τ_{21}=−0.3125	τ_{31}=1.3204	τ_{32}=0.5128	
	303.2	τ_{12}=0.5131	τ_{13}=6.5671	τ_{23}=0.8421	0.0080
		τ_{21}=−1.3521	τ_{31}=2.1753	τ_{32}=0.4927	
	308.2	τ_{12}=0.2131	τ_{13}=3.5671	τ_{23}=0.7414	0.0230
		τ_{21}=0.1125	τ_{31}=1.7204	τ_{32}=0.1927	
	318.2	τ_{12}=0.9414	τ_{13}=2.4257	τ_{23}=1.6842	0.0068
		τ_{21}=−1.2572	τ_{31}=3.4215	τ_{32}=0.2485	
UNIQUAC[b]	298.2	τ_{12}=5.1651	τ_{13}=0.5226	τ_{23}=4.1030	0.0123
		τ_{21}=1.8724	τ_{31}=0.1949	τ_{32}=0.4010	
	303.2	τ_{12}=4.7810	τ_{13}=0.5872	τ_{23}=0.6721	0.0097
		τ_{21}=0.9842	τ_{31}=0.2752	τ_{32}=4.0125	
	308.2	τ_{12}=5.7982	τ_{13}=0.6158	τ_{23}=0.5710	0.0211
		τ_{21}=0.4384	τ_{31}=0.3425	τ_{32}=3.9125	
	318.2	τ_{12}=4.9970	τ_{13}=0.4732	τ_{23}=0.5421	0.0083
		τ_{21}=1.0182	τ_{31}=0.3542	τ_{32}=4.3789	

[a] $\tau_{ij}=(g_{ij}-g_{jj})/RT$. τ_{ij} is a NRTL model binary interaction parameter (dimensionless).
[b] $\tau_{ij}=\exp(-\varepsilon_{ij})/RT$. τ_{ij} is a UNIQUAC model binary interaction parameter (dimensionless).

separating the solvent-acetic acid mixture in the post-extraction distillation process. Considering the distribution coefficients, selectivity, and the boiling point difference, we conclude that 1-nonanol is an attractive solvent to extract acetic acid from a dilute aqueous mixture. Using the Gibbs energy minimization method, we correlated the experimental data with NRTL and UNIQUAC models to obtain binary interaction parameters. And we used Graphical User Interface to confirm the consistency of binary interaction parameters. The small RMSD values obtained in our analysis suggest that both NRTL and UNIQUAC models can be used for both water/acetic acid/1-nonanol and water/acetic acid/1-decanol systems. The new LLE data presented in this paper will provide an important design basis to develop more effective and cost-effective acetic acid extraction processes.

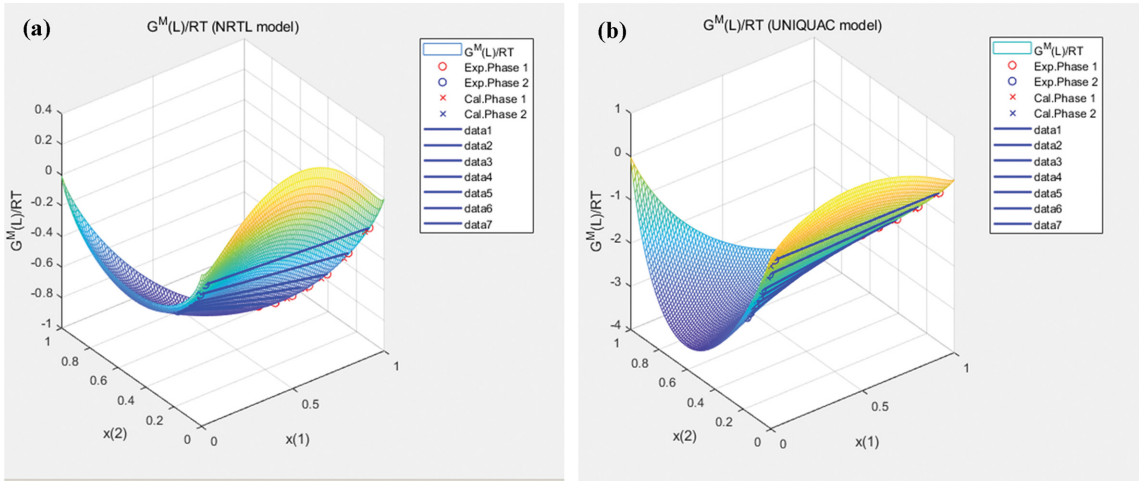

Fig. 14. Calculated G^M/RT surface and experimental LLE tie lines for water/acetic acid/1-nonanol system at 303.2 K: (a) NRTL model, (b) UNIQUAC model.

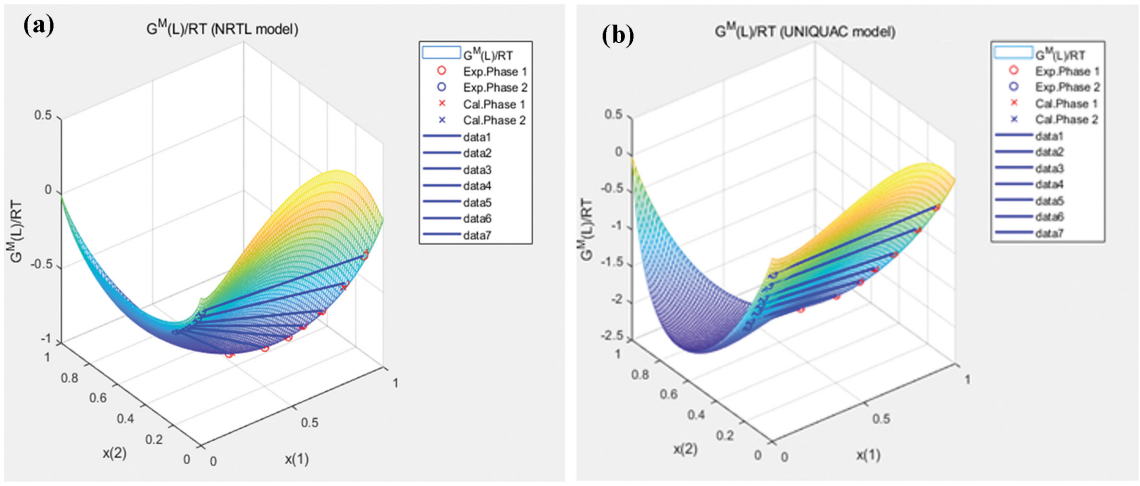

Fig. 15. Calculated G^M/RT surface and experimental LLE tie lines for water/acetic acid/1-decanol system at 303.2 K: (a) NRTL model, (b) UNIQUAC model.

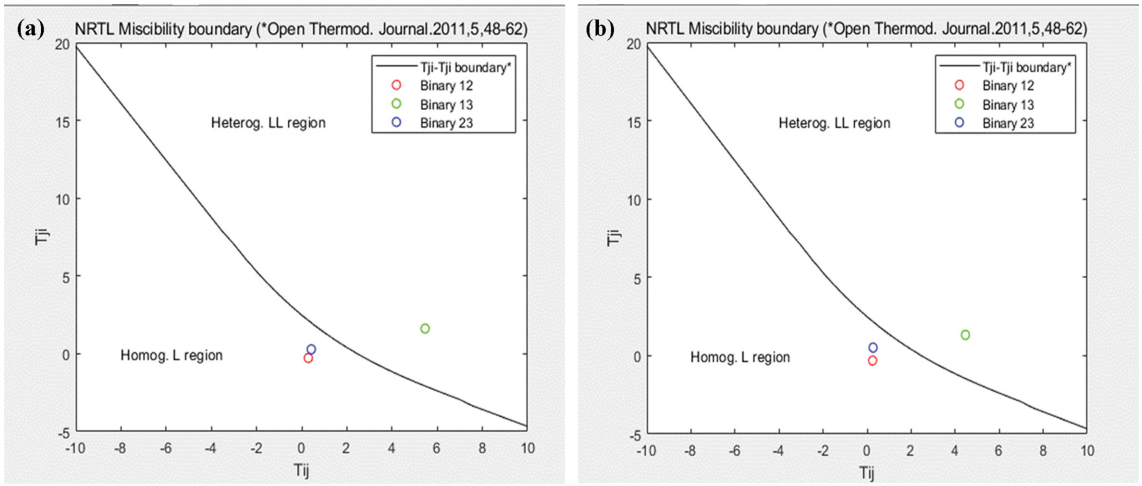

Fig. 16. NRTL binary parameter miscibility boundary for (a) water/acetic acid/1-nonanol system, (b) water/acetic acid/1-decanol system at 303.2 K.

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