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Salting-Out Effect of NaCl and KCl on the Liquid−Liquid Equilibrium of Water + 2-Methylpropanoic Acid + (1-Methylethyl)-benzene System at Several Temperatures

Javad Saien* and Mahdi Norouzi

Department of Applied Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran

ABSTRACT: The salting-out effect of NaCl and KCl on the liquid−liquid equilibrium (LLE) of the ternary system of {water (1) + 2-methylpropanoic acid (2) + (1-methylethyl)-benzene (3)}, a recommended system for liquid−liquid extraction investigations, was studied at temperatures of (288.15, 298.15, and 313.15) K. The generated data for salt-free system have been used to estimate the binary molecular interaction parameters for the nonrandom two-liquid (NRTL) activity coefficient model. Results show that this model reproduces very good tie lines by estimated binary molecular interaction coefficients. The distribution coefficient of 2-methylpropanoic acid between organic/aqueous phases increases with its concentration, both in salt-free and in the presence of salt cases; however, it decreases moderately with temperature, within the range used. Adding a 0.05 mass fraction (based on mass of initial water) NaCl leads to an average enhancement of about 4 4% in distribution coefficient, and hence, it reaches to about 124 % by adding 0.10 mass fraction of this salt. The appropriate enhancement achievement with KCl are about (38 and 121) %, respectively. The Othmer−Tobias equation was used to examine the reliability of the experimental results, and an excellent agreement was revealed.

INTRODUCTION

Many attempts have been made for the solvent extraction of carboxylic acids from aqueous solutions. Liquid−liquid equilibrium (LLE) measurements and phase behavior of ternary systems including carboxylic acids have been the subject of much research in recent years in that LLE data are required for the design of liquid−liquid extraction units.[1−5]

The presence of dissolved salts causes us to alter the equilibrium behavior of these systems. This phenomenon is termed "salting-out" which leads to an increase in the distribution coefficient of an extractable species from aqueous phase in the presence of a salt. This matter can be explained by the fact that, by solvating ions, some of the water becomes unavailable and, therefore, the solute tendency from aqueous phase to organic phase is favored. Salting-out can be used to improve separation in processes such as extraction because of altering distribution coefficient, rectification for altering azeotropic conditions, absorption, and distillation for altering distribution coefficient.[6−11] Increasing the amount of dissolved salts usually causes the increase in extraction efficiency of the solute, but the raffinate phase will have a higher concentration of dissolved salt. So, a lower salt concentration is usually preferred.

Many solvents have been used for the extraction of carboxylic acids of dilute aqueous solutions. The {water + 2-methylpropanoic acid + (1-methylethyl)-benzene} ternary system is of practical interest in that it has been a test system for column contactors for liquid−liquid extraction.[12] (1-Methylethyl)-benzene may be considered as a suitable solvent for extraction of carboxylic acids from water, having low vapor pressure, capability to form two phases at low temperatures, and rapid phase separation due to its low density and low viscosity. This chemical system is known as a high interfacial tension system that is 32.3 $mN \cdot m^{-1}$ at 298.15 K.[13] Also, it has the advantage that (1-methylethyl)-benzene is not a very flammable liquid.[14] It is notable that previous LLE data for the extraction of different carboxylic acids from water using (1-methylethyl)-benzene solvent have been reported in two articles by Soares et al.[14] and Cehreli.[15]

In this work, LLE data for the {water + 2-methylpropanoic acid + (1-methylethyl)-benzene} ternary system are to be obtained and used to obtain the parameters of nonrandom two-liquid (NRTL) activity coefficient using an Aspen Plus simulator (V 11.1). The effects of NaCl and KCl electrolytes on the LLE data for this system are to be investigated using (0.05 and 0.10) mass fractions of initial water, at different temperatures. The reliability of experimental tie line data of ternary system with and without salts is to be ascertained with the Othmer−Tobias correlation.

EXPERIMENTAL SECTION

Chemicals. All materials were purchased from Merck Company. (1-Methylethyl)-benzene and 2-methylpropanoic acid were with mass fraction purities more than 0.995 and were used without further purification. Sodium chloride and potassium chloride were analytical purity grade and dried in oven at 150 °C before use. Standard 0.1 $mol \cdot kg^{-1}$ ($\pm$ 0.2 %) sodium hydroxide solutions (prepared by adding the solution of a tube of its Merck product to distilled water in a 1000 mL volumetric flask) were used for titration. Water was bidistilled before utilization.

Apparatus and Procedure. The LLE data measurements were made in an equilibrium jacketed cell equipped with a

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magnetic stirrer at the temperatures under study, (288.15, 298.15, and 313.15) K. The temperature was regulated at the desired value, using a thermostat (Julabo, Germany) with an uncertainty of ± 0.1 K. This apparatus was calibrated once with bidistilled water by means of an accurate thermometer (Amadigit, ad 3000th, Thermometer Percica, Germany). An electronic Ohaus (Adventurer Pro AV264, Switzerland) balance with the uncertainty of ± 0.1 mg was used in all experiments. All experiments were conducted under ambient pressure.

To determine the tie line data, ternary mixtures of known overall compositions lying within the two-phase region were prepared by mass. After vigorously stirring the content of the equilibrium cell for 1 h, the samples were allowed to rest for 4 h to reach equilibrium. Samples were taken from each phase and analyzed. For the salting-out experiments, the appropriate salt amount was added to the solution prior to stirring.

Sample Analysis. Taken samples from each phase were weighed and titrated with 0.1 $\text{mol}\cdot\text{kg}^{-1}$ sodium hydroxide solutions, in the presence of phenolphthalein as the indicator. The appropriate added sodium hydroxide volumes for titration, within (115 to 1320) μL, were obtained from a mircroliter-syringe with the uncertainty of 5 μL. For each phase sample, the titration was repeated four times, and the average was used. The sample taken from organic phase was also analyzed using gas chromatography (GC) (Shimadzu 14B), equipped with a flame ionization detector (FID). A capillary column (25 m long, 0.22 mm internal diameter, 0.5 μm film thickness) was utilized to separate organic components. The oven temperature remained at 160 °C for 1 min and increased to 170 °C with the rate of 2 $°\text{C}\cdot\text{min}^{-1}$. The detector temperature was kept at 250 °C and injection port temperature held at 220 °C. Injections were performed on the split-less mode. Nitrogen was used as a carrier at a constant rate, and 0.2 μL of a sample was injected. The injection of the organic phase was repeated four times, and the average was used. To calibrate the GC, the standard mixtures were prepared by mass and injected to GC; the relative response factor (RRF) of the detector for (1-methylethyl)-benzene (component 3) to 2-methylpropanoic acid (component 2) was determined as eq 1 in GC calculation, according to reported works.[16,17]

$$(\text{RRF}) = \frac{(\text{RF}_3)}{(\text{RF}_2)} = \left[\frac{A_2}{A_3}\right]_S \left[\frac{w_3}{w_2}\right]_S \tag{1}$$

where RF, A, and w represent the GC response factor, the peak area, and the mass fraction; also subscript S represents the standard.

The (1-methylethyl)-benzene mass fraction in the unknown mixture organic phase, $(w_3)_Z$, was calculated by eq 2:

$$(w_3)_Z = \frac{(A_3)_Z}{(A_3)_Z + \dfrac{(A_2)_Z}{(\text{RRF})}} \tag{2}$$

The water (component 1) mass fraction in the organic phase was calculated by subtracting (1-methylethyl)-benzene and 2-methylpropanoic acid mass fractions of unit.

The mass fraction of water and (1-methylethyl)-benzene in the aqueous phase can be calculated by simultaneous solving eqs 3 and 4, which are used to obtain the mass of organic and aqueous phases in equilibrium:

$$m_{\text{org}}\cdot(w_2)_{\text{org}} + m_{\text{aq}}\cdot(w_2)_{\text{aq}} = m_2 \tag{3}$$

$$m_{\text{org}} + m_{\text{aq}} = m_1 + m_2 + m_3 \tag{4}$$

where m represents the mass. Also, the subscripts aq and org stand for aqueous and organic phases, respectively. Having m_{aq} and m_{org} values, the mass fraction of (1-methylethyl)-benzene and water in aqueous phase can be obtained by eqs 5 and 6:

$$(w_3)_{\text{aq}} = \frac{m_3 - [m_{\text{org}}\cdot(w_3)_{\text{org}}]}{m_{\text{aq}}} \tag{5}$$

$$(w_1)_{\text{aq}} = 1 - (w_3)_{aq} - (w_2)_{\text{aq}} \tag{6}$$

The standard uncertainty for the measured mass fractions is $u(w) = 0.0005$.

RESULTS AND DISCUSSION

The experimental tie line data for the {water (1) + 2-methylpropanoic acid (2) + (1-methylethyl)-benzene (3)} ternary system at different temperatures are presented in Table 1. The distribution coefficient of 2-methylpropanoic acid between phases (D), given in this table, is according to equation:

$$D = \frac{w_{23}}{w_{21}} \tag{7}$$

where w_{21} and w_{23} are the mass fractions of 2-methylpropanoic acid in aqueous and in organic phases, respectively. The results of LLE show that the use of (1-methylethyl)-benzene for the

Table 1. Tie Line Data for {Water (1) + 2-Methylpropanoic Acid (2) + (1-Methylethyl)-benzene (3)} System

T/K	organic phase			aqueous phase			D
	w_{33}	w_{23}	w_{13}	w_{31}	w_{21}	w_{11}	
288.15	0.9408	0.0574	0.0018	0.0034	0.0211	0.9755	2.720
	0.8547	0.1429	0.0024	0.0022	0.0400	0.9578	3.570
	0.7515	0.2452	0.0033	0.0020	0.0563	0.9417	4.354
	0.6909	0.3045	0.0046	0.0023	0.0644	0.9333	4.726
	0.6257	0.3688	0.0055	0.0035	0.0728	0.9237	5.064
	0.5597	0.4339	0.0064	0.0014	0.0819	0.9168	5.301
	0.5041	0.4861	0.0099	0.0039	0.0881	0.9080	5.517
	0.4564	0.5292	0.0143	0.0036	0.0938	0.9026	5.643
298.15	0.9469	0.0518	0.0013	0.0020	0.0218	0.9763	2.382
	0.8990	0.0982	0.0029	0.0025	0.0311	0.9663	3.151
	0.8499	0.1468	0.0033	0.0024	0.0407	0.9569	3.609
	0.7878	0.2074	0.0047	0.0037	0.0518	0.9445	4.003
	0.7224	0.2724	0.0052	0.0034	0.0612	0.9354	4.453
	0.6499	0.3434	0.0067	0.0019	0.0720	0.9261	4.767
	0.6108	0.3811	0.0081	0.0035	0.0773	0.9192	4.929
	0.5626	0.4286	0.0088	0.0038	0.0834	0.9128	5.139
	0.4958	0.4920	0.0122	0.0025	0.0906	0.9069	5.429
313.15	0.9447	0.0508	0.0045	0.0025	0.0229	0.9747	2.224
	0.8991	0.0964	0.0045	0.0026	0.0322	0.9652	2.997
	0.8658	0.1280	0.0062	0.0033	0.0394	0.9573	3.247
	0.8111	0.1824	0.0066	0.0048	0.0495	0.9458	3.687
	0.7581	0.2351	0.0068	0.0070	0.0582	0.9349	4.041
	0.7010	0.2913	0.0077	0.0050	0.0664	0.9287	4.389
	0.6299	0.3620	0.0081	0.0039	0.0765	0.9196	4.732
	0.5364	0.4497	0.0139	0.0055	0.0886	0.9059	5.075

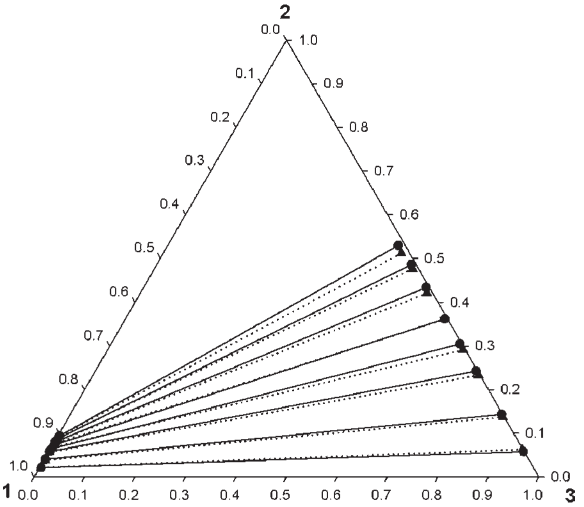

Figure 1. Ternary system of {water (1) + 2-methylpropanoic acid (2) + (1-methylethyl)-benzene (3)} at 288.15 K. ● and solid line, experimental tie lines; ▲ and dotted line, NRTL tie lines.

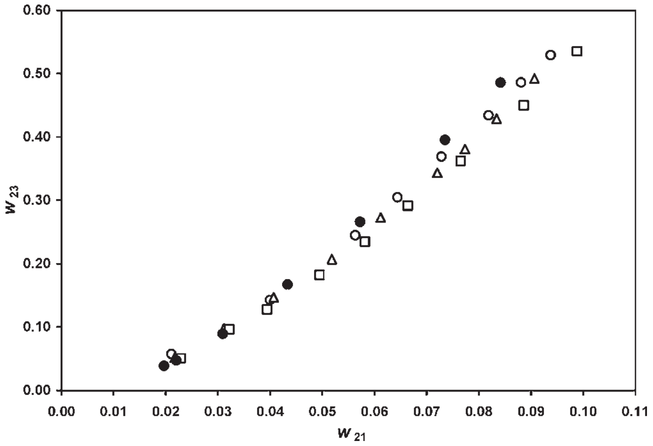

Figure 2. Distribution of 2-methylpropanoic acid between phases at different temperatures. ○, 288.15 K; △, 298.15 K; □, 313.15 K; ●, data from Soares et al.[14] at 288.15 K.

extraction of 2-methylpropanoic acid from its aqueous solution provides a distribution coefficient ranging from 2.222 to 5.643 within the concentration and temperature ranges of this study.

(1-Methylethyl)-benzene has a negligible miscibility with water and a suitable coefficient distribution for extraction 2-methylpropanoic acid from dilute water solution, while the extract phase has a small amount of water. Figure 1 shows the ternary diagram of {water + 2-methylpropanoic acid + (1-methylethyl)-benzene} at 288.15 K. Similar plots are appropriate at either of the other temperatures.

Data for salt-free system are illustrated in Figure 2 by plotting the mass fraction of 2-methylpropanoic acid in the organic phase versus that of the aqueous phase, at different temperatures. Results show that the temperature (within the used range) has no significant influence on distribution at low amounts of 2-methylpropanoic acid; however, at high amounts (w_{21} above 0.06), a higher distribution coefficient is achieved at lower temperatures.

Table 2. NRTL Coefficients of the Equations for Binary Interaction Parameters for the {Water (1) + 2-Methylpropanoic Acid (2) + (1-Methylethyl)-benzene (3)} System

component *i*:	2	3	3
component *j*:	1	2	1
a_{ij}	3.329	0.0	0.0
a_{ji}	1.747	0.0	0.0
b_{ij}	382.591	3.462	1062.714
b_{ji}	462.629	359.550	2069.634
c_{ij}	0.470	0.3	0.3

It has to be noted that the obtained mass fractions are very close to those reported by Soares et al.[14] (salt free system). A comparison between data at 228.15 K is presented in Figure 2.

The relationship of the LLE can be represented with an activity coefficient model. In this model, the basic relationships for every component *i* in two coexistent liquid phases of a system at equilibrium are:

$$x_i^{\mathrm{I}}\gamma_i^{\mathrm{I}} = x_i^{\mathrm{II}}\gamma_i^{\mathrm{II}} \tag{8}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \tag{9}$$

$$\sum_i x_i^{\mathrm{II}} = 1 \tag{10}$$

where x_i^{I}, x_i^{II}, γ_i^{I}, and γ_i^{II} are the mole fraction and activity coefficient of component *i* in phases I and II, respectively.

The NRTL activity coefficient model was used for correlating experimental data. In this regard, the activity coefficient, γ_i, for a component *i* is given by eq 11,[18]

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_v x_v \tau_{vj} G_{vj}}{\sum_k x_k G_{kj}} \right) \tag{11}$$

where *x* is the mole fraction, *τ* and *G* are binary parameters for NRTL model, and *i*, *j*, *k*, and *v* are indices, each of them for all of the components.

The binary interaction parameters can be calculated using the following equations,[19,20]

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{12}$$

$$\alpha_{ij} = \alpha_{ji} = c_{ij} \tag{13}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{14}$$

where α is the nonrandomness parameter and a_{ij}, b_{ij}, and c_{ij} are NRTL coefficients of the equations for binary interaction parameters. These can be determined from LLE data regression using Aspen Plus (Version 11.1). This software employs an objective function called "maximum likelihood" and an algorithm called "Britt-Luecke" to correlate model parameters.

Table 2 presents the coefficients that were retrieved from Aspen Plus based on the above equations to calculate the binary interaction parameters for the NRTL model. It has to be noted that a recommended value of 0.30 is considered for

Table 3. Tie Line Data for the {Water (1) + 2-Methylpropanoic Acid (2) + (1-Methylethyl)-benzene (3)} System with (0.05 and 0.10) Mass Fractions of Initial Water of NaCl or KCl at 288.15 K

organic phase			aqueous phase			
w_{33}	w_{23}	w_{13}	w_{31}	w_{21}	w_{11}	D
			0.05 NaCl			
0.9245	0.0716	0.0039	0.0011	0.0193	0.9796	3.706
0.8813	0.1129	0.0058	0.0029	0.0237	0.9734	4.768
0.8324	0.1602	0.0074	0.0034	0.0304	0.9662	5.270
0.7209	0.2709	0.0082	0.0025	0.0412	0.9562	6.570
0.6472	0.3445	0.0083	0.0042	0.0489	0.9469	7.039
0.5470	0.4387	0.0143	0.0049	0.0583	0.9368	7.529
0.5014	0.4833	0.0153	0.0042	0.0616	0.9343	7.849
0.4351	0.5479	0.0170	0.0022	0.0683	0.9295	8.024
0.3704	0.6081	0.0215	0.0022	0.0754	0.9224	8.061
			0.05 KCl			
0.8885	0.1084	0.0030	0.0024	0.0247	0.9729	4.390
0.7736	0.2203	0.0061	0.0032	0.0375	0.9593	5.875
0.7302	0.2622	0.0076	0.0013	0.0415	0.9572	6.316
0.6943	0.2972	0.0085	0.0043	0.0467	0.9490	6.501
0.6405	0.3504	0.0091	0.0024	0.0518	0.9458	6.761
0.5943	0.3959	0.0097	0.0026	0.0556	0.9418	7.116
0.5408	0.4457	0.0135	0.0045	0.0602	0.9353	7.409
0.4853	0.4973	0.0173	0.0020	0.0655	0.9325	7.592
0.4374	0.5446	0.0180	0.0042	0.0697	0.9261	7.816
0.3719	0.6082	0.0199	0.0034	0.0794	0.9172	7.767
			0.10 NaCl			
0.9315	0.0655	0.0030	0.0024	0.0103	0.9872	6.335
0.8857	0.1113	0.0030	0.0016	0.0143	0.9842	7.517
0.7952	0.1988	0.0060	0.0045	0.0216	0.9739	9.219
0.7191	0.2734	0.0076	0.0031	0.0275	0.9694	9.955
0.5992	0.3912	0.0097	0.0027	0.0357	0.9616	10.983
0.5664	0.4187	0.0149	0.0043	0.0383	0.9574	11.225
0.5306	0.4527	0.0166	0.0030	0.0408	0.9562	11.380
0.4758	0.5063	0.0179	0.0028	0.0456	0.9517	11.405
0.4336	0.5479	0.0185	0.0046	0.0485	0.9469	11.528
0.3670	0.6139	0.0191	0.0025	0.0543	0.9432	11.509
			0.01 KCl			
0.8847	0.1119	0.0034	0.0025	0.0151	0.9825	7.426
0.7792	0.2150	0.0057	0.0023	0.0233	0.9744	9.231
0.7145	0.2787	0.0069	0.0013	0.0285	0.9703	9.782
0.6696	0.3218	0.0086	0.0042	0.0317	0.9641	10.146
0.5981	0.3926	0.0093	0.0033	0.0362	0.9604	10.833
0.5697	0.4167	0.0137	0.0020	0.0383	0.9597	10.878
0.5108	0.4726	0.0166	0.0042	0.0428	0.9530	11.052
0.4748	0.5069	0.0183	0.0039	0.0456	0.9506	11.1241
0.4401	0.5406	0.0192	0.0012	0.0481	0.9506	11.230
0.3465	0.6321	0.0214	0.0037	0.0563	0.9399	11.223

Table 4. Tie Line Data for the {Water (1) + 2-Methylpropanoic Acid (2) + (1-Methylethyl)-benzene (3)} System with (0.05 and 0.10) Mass Fractions of Initial Water of NaCl or KCl at 298.15 K

organic phase			aqueous phase			
w_{33}	w_{23}	w_{13}	w_{31}	w_{21}	w_{11}	D
			0.05 NaCl			
0.8965	0.1020	0.0015	0.0018	0.0238	0.9743	4.285
0.8483	0.1478	0.0039	0.0012	0.0300	0.9688	4.922
0.7767	0.2191	0.0043	0.0025	0.0368	0.9606	5.952
0.7122	0.2816	0.0062	0.0028	0.0427	0.9545	6.598
0.5841	0.4026	0.0133	0.0027	0.0567	0.9406	7.100
0.5026	0.4801	0.0174	0.0012	0.0624	0.9364	7.699
0.4260	0.5535	0.0205	0.0015	0.0696	0.9290	7.958
0.3563	0.6180	0.0257	0.0028	0.0775	0.9197	7.975
			0.05 KCl			
0.8893	0.1077	0.0030	0.0021	0.0242	0.9737	4.444
0.8051	0.1895	0.0054	0.0029	0.0348	0.9624	5.449
0.6454	0.3461	0.0085	0.0019	0.0506	0.9474	6.836
0.5831	0.4072	0.0098	0.0035	0.0578	0.9387	7.039
0.5185	0.4680	0.0135	0.0013	0.0636	0.9352	7.364
0.4900	0.4935	0.0165	0.0036	0.0676	0.9288	7.301
0.4055	0.5759	0.0186	0.0046	0.0753	0.9201	7.646
0.3571	0.6231	0.0198	0.0015	0.0787	0.9199	7.921
			0.01 NaCl			
0.9464	0.0515	0.0021	0.0028	0.0098	0.9875	5.263
0.8569	0.1403	0.0028	0.0024	0.0166	0.9811	8.470
0.8137	0.1830	0.0033	0.0028	0.0200	0.9772	9.139
0.7517	0.2393	0.0090	0.0040	0.0247	0.9713	9.678
0.7070	0.2837	0.0094	0.0031	0.0279	0.9693	10.155
0.6037	0.3851	0.0111	0.0041	0.0362	0.9617	10.638
0.5410	0.4449	0.0141	0.0017	0.0403	0.9581	11.052
0.4214	0.5582	0.0205	0.0014	0.0507	0.9539	10.999
0.3473	0.6266	0.0261	0.0043	0.0564	0.9372	11.117
			0.01 KCl			
0.9084	0.0886	0.0031	0.0022	0.0133	0.9845	6.634
0.7595	0.2351	0.0054	0.0018	0.0241	0.9741	9.740
0.6874	0.3053	0.0073	0.0038	0.0297	0.9665	10.282
0.6504	0.3413	0.0083	0.0016	0.0339	0.9646	10.071
0.5989	0.3913	0.0098	0.0042	0.0365	0.9593	10.718
0.5520	0.4338	0.0142	0.0035	0.0398	0.9567	10.890
0.4951	0.4887	0.0162	0.0022	0.0443	0.9535	11.035
0.4426	0.5386	0.0188	0.0037	0.0494	0.9468	10.894
0.3472	0.6325	0.0203	0.0024	0.0585	0.9390	10.803

$c_{ij} = c_{ji}$ by software for nonpolar—polar nonassociated liquids,[19] that is, (1-methylethyl)-benzene—2-methylpropanoic acid and (1-methylethyl)-benzene—water in this work. The obtained root-mean-square deviation (rmsd) value between experimental and calculated data, defined as:

$$\mathrm{rmsd} = \sqrt{\frac{\sum_i \sum_j \sum_k (w_{ipq}^{\mathrm{exp}} - w_{ipq}^{\mathrm{cal}})^2}{6N}} \qquad (15)$$

where w_{ipq}^{exp} and w_{ipq}^{cal} are experimental and calculated mass fractions of component $i = 1, 2, 3$ in phases, $p =$ I, II and on tie lines, $q = 1, 2, ...; N$, for all data, is less than 0.032, confirming the reliability of the results.[21] Figure 1 shows typically that the

Table 5. Tie Line Data for the {Water (1) + 2-Methylpropanoic Acid (2) + (1-Methylethyl)-benzene (3)} System with (0.05 and 0.10) Mass Fractions of Initial Water of NaCl or KCl at 313.15 K

organic phase			aqueous phase			
w_{33}	w_{23}	w_{13}	w_{31}	w_{21}	w_{11}	D
			0.05 NaCl			
0.8917	0.1072	0.0011	0.0012	0.0255	0.9733	4.207
0.8602	0.1382	0.0016	0.0041	0.0281	0.9678	4.917
0.7967	0.1990	0.0042	0.0034	0.0349	0.9617	5.707
0.7219	0.2707	0.0073	0.0026	0.0427	0.9548	6.341
0.6017	0.3880	0.0103	0.0032	0.0535	0.9433	7.258
0.5174	0.4813	0.0014	0.0026	0.0586	0.9388	8.215
0.4839	0.5025	0.0137	0.0031	0.0600	0.9370	8.381
0.4203	0.5619	0.0178	0.0034	0.0655	0.9311	8.576
			0.05 KCl			
0.8905	0.1069	0.0027	0.0022	0.0245	0.9733	4.367
0.7642	0.2292	0.0066	0.0011	0.0393	0.9596	5.838
0.6555	0.3359	0.0086	0.0032	0.0516	0.9452	6.512
0.5433	0.4430	0.0138	0.0043	0.0623	0.9334	7.111
0.5197	0.4660	0.0143	0.0036	0.0653	0.9311	7.140
0.4921	0.4920	0.0159	0.0043	0.0679	0.9278	7.242
0.4321	0.5500	0.0180	0.0026	0.0741	0.9233	7.418
0.4013	0.5795	0.0192	0.0032	0.0772	0.9195	7.502
			0.01 NaCl			
0.9473	0.0508	0.0019	0.0024	0.0112	0.9863	4.523
0.9012	0.0969	0.0019	0.0033	0.0146	0.9820	6.628
0.8644	0.1330	0.0027	0.0036	0.0166	0.9768	7.996
0.8156	0.1816	0.0029	0.0027	0.0202	0.9757	9.007
0.7409	0.2509	0.0083	0.0019	0.0265	0.9706	9.454
0.6548	0.3347	0.0105	0.0031	0.0327	0.9602	10.232
0.5652	0.4220	0.0128	0.0013	0.0393	0.9544	10.745
0.4693	0.5150	0.0157	0.0037	0.0481	0.9392	10.714
			0.01 KCl			
0.9244	0.0726	0.0030	0.0032	0.0115	0.9853	6.330
0.8472	0.1485	0.0043	0.0022	0.0186	0.9792	7.979
0.7921	0.2027	0.0052	0.0029	0.0230	0.9742	8.828
0.7289	0.2648	0.0063	0.0035	0.0268	0.9696	9.868
0.6728	0.3192	0.0080	0.0042	0.0310	0.9648	10.299
0.6233	0.3675	0.0092	0.0019	0.0356	0.9625	10.325
0.5729	0.4135	0.0136	0.0035	0.0396	0.9569	10.436
0.4489	0.5335	0.0176	0.0027	0.0509	0.9464	10.477
0.3772	0.6035	0.0193	0.0021	0.0589	0.9389	10.245

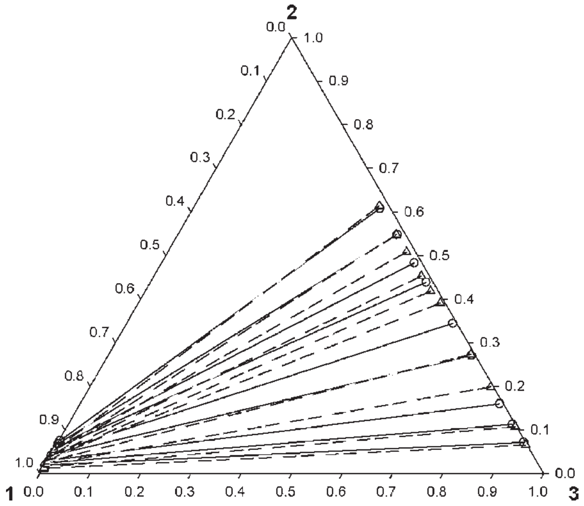

Figure 3. Ternary system of {water (1) + 2-methylpropanoic acid (2) + (1-methylethyl)-benzene (3)} at 288.15 K; ○ and solid line, tie lines with 0.05 mass fraction of NaCl; △ and dashed lines, tie lines with 0.10 mass fraction of NaCl.

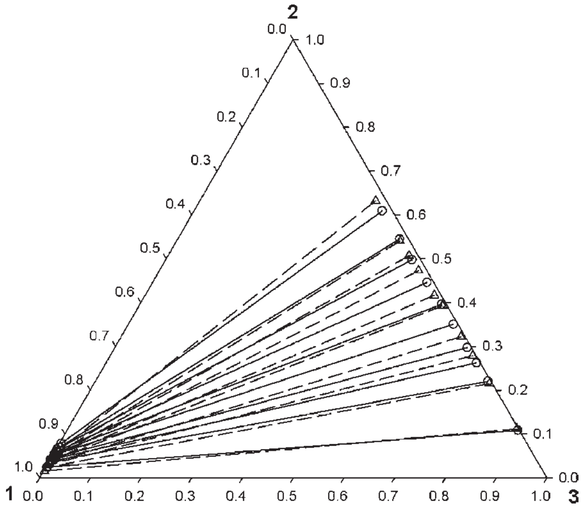

Figure 4. Ternary system of {water (1) + 2-methylpropanoic acid (2) + (1-methylethyl)-benzene (3)} at 288.15 K. ○ and solid lines, tie lines with 0.05 mass fraction KCl, △ and dashed lines, tie lines with 0.10 mass fraction KCl.

NRTL equation can reproduce very good tie lines for the used ternary chemical system.

The LLE data with (0.05 and 0.10) mass fractions (based on mass of initial water) for NaCl and KCl added salts, at different temperatures, are listed in Tables 3 to 5.

The presence of dissolved salts increases the solubility of 2-methylpropanoic acid in organic phase. In Figures 3 and 4, the effect of the salt presence on the distribution of 2-methylpropanoic acid at 288.15 K is shown. Similar tie lines are appropriate for the other temperatures. Adding 0.05 mass fraction of NaCl leads to an average (with respect to solute concentration and temperature) enhancement of about 44 % in distribution coefficient and, hence, reaches about 124 % by adding 0.10 mass fraction of this salt. The appropriate enhancement with KCl salt are about (38 and 121) %, respectively.

Figure 5 presents a comparison between the results for salt-free case and with the presence of NaCl and KCl salts at 288.15 K. In all cases, the distribution coefficient first increases significantly and then moderately as the solute concentration increases. Meanwhile, the effectiveness of NaCl in salting-out is slightly more than KCl, within concentrations investigated in this study and based on salt mass fraction. There is similar behavior at other temperatures. Several previous works on mass transfer and equilibrium distribution of a solute between phases show the similar abilities in salting-out by the used salts.[22,23]

The salting-out effect of NaCl at different temperatures is presented in Figure 6. A mild variation is pronounced within the

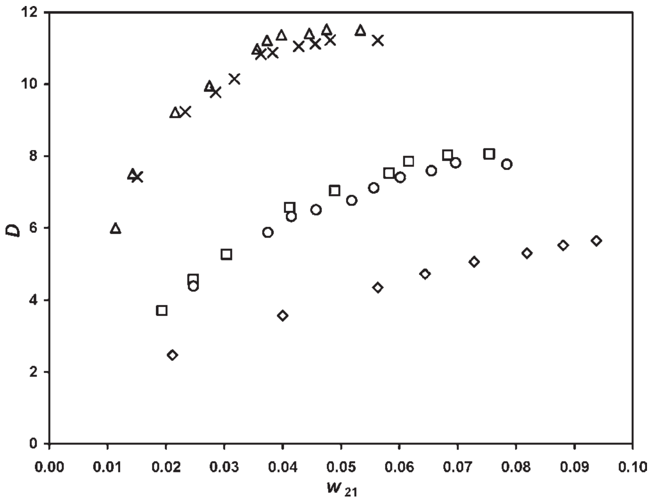

Figure 5. 2-Methylpropanoic acid distribution coefficient versus its mass fraction in the aqueous phase with the used salts at 288.15 K. ◊, salt-free; ○, 0.05 mass fraction KCl; □, 0.05 mass fraction NaCl; ×, 0.10 mass fraction KCl; △, 0.10 mass fraction NaCl.

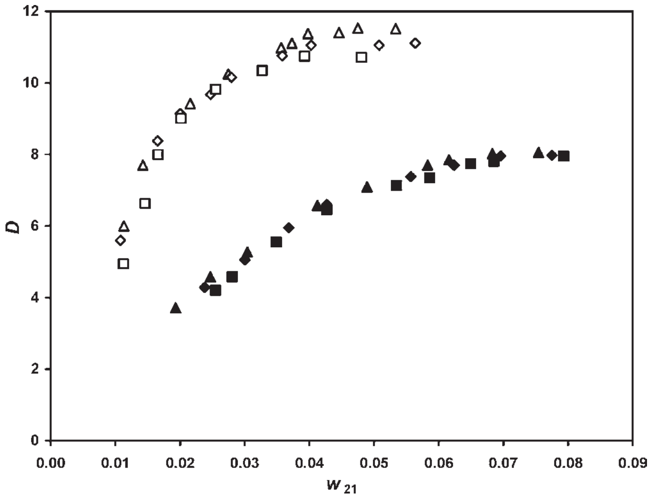

Figure 6. 2-Methylpropanoic acid distribution coefficient versus its mass fraction in the aqueous phase with NaCl addition at the used temperatures. △, 0.10 mass fraction and 288.15 K; ◊, 0.10 mass fraction and 298.15 K; □, 0.10 mass fraction and 313.15 K; ▲, 0.05 mass fraction and 288.15 K; ◆, 0.05 mass fraction and 298.15 K; ■, 0.05 mass fraction and 313.15 K.

used temperatures. The lower temperature of 288.15 K provides the higher solute solubility in the organic phase, and it decreases as the temperature increases. The highest difference for the distribution coefficient, within the used temperatures, is about 7.2 % with the 0.10 mass fraction of NaCl or KCl.

The reliability of the experimentally measured tie-line data can be ascertained by applying the Othmer−Tobias correlation:[24]

$$\ln\left(\frac{1-w_{33}}{w_{33}}\right) = a + b\ln\left(\frac{1-w_{11}}{w_{11}}\right) \qquad (16)$$

where a and b are the intercept and slope of logarithmic variations, respectively.

The values of parameters a and b are listed in Table 6, together with the coefficients of determination (R^2). As the given coefficient of determination values indicate, there is a good agreement between obtained data and eq 16 (the minimum R^2 is 0.989), indicating a high degree of consistency of the related data.

Table 6. Parameters of the Othmer−Tobias Equation for the Used System with (0.05 and 0.10) Mass Fractions of Initial Water of NaCl or KCl and without Salt

state	T/K	a	b	R^2
salt free	288.15	4.554	2.009	0.995
	298.15	4.419	1.988	0.991
	313.15	4.017	1.886	0.991
0.05 NaCl	288.15	2.150	5.710	0.991
	298.15	2.295	6.136	0.994
	313.15	2.556	6.926	0.992
0.10 NaCl	288.15	2.014	6.111	0.992
	298.15	2.165	6.632	0.991
	313.15	1.783	4.806	0.990
0.05 KCl	288.15	2.232	5.860	0.992
	298.15	2.197	5.768	0.989
	313.15	2.144	5.572	0.990
0.10 KCl	288.15	2.067	6.248	0.990
	298.15	2.009	6.041	0.994
	313.15	2.011	5.979	0.998

■ CONCLUSIONS

LLE data were collected for the ternary system of {water + 2-methylpropanoic acid + (1-methylethyl)-benzene} at (288.15, 298.15, and 313.15) K and under ambient pressure, with and without salts. According to the results, (1-methylethyl)-benzene provides a distribution coefficient of more than 6.641 and 3.799 (average at the highest used temperature) for the extraction of 2-methylpropanoic acid from aqueous solutions in the presence and absence of salts, respectively. The NRTL model with the estimated molecular interaction coefficients, obtained with the aid of Aspen Plus simulator, gives the tie lines very close to experimental ones for salt-free results. The presence of only (0.05 and 0.10) mass fractions of initial water of NaCl or KCl causes significant increase in distribution coefficient of 2-methylpropanoic acid between organic and aqueous phases. In this regard, the influence of temperature, within the range used, is moderate. The NaCl salt provides a relatively more effective salting-out of 2-methylpropanoic acid under identical conditions. The reliability of experimental tie line data has been tested by the Othmer−Tobias equation with high accuracy.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +988118282807. Fax: +988118257407. E-mail: saien@basu.ac.ir.

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