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Salt effect on the liquid-liquid equilibrium of water-furfuryl alcohol-furfural system at 298.15 K

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Abstract−Salt effect on the liquid phase equilibrium of the water-furfuryl alcohol-furfural system at 298.15 K was studied. The effects of salt concentration (1, 3 and 10% w/wNaCl) and type of salt (LiCl, KCl and RbCl) were investigated. The solubility and tie-line data of these systems were determined by experimental analysis. The results showed that addition of salt significantly affected the two-phase region of ternary system; the enlargement of two-phase region occurred with an increase of salt concentration in initial aqueous phase and the type of the salt in the following order: LiCl>NaCl>KCl>RbCl. Distribution coefficients and separation factors were also calculated. The reliability of the LLE experimental results was validated by the Othmer-Tobias equation, Hand equation and Bachman equation. NRTL was employed to correlate the results obtained by the modeling with the experimental data. Good correlation result was confirmed by the rmsd values of less than 0.3%.

Keywords: Salt Effect, Furfuryl Alcohol, Furfural, Liquid-liquid Equilibrium, Tie-line Data

INTRODUCTION

Furfuryl alcohol (FAL) is used mainly for the production of thermostatic resins, liquid resins for strengthening ceramics, as well as in the production of various synthetic fibers, rubber-resins and polymer concrete. In addition, it is used as a chemical intermediate, employed for the manufacture of dispersing agents, lysine, lubricants and plasticizers [1]. Furfuryl alcohol is produced by catalytic hydrogenation of furfural in vapor or liquid phase [2,3]. Since in the technology of furfural synthesis is produced furfural-waste stream, it is convenient to perform hydrogenation in aqueous phase [4]. Due to the toxicity of furfuryl alcohol together with its adverse environmental impact, its removal of from wastewater before discharging to the environment is very important.

Liquid-liquid extraction has been widely used for the separation and wastewater treatment processes because of industrially applicable and economical methods. In this process, a solution is brought into contact with a second liquid that is immiscible or partially miscible with the first one. One or more components can transfer from the solution into the solvent. The addition of salt to a mixture of solvents can lead to great changes in their composition. In the presence of salt, the solvent mixture must be considered both in process design and operation, because it can significantly change the interaction among the various solvent solute molecules, resulting in shifting their two-phase equilibrium composition [5]. Liquid-liquid equilibrium is the result of intermolecular forces, mainly of hydrogen-bonding type. When the ions are solvated, part of the water molecules become unavailable for the solution, and they are "salted out" from the aqueous phase. On the other hand, when a polar solvent is added to an aqueous salt solution, it captures the water molecules that were solvating the ions, in a "salting in" effect. These effects of the addition of a salt on the thermodynamic equilibrium can be seen in two ways: graphically, by change in the size of the two-phase region and the slope of the tie-lines; and quantitatively, by changes in the distribution coefficient of solute and the solvents selectivity [6,7]. Addition of salt to an aqueous solution of an organic compound can also result in either increase or decrease in solubility of the solute in the solution [8]. Adding salt has demonstrated to be beneficial in separation, purification, distillation, and solvent extraction processes [9].

In recent years, the liquid-liquid equilibrium (LLE) and effects of salt on the liquid-liquid equilibrium systems have been studied. The salt effect on the liquid-liquid equilibrium of water+diethanolamine+isobutanol/cyclohexanol) systems was investigated by Ghalami-Choobar et al. [10]. The effect of salt on the solubility and tie-line data was studied by Wannachod et al. [11] for water+formic acid+MIBK and the effect of NaCl for furfuryl alcohol+n-butanol+water system [12]. Their results shown that addition of salt to the systems can significantly improve the extraction efficiency. However, the salt effect on the LLE of investigated systems water+furfuryl alcohol+furfural has not been reported in the literature.

In this study, the effect of salts on the solubility and tie-line data

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for the ternary systems consisting of water, furfuryl alcohol and furfural at 298.15 K and atmospheric pressure was investigated. The reliability of experimental results was validated using the Othmer-Tobias, Hand and Bachman equation. Distribution coefficient and separation factors were evaluated for the investigated systems. NRTL model was employed to correlate the results obtained by the modeling of experimental data.

EXPERIMENTAL

1. Materials

Materials of consisting of furfuryl alcohol ($C_5H_4O_2$, MW 96.08 g/mol), sodium chloride (NaCl, MW 22.99 g/mol), lithium chloride (LiCl, MW 42.39 g/mol), potassium chloride (KCl, MW 74.55 g/mol) and rubidium chloride (RbCl, MW 120.92 g/mol) were used in this work without further purification. Furfural ($C_5H_6O_2$, MW 98.10 g/mol) was purified by vacuum distillation and stored at −15 °C. The source and mass fraction purity of materials are listed in Table 1. Distilled water was used throughout all the experiments.

Table 1. Source and mass fraction purity of materials

Material	Source	Mass fraction purity	Analysis method
Furfuryl alcohol	Sigma-Aldrich	0.99	GC
Furfural	Sigma-Aldrich	0.99	GC
Lithium chloride	Sigma-Aldrich	0.99	-
Sodium chloride	Merck	-	-
Potassium chloride	Sigma-Aldrich	0.99	-
Rubidium chloride	Sigma-Aldrich	0.99	-

2. Apparatus and Procedure

First, a certain amount of salts (LiCl, NaCl, KCl, RbCl) were weighed accurately in order to prepare a salt solution. The solubility data for the ternary systems consisting of water (aqueous salt solution), furfuryl alcohol and furfural were studied by direct measurement method in organic-rich and aqueous-rich phases at equilibrium. Binary mixtures of furfuryl alcohol and furfural with known composition were prepared in closed glass cells and titrated with water until they became turbid. The end point of titration was achieved when the mixtures remained turbid for 2 h. During this period, the glass cells were agitated periodically to observe the turbidity. These procedures were carried out to determine the solubility curve of the organic-rich phase. For the aqueous-rich phase, binary mixtures of furfuryl alcohol and water were prepared and the organic solvent was added to titration. All measurements were repeated at least three times.

After reaching equilibrium compositions, the tie-line data were studied at 298.15 K. Heterogeneous ternary mixtures were prepared with known overall composition. The mixtures were centrifuged and left for 14 h to ensure separation. These periods were long enough for samples reaching two equilibrium liquid layers: organic-rich and aqueous-rich. Then, the organic-rich phase was carefully withdrawn from the top layer of the glass cell by syringe and weighed. The aqueous-rich phase was also weighed and analyzed by gas chromatography. Finally, the compositions of all components were calculated directly based on analytical results. Triangular phase diagrams for all systems of LLE data were plotted using the ProSim program.

3. Analysis

Samples from the phases were analyzed by gas chromatography (Hewlett Packard 5890 Series II with FID detector) using a glass

Table 2. Experimental solubility data in mass fractions for water(1)+furfuryl alcohol(2)+furfural(3) with different NaCl concentration at 298.15 K and atmospheric pressure

Without salt[a]			1%NaCl			3%NaCl			10%NaCl		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
0.0457	0.000	0.9543	0.0306	0.0000	0.9694	0.0315	0.0000	0.9685	0.0280	0.0000	0.9720
0.058	0.0758	0.8662	0.0664	0.1752	0.7584	0.0378	0.0661	0.8961	0.0335	0.0812	0.8853
0.0717	0.1458	0.7825	0.0768	0.2261	0.6971	0.0444	0.1374	0.8183	0.0387	0.1621	0.7992
0.0872	0.2155	0.6973	0.0996	0.3240	0.5764	0.0539	0.2197	0.7265	0.0456	0.2299	0.7245
0.1017	0.2904	0.6079	0.1285	0.4223	0.4492	0.0650	0.2920	0.6439	0.0534	0.2957	0.6509
0.1187	0.3700	0.5113	0.1605	0.5138	0.3257	0.0736	0.3597	0.5667	0.0579	0.3748	0.5673
0.1438	0.4250	0.4312	0.1940	0.5819	0.2241	0.0939	0.4815	0.4246	0.0639	0.4633	0.4728
0.1918	0.4932	0.3150	0.2513	0.6139	0.1348	0.1073	0.5598	0.3329	0.0699	0.5506	0.3795
0.2607	0.5211	0.2182	0.2963	0.6120	0.0917	0.1288	0.6517	0.2195	0.0753	0.6268	0.2979
0.3233	0.5233	0.1534	0.3584	0.5856	0.0560	0.1642	0.7354	0.1004	0.0793	0.6873	0.2334
0.3776	0.5046	0.1178	0.4542	0.5179	0.0279	0.1770	0.7626	0.0604	0.0850	0.7607	0.1543
0.4636	0.4546	0.0818	0.5829	0.3974	0.0197	0.2041	0.7959	0.0000	0.0867	0.8190	0.0942
0.5522	0.3850	0.0628	0.6831	0.3014	0.0155	0.7835	0.2165	0.0000	0.0928	0.9072	0.0000
0.6519	0.2975	0.0506	0.7728	0.2035	0.0237	0.8400	0.1521	0.0079	0.9011	0.0989	0.0000
0.7900	0.1511	0.0589	0.8611	0.0987	0.0402	0.8792	0.1048	0.0160	0.9228	0.0698	0.0074
0.8480	0.0801	0.0719	0.8947	0.0510	0.0543	0.9161	0.0492	0.0347	0.9369	0.0416	0.0215
0.9135	0.0000	0.0865	0.9236	0.0000	0.0764	0.9380	0.0000	0.0620	0.9500	0.0000	0.0500

[a] Data from literature [12]

Table 3. Experimental solubility data in mass fractions for water(1)+furfuryl alcohol(2)+furfural(3) with various salts at 298.15 K and atmospheric pressure

1%LiCl			1%NaCl			1%KCl			1%RbCl		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
0.0263	0.0000	0.9737	0.0306	0.0000	0.9694	0.0495	0.0000	0.9505	0.0417	0.0000	0.9583
0.0459	0.0973	0.8568	0.0664	0.1752	0.7584	0.0673	0.1245	0.8082	0.0650	0.1166	0.8184
0.0692	0.2056	0.7252	0.0768	0.2261	0.6971	0.0910	0.2324	0.6766	0.0828	0.1881	0.7292
0.0925	0.3094	0.5981	0.0996	0.3240	0.5764	0.1073	0.2949	0.5978	0.0987	0.2718	0.6295
0.1322	0.4464	0.4213	0.1285	0.4223	0.4492	0.1400	0.4252	0.4347	0.1198	0.3531	0.527
0.1679	0.5461	0.2860	0.1605	0.5138	0.3257	0.1796	0.5173	0.3031	0.1454	0.4260	0.4286
0.2132	0.6120	0.1748	0.1940	0.5819	0.2241	0.2133	0.5650	0.2217	0.1852	0.4940	0.3208
0.2579	0.6285	0.1136	0.2513	0.6139	0.1348	0.2466	0.5875	0.1659	0.2488	0.5589	0.1923
0.3037	0.6233	0.0730	0.2963	0.6120	0.0917	0.3050	0.5913	0.1037	0.3008	0.5612	0.1383
0.3892	0.5762	0.0346	0.3584	0.5856	0.0560	0.3812	0.5539	0.0649	0.3633	0.5367	0.1000
0.4998	0.4869	0.0132	0.4542	0.5179	0.0279	0.4541	0.4965	0.0495	0.4664	0.4714	0.0622
0.6196	0.3729	0.0073	0.5829	0.3974	0.0197	0.5427	0.4257	0.0316	0.5437	0.4066	0.0497
0.7003	0.2918	0.0078	0.6831	0.3014	0.0155	0.6098	0.3633	0.0268	0.6468	0.3137	0.0395
0.7906	0.1991	0.0103	0.7728	0.2035	0.0237	0.7229	0.2543	0.0227	0.6893	0.2694	0.0413
0.8651	0.1037	0.0312	0.8611	0.0987	0.0402	0.7993	0.1696	0.0308	0.7645	0.1920	0.0435
0.8878	0.0680	0.0442	0.8947	0.0510	0.0543	0.8743	0.0755	0.0502	0.8413	0.1056	0.0531
0.9233	0.0000	0.0766	0.9236	0.0000	0.0764	0.9179	0.0000	0.0821	0.9195	0.0000	0.0805

column (1.4 m×3 mm) packed with 5% C20M+5% SE. The injection and the detector temperatures were 435.15 K. The flow rate of carrier gas (helium) was maintained at 40 $cm^3 \cdot min^{-1}$. The external standard method was used to analyze the content of the three components. To obtain quantitative results, each analysis was done in triplicate.

RESULTS AND DISCUSSION

1. Experimental Solubility and Tie-line Data

Experimental solubility data for the systems of water+FAL+furfural with addition of salts at 298.15 K and atmospheric pressure are shown in Tables 2 and 3 and Figs. 1 and 2. The investigated systems exhibited type-1 behavior of LLE [13], which has only one liquid pair of partially miscible (water+furfural) and two pairs of completely miscible (water+FAL) and (FAL+furfural). For all systems with salts, the two-phase region is larger than the system without salts, and the region is larger when the concentration of salt increased. This region depends on the mutual solubility of water and furfural. It can be explained that salt ions in the aqueous solution solvated, water being the preferred component for solvation. In hydration theory [14], it is assumed that each salt ion binds with water molecules. This bound water was then unavailable for furfuryl alcohol and furfural. Therefore, furfuryl alcohol

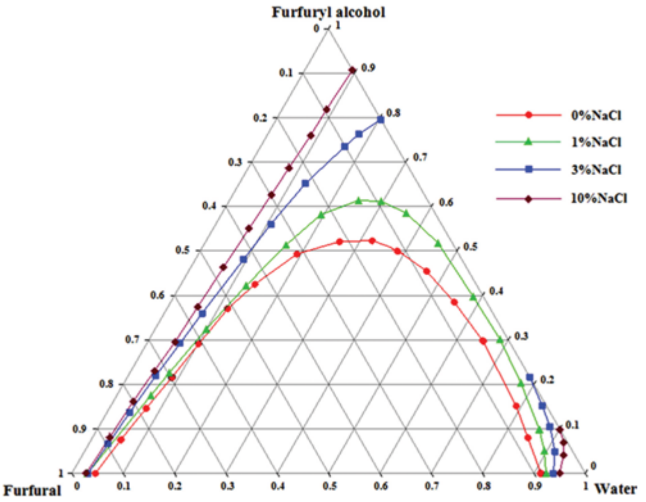

Fig. 1. Solubility curves for water+furfuryl alcohol+furfural with addition of different NaCl concentration at 298.15 K and atmospheric pressure.

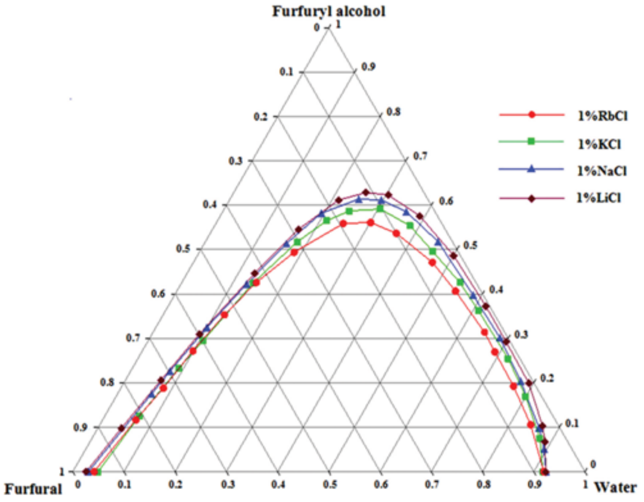

Fig. 2. Solubility curves for water+furfuryl alcohol+furfural with addition of various salts at 298.15 K and atmospheric pressure.

Table 4. Experimental tie-line data in mass fractions for the ternary systems of water(1)+furfuryl alcohol(2)+furfural(3) with different NaCl concentration at 298.15 K and atmospheric pressure

Aqueous-rich phase			Organic-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
1%NaCl					
0.9212	0.0077	0.0711	0.0523	0.0925	0.8552
0.9165	0.0172	0.0663	0.0673	0.1734	0.7593
0.9083	0.0303	0.0614	0.0807	0.2412	0.6781
0.8982	0.0473	0.0545	0.098	0.3108	0.5912
0.8776	0.0774	0.045	0.1204	0.3899	0.4897
0.8496	0.115	0.0354	0.1468	0.4708	0.3824
3%NaCl					
0.9314	0.0134	0.0552	0.0512	0.1828	0.766
0.9274	0.0247	0.0479	0.0667	0.2788	0.6545
0.9173	0.0416	0.0411	0.0783	0.3729	0.5488
0.9146	0.0529	0.0325	0.0862	0.4388	0.475
0.9058	0.068	0.0262	0.0987	0.4953	0.406
0.8905	0.0887	0.0208	0.1058	0.5593	0.3349
10%NaCl					
0.9508	0.0061	0.0431	0.0366	0.0996	0.8638
0.9452	0.0153	0.0395	0.0468	0.2242	0.729
0.9428	0.0266	0.0306	0.0586	0.3635	0.5779
0.9371	0.0379	0.025	0.0672	0.4671	0.4657
0.9341	0.0473	0.0186	0.0732	0.5725	0.3543
0.9294	0.0567	0.0139	0.0780	0.6478	0.2742

Table 5. Experimental tie-line data in mass fractions for the ternary systems of water(1)+furfuryl alcohol(2)+furfural(3) with various salt at 298.15 K and atmospheric pressure

Aqueous-rich phase			Organic-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
1%LiCl					
0.9190	0.0077	0.0733	0.0468	0.0968	0.8564
0.9139	0.0190	0.0671	0.0686	0.1903	0.7411
0.9064	0.0340	0.0596	0.0884	0.2845	0.6271
0.8932	0.0605	0.0463	0.1181	0.388	0.4939
0.8777	0.0849	0.0374	0.1408	0.4633	0.3959
0.8552	0.1169	0.0279	0.1670	0.5348	0.2982
1%KCl					
0.9147	0.0077	0.0776	0.0608	0.0785	0.8607
0.9100	0.0172	0.0728	0.0748	0.1583	0.7669
0.9015	0.0341	0.0644	0.0977	0.2430	0.6593
0.8881	0.0604	0.0515	0.1216	0.3353	0.5431
0.8626	0.0925	0.0449	0.1367	0.4031	0.4602
0.8358	0.1263	0.0379	0.1526	0.4595	0.3879
1%RbCl					
0.9102	0.0133	0.0765	0.0632	0.1000	0.8368
0.9004	0.0265	0.0731	0.082	0.1734	0.7446
0.8861	0.0454	0.0685	0.0958	0.2468	0.6574
0.868	0.0717	0.0603	0.1152	0.3221	0.5627
0.8483	0.0981	0.0536	0.1356	0.3823	0.4821
0.8104	0.1414	0.0482	0.1623	0.4501	0.3876

and furfural tend to be less soluble in water. As shown in Fig. 1, enlargement of the two-phase region occurred when the concentration of salt in the initial aqueous phase increased. These results are consistent with data reported by Wannachod [12] and Wang [15]. With the addition of various types of metal chlorides, the two-phase region increased in the following order of salts: LiCl>NaCl>KCl>RbCl, as shown in Fig. 2. It is in agreement with the result reported by Hasseine [16]. So, the results show that addition of salts is an important factor influencing the two-phase region of the studied systems.

The tie-line data for these systems are shown in Tables 4 and 5, and the corresponding triangular phase diagrams are presented in Figs. 3 through 8. The slope of the tie-line in the phase diagrams

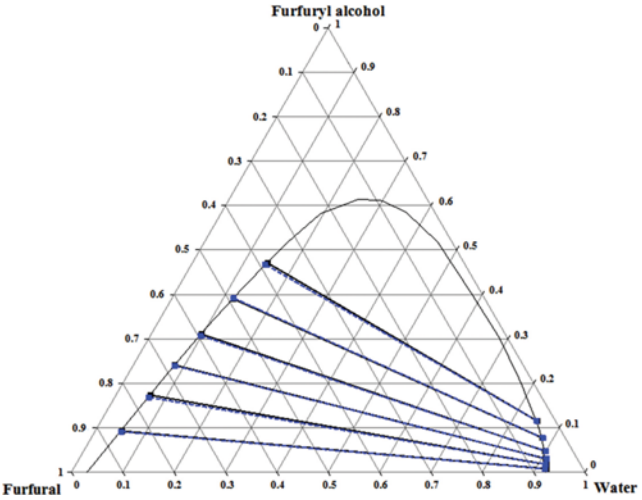

Fig. 3. Ternary diagram for the LLE system of water+furfuryl alcohol+furfural+1%NaCl at 298.15 K and atmospheric pressure; (-□-) experimental tie-line data and (-■-) calculated NRTL data.

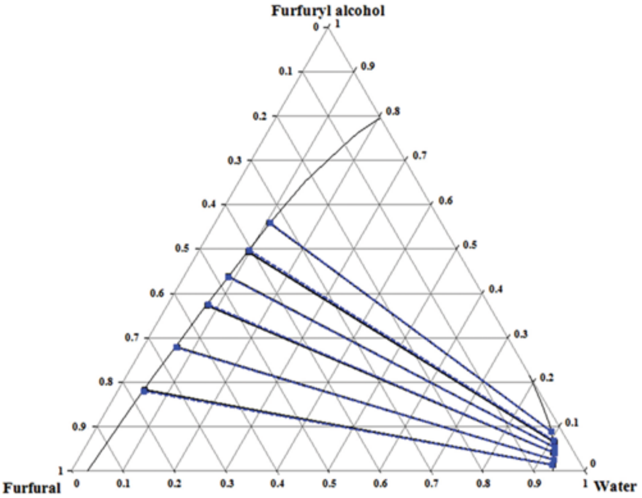

Fig. 4. Ternary diagram for the LLE system of water+furfuryl alcohol+furfural+3%NaCl at 298.15 K and atmospheric pressure; (-□-) experimental tie-line data and (-■-) calculated NRTL data.

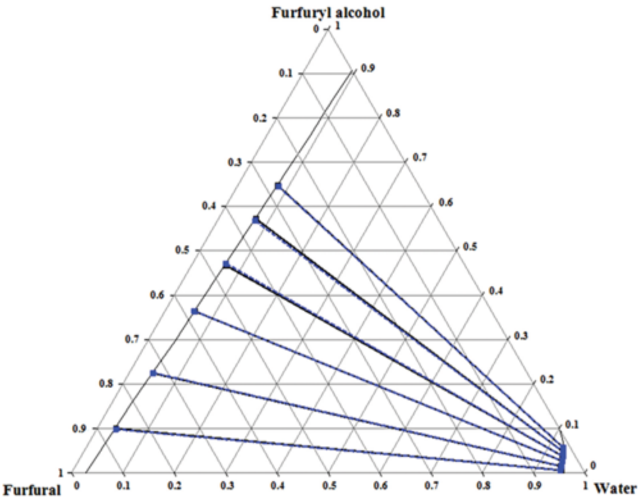

Fig. 5. Ternary diagram for the LLE system of water+furfuryl alcohol+furfural+10%NaCl at 298.15 K and atmospheric pressure; (-□-) experimental tie-line data and (-■-) calculated NRTL data.

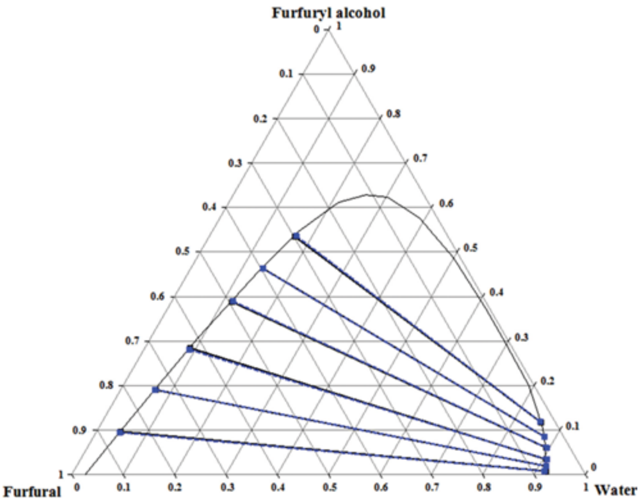

Fig. 6. Ternary diagram for the LLE system of water+furfuryl alcohol+furfural+1%LiCl at 298.15 K and atmospheric pressure; (-□-) experimental tie-line data and (-■-) calculated NRTL data.

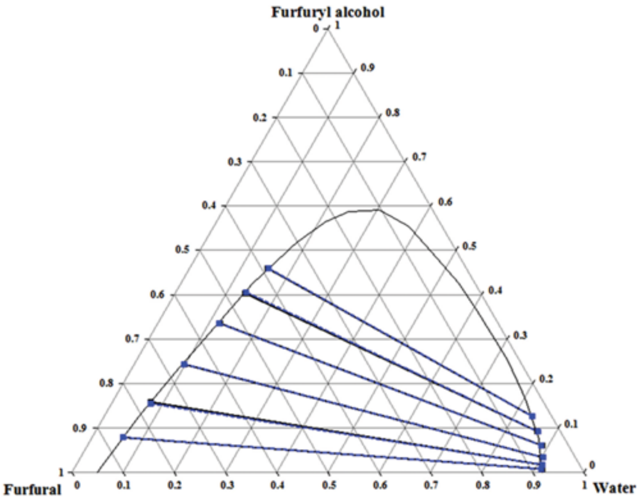

Fig. 7. Ternary diagram for the LLE system of water+furfuryl alcohol+furfural+1%KCl at 298.15 K and atmospheric pressure; (-□-) experimental tie-line data and (-■-) calculated NRTL data.

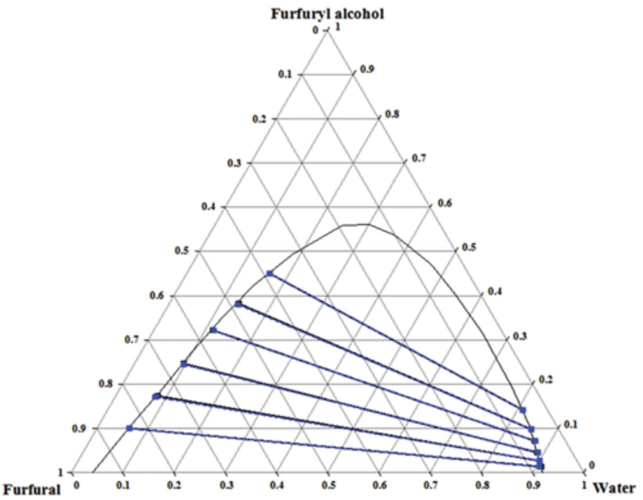

Fig. 8. Ternary diagram for the LLE system of water+furfuryl alcohol+furfural+1%RbCl at 298.15 K and atmospheric pressure; (-□-) experimental tie-line data and (-■-) calculated NRTL data.

demonstrated that FAL is more soluble in furfural than in water. This may be due to the intermolecular interaction of FAL with furfural and water, mainly of the hydrogen-bonding. In water, FAL formed the weak hydrogen bonds with molecules of water [17].

2. Distribution Coefficients and Separation Factors

To evaluate the effectiveness of the FAL extraction, distribution coefficients (D) and separation factors (S) were determined from the experimental tie-line data. The distribution coefficients (D) and the separation factor (S) were calculated by Eq. (1) as shown below:

$$S=\frac{D_2}{D_1}=\frac{W_{23}/W_{21}}{W_{13}/W_{11}} \qquad (1)$$

where D_1 and D_2 are the distribution coefficients of water and FAL, w_{11} and w_{21} are the mass fractions of water and FAL in the aqueous-rich phase, w_{13} and w_{23} are the mass fractions of water and FAL in the organic-rich phase, respectively.

The experimental values of distribution coefficients and separation factors are listed in Tables 6 and 7, and the variation of the separation factor as a function of the mass fraction of furfuryl alcohol in aqueous-rich phase is shown in Fig. 9. The results were presented and compared for experiments performed with or without salt: the separation factor increases with the increasing of the salt concentration. It is known that the presence of salt can significantly change the equilibrium composition. When salt is added, each salt ion attacks surrounding water molecules, forming hydration shells [9]. The water molecules surrounding the ions are unavailable to act as a solvent for FAL, so that it is less soluble and

Table 6. Distribution coefficients and separation factor for the system of water+furfuryl alcohol+furfural with different NaCl concentration at 298.15 K and atmospheric pressure

Without salt[a]			1%NaCl			3%NaCl			10%NaCl		
D_2	D_1	S	D_2	D_1	S	D_2	D_1	S	D_2	D_1	S
4.0847	0.0748	54.5752	12.0130	0.0568	211.5940	13.6418	0.0550	248.1634	16.3279	0.0385	424.1677
4.9075	0.0956	51.3279	10.0814	0.0734	137.2897	11.2874	0.0719	156.9412	14.6536	0.0495	295.9525
4.4555	0.1128	39.5011	7.9604	0.0888	89.5964	8.9639	0.0854	105.0144	13.6654	0.0622	219.8592
4.2946	0.1323	32.4551	6.5708	0.1091	60.2236	8.2949	0.0942	88.0106	12.3245	0.0717	171.8650
3.3082	0.2034	16.2658	5.0375	0.1372	36.7183	7.2838	0.1090	66.8459	12.1036	0.0784	154.4531
2.7091	0.2478	10.9321	4.0939	0.1728	23.6934	6.3055	0.1188	53.0725	11.4250	0.0839	136.1338

[a] Data from literature [12]

Table 7. Distribution coefficients and separation factor for the system of water+furfuryl alcohol+furfural with various salt at 298.15 K and atmospheric pressure

1%LiCl			1%NaCl			1%KCl			1%RbCl		
D_2	D_1	S	D_2	D_1	S	D_2	D_1	S	D_2	D_1	S
12.5714	0.0509	246.8620	12.0130	0.0568	211.5940	10.1948	0.0665	153.3748	7.5188	0.0694	108.2850
10.0158	0.0751	133.4319	10.0814	0.0734	137.2897	9.2035	0.0822	111.9676	6.5434	0.0911	71.8497
8.3676	0.0975	85.7968	7.9604	0.0888	89.5964	7.1261	0.1084	65.7541	5.4361	0.1081	50.2813
6.4132	0.1322	48.5037	6.5708	0.1091	60.2236	5.5513	0.1369	40.5438	4.4923	0.1327	33.8485
5.4570	0.1604	34.0172	5.0375	0.1372	36.7183	4.3578	0.1585	27.4987	3.8970	0.1598	24.3795
4.5749	0.1953	23.4276	4.0939	0.1728	23.6934	3.6382	0.1826	19.9265	3.1832	0.2003	15.8943

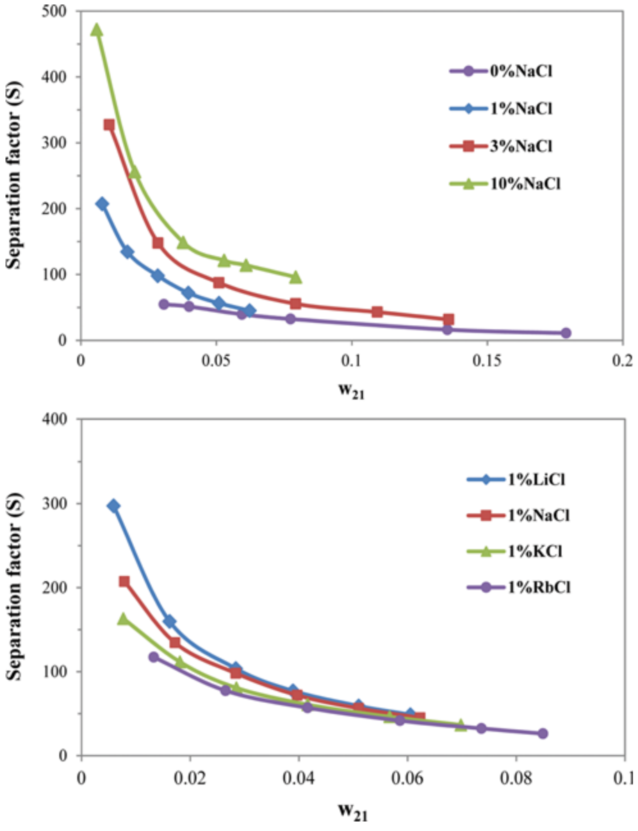

Fig. 9. Separation factor (S) plotted against the mass fraction of FAL in the aqueous phase at 298.15 K and atmospheric pressure.

enriched in the organic phase. Therefore, the addition of salt decreases the mutual solubility of the system and increases the two-phase region. The influence of the salt on the salting-out effect is in the order of LiCl>NaCl>KCl>RbCl. However, the effect of salt concentration was more significant than the effect of type of salt. These results indicated that the addition of salts is beneficial for the separation of FAL from its aqueous solution.

3. Reliability of Tie-line Data

The consistency of experimental tie-line data can be determined by applying, for example, the Otmer-Tobias [18], Hand [19] and Bachman [20] correlation as shown in Eq. (2)-(4), respectively:

$$\ln\left[\frac{1-w_{33}}{w_{33}}\right]=A+B\ln\left[\frac{1-w_{11}}{w_{11}}\right] \tag{2}$$

$$\ln\left[\frac{w_{21}}{w_{11}}\right]=A'+B'\ln\left[\frac{w_{23}}{w_{13}}\right] \tag{3}$$

$$w_{23}=A''+B''\left[\frac{w_{23}}{w_{11}}\right] \tag{4}$$

where w_{11} is the mass fraction of water in the aqueous-rich phase, w_{33} is the mass fraction of the furfural in the organic-rich phase, and w_{21} and w_{23} are the mass fractions of FAL in the aqueous-rich phase and the organic-rich phase, respectively. A, B, A′, B′, A″ and B″ are the parameters of the Othmer-Tobias, Hand and Bachman correlation equation. The linearity of the plots indicates consistency with experimental data. The values of parameters A, B, A′, B′, A″ and B″ and the values of corresponding correlation coefficient (R^2) are given in Tables 8 and 9. The comparison of these

Table 8. Values of Othmer-Tobias and Bachman parameters for the system of water+furfuryl alcohol+furfural with different NaCl concentration at 298.15 K and atmospheric pressure

NaCl conc. (%w/w)	Othmer-Tobias			Hand			Bachman		
	A	B	R^2	A′	B′	R^2	A″	B″	R^2
1	5.5613	2.8317	0.9185	−2.2069	1.1656	0.9989	0.0171	0.9159	0.9918
3	8.3929	3.5453	0.9347	−2.2069	0.9954	0.9969	0.0151	0.8749	0.9995
10	20.1132	7.3825	0.9815	−2.7792	0.7490	0.9844	0.0076	0.9253	0.9999

Table 9. Values of Othmer-Tobias and Bachman parameters for the system of water+furfuryl alcohol+furfural with various salt at 298.15 K and atmospheric pressure

Salt	Othmer-Tobias			Hand			Bachman		
	A	B	R^2	A′	B′	R^2	A″	B″	R^2
1%LiCl	7.7919	3.7740	0.9244	−2.5088	1.0193	0.9974	0.0295	0.8260	0.9918
1%NaCl	5.5613	2.8317	0.9185	−2.2069	1.1656	0.9989	0.0171	0.9159	0.9918
1%KCl	5.1956	2.7664	0.8733	−2.1117	1.1375	0.9982	0.0234	0.8572	0.9965
1%RbCl	4.0331	2.3462	0.9568	−1.9013	1.0980	0.9997	0.0269	0.8213	0.9974

results shows that the R^2 value for the Othmer-Tobias equation does not fit the results satisfactorily, while for the Hand and Bachman equation a good linear fit is achieved. This indicates that the Hand and Bachman equation can be used to correlate the tie-line data of the studied ternary mixtures.

4. Correlation Model

The relationship of the experimental tie-line data obtained at 298.15 K and atmospheric pressure for investigated ternary system can be represented by the NRTL model. In this model, the basic relationships for every component i in the aqueous-rich and organic-rich phases at equilibrium are as follows:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \tag{5}$$

$$\Sigma x_i^I = \Sigma x_i^{II} = 1 \tag{6}$$

where x_i^I, x_i^{II}, γ_i^I and γ_i^{II} are the mole fractions and activity coefficients of component i in the aqueous-rich (I) and organic-rich (II) phases, respectively.

The activity coefficient (i) in the NRTL model is expressed as [21]:

$$\ln\gamma_1 = \frac{\Sigma_{j=1}^{3}\tau_{ji}G_{ji}x_j}{\Sigma_{k=1}^{3}G_{ki}x_k} + \Sigma_{j=1}^{3}\frac{x_jG_{ij}}{\Sigma_{k=1}^{3}G_{kj}x_k}\left(\tau_{ij} - \frac{\Sigma_{k=1}^{3}x_k\tau_{kj}G_{kj}}{\Sigma_{k=1}^{3}G_{kj}x_k}\right) \tag{7}$$

where x_i is the mole fraction of component i, the parameters τ_{ij}, τ_{ji}, τ_{kj}, G_{ij}, G_{ji}, G_{ki} and G_{kj} are the adjustable parameters for each binary pair in the NRTL model and i, j, k are the indices for the compo-

Table 10. NRTL (α=0.2) binary interaction parameters (b_{ij} and b_{ji}) and rmsd values for the systems investigated

Ternary system	i-j	b_{ij}	b_{ji}	rmsd (%)
Water+FAL+furfural+ 1%NaCl	1-2	929.2853	−194.5398	0.2364
	1-3	−1084.0682	2101.5323	
	2-3	−188.1432	−338.9594	
Water+FAL+furfural+ 3%NaCl	1-2	990.9472	−61.3956	0.1589
	1-3	−1054.3207	2136.9678	
	2-3	30.7002	−436.3064	
Water+FAL+furfural+ 10%NaCl	1-2	1151.0912	67.2290	0.1678
	1-3	−957.2717	2135.7894	
	2-3	198.5662	−275.3965	
Water+FAL+furfural+ 1%LiCl	1-2	1082.9453	−198.6650	0.1701
	1-3	−1102.3151	2135.7882	
	2-3	−188.1432	−189.5194	
Water+FAL+furfural+ 1%KCl	1-2	803.0303	−214.4733	0.1386
	1-3	−1071.4401	2049.9634	
	2-3	12.3082	−645.3972	
Water+FAL+furfural+ 1%RbCl	1-2	931.1243	−208.9167	0.1558
	1-3	−1074.6727	2046.6850	
	2-3	−178.0333	−208.4058	

nents. These adjustable parameters can be calculated as follows:

$$\tau_{ij}=a_{ij}+\frac{b_{ij}}{T}+e_{ij}\ln T \tag{8}$$

$$\alpha_{ij}=\alpha_{ji}=c_{ij} \tag{9}$$

$$G_{ij}=\exp(-\alpha_{ij}\tau_{ij}) \tag{10}$$

where a_{ij}, b_{ij}, c_{ij} and e_{ij} are the NRTL coefficients for the binary interaction parameters and α_{ij} and α_{ji} are the non-randomness parameters.

We determined the value of the non-randomness parameter (α) of the NRTL model and took the appropriate value to be 0.2. The binary interaction parameters (b_{ij} and b_{ji}) of the NRTL model for the ternary system were obtained using the experimental LLE data as listed in Table 10. The modeling results were correlated with the experimental tie-line data of each ternary system as shown in Figs. 2 through 5. The correlation of both results in terms of root-mean square deviation (rmsd) is listed in Table 10. The rmsd value was calculated by the difference between the experimental and modeling mass fractions as follows:

$$\mathrm{rmsd}=100\sqrt{\frac{\Sigma_{k=1}\Sigma_{j=1}\Sigma_{i=1}(w_{ijk}^{expt}-w_{ijk}^{cal})}{6n}} \tag{11}$$

where n is the number of tie-lines, w^{expt} and w^{cal} are the experimental and modeling mass fractions, respectively. Subscript i is the component, j is the phase and k=1, 2, …, n is the number of tie-lines. As can be seen in Table 10, the modeling results of the NRTL model provide a good correlation with the experimental results of all investigated ternary systems. Low rmsd values for the NRTL model confirm its ability to predict the LLE data obtained in this work.

CONCLUSIONS

The solubility and tie-line data of the water-FAL-furfural system with the addition of salt were studied at 298.15 K and atmosphere pressure. The effects of salt concentration (1-10%NaCl) and type of salt (1%LiCl, 1%KCl and 1%RbCl) were investigated. The results showed that the enlargement of two-phase region occurred with an increase of salt concentration in initial aqueous phase and the type of the salt in the following order: LiCl>NaCl>KCl>RbCl. The distribution coefficients and separation factors were calculated to evaluate the effectiveness of the FAL extraction. The results indicated that the addition of salts has a beneficial effect on the separation of FAL from its aqueous solution.

The reliability of the LLE experimental results was validated using the Othmer-Tobias equation, Hand equation and Bachman equation. The Hand and Bachman equations are agreeable to correlate the tie-line data obtained in this work. NRTL was employed to correlate the results obtained by the modeling of the experimental data. The rmsd values lower than 0.3% confirms good correlation of the result.

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