Separation of Formic Acid from Aqueous Solutions by Liquid Extraction Technique at Different Temperatures

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(Received 2 November 2018, Accepted 4 January 2019)

In this study, the separation of formic acid from aqueous solutions was investigated. Liquid-liquid equilibrium (LLE) data including tie-lines was reported for a ternary mixture of water + formic acid + 2-methylpropyl ethanoate at (293.15-323.15) K and atmospheric pressure. The system shows type-I phase behavior based on Treybal classification because only one partially miscible binary mixture (water + 2-methylpropyl ethanoate) was observed. The composition of tie-lines was determined by cloud point method and refractive index measurements. The results show that the solubility of formic acid in the water-rich phase is more than that in the solvent-rich phase. The extracting capability of the solvent was ascertained by determination of the distribution coefficients and separation factors. The reliability of tie-line data was verified by Othmer-Tobias and Hand equations. The experimental data were correlated with NRTL and UNIQUAC models and the binary interaction parameters were determined. The values of the root-mean-square deviation (RMSD) were confirmed the quality the correlations.

Keywords: Liquid-liquid equilibrium, NRTL, UNIQUAC, Formic acid, 2-Methylpropyl ethanoate

INTRODUCTION

Formic acid is one of the most commonly used chemicals in different industries such as pesticide, leather, rubber, printing, pharmaceutical, food, *etc*. [1-4]. Formic acid also is the greatest organic fuel used for energy generation in direct liquid fuel cells [5-8]. During the chemical synthesis or fermentation processes for the production of formic acid, aqueous solutions are achieved. In general, the separation of formic acid from industrial wastewaters or aqueous solutions is very important and holds considerable interest due to its economic benefits and widespread application in chemical industries [2-3,9]. As water and formic acid form an azeotropic binary mixture, efficient separation by distillation method is impossible or expensive [2-3,10]. Liquid extraction can be used as an efficient method for the separation of formic acid from

wastewaters or dilute solutions. Liquid-liquid equilibria (LLE) data can be helpful in developing the separation processes [11-13]. The selection of adequate solvent is very important in liquid extraction and many solvents have been studied to improve the extraction of formic acid from aqueous solutions [2,9-10,14-16]. Esters are adequate for this purpose for their stability, low solubility in water, low toxicity and low cost.

In this study, the separation of formic acid from dilute solutions by LLE technique has been considered. 2-Methylpropyl ethanoate was used as a solvent and the results were compared with the other used esters (ethyl ethanoate and butyl ethanoate) [15] for extraction of formic acid from water.

Formic acid and water are self-associated through hydrogen bonding [1]. The hydrophilic interaction between the -COOH group of the acid with water molecules leads to the formation of a new H-bond and the released energy can help the disruption of water and acid molecules. Esters are polar molecules, so they have dipole-dipole interactions as

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well as van der Waals dispersion forces. They do not form hydrogen bonds in the pure state but hydrogen bond with water molecules will occur. So, the solvent used for the extraction of formic acid from water should be able to overcome these complex interactions.

The LLE data were determined for (water + formic acid + 2-methylpropyl ethanoate) ternary mixture by cloud point method at $T = (293.15\text{-}323.15)$ K and atmospheric pressure. The tie lines compositions were determined using refractive index measurements of the cloudy samples and the experimental data were correlated by applying two local composition models (NRTL and UNIQUAC). In addition, the reliability of the tie-line data was examined by the Othmer-Tobias [17] and Hand [18] equations.

EXPERIMENTAL

Materials

In Table 1, details of the chemicals used in this study are shown. Formic acid and 2-methylpropyl ethanoate were purchased from Merck and used without further purification. During the experiments, bidistilled water was used. The measured refractive indices of the pure substances along with the corresponding literature values are given in Table 1 [9,19-20].

Apparatus and Procedure

The solubility and tie-line data were obtained for (water + formic acid + 2-methylpropyl ethanoate) ternary mixture at $T = (293.15\text{-}323.15)$ K using a jacketed glass extraction cell with about 10 cm^3 volume. The isothermal conditions were provided by connecting the cell to a thermostat (RE 104, LAUDA, Germany) with an accuracy of ±0.1 K. The experiments were performed in two steps. First, calibration curves were determined from solubility data obtained by the cloud point method [21] at each temperature. In this method, known compositions of binary mixtures in the water-rich (water + formic acid) and solvent-rich (2-methylpropyl ethanoate + formic acid) regions were prepared in a glass extraction cell gravimetrically and stirred enough. Then, the binary mixtures were titrated by the third component (water or 2-methylpropyl ethanoate) until the cloudy samples were observed (end point). The refractive index of the samples was measured with an

automatic refractometer (Abbemat 3200, Anton Paar) with an accuracy of 0.0001 and the standard curves were generated. Figure 1 represents a typical standard curve for formic acid in aqueous and organic phases at 293.15 K. Second, different known compositions of water, formic acid and 2-methylpropyl ethanoate were introduced into the glass equilibrium cells. An Axis balance (ALN220 model) with the uncertainty of ±0.1 mg was used for the weighing. The mixtures were shaken sufficiently and left to settle down into a raffinate and extract phases for 12 h inside a water bath. The samples from each phase were taken by glass syringes with a capacity of 5 ml and their refractive indices were measured. The composition of each phase was obtained by the standard curves with an uncertainty of less than $\pm 1 \times 10^{-4}$ in mass fraction.

RESULTS AND DISCUSSION

Experiments

The experimental tie-line data for (water + formic acid + 2-methylpropyl ethanoate) ternary mixture at $T = (293.15\text{-}323.15)$ K and atmospheric pressure are reported in Table 2 and are graphically represented in Figs. 2 and 3. The compositions were expressed in mass fraction (w_i, $i = 1, 2, 3$).

The binary mixtures (water + formic acid) and (formic acid + 2-methylpropyl ethanoate) are miscible and water + 2-methylpropyl ethanoate mixture is partially miscible so the ternary mixture is classified as Treybal's type I. It is found that the effect of temperature on the immiscible region is insignificant in the studied temperature range.

It can be seen from the figures that the solubility of formic acid in the water-rich phase is more than that in the solvent-rich phase. Both formic acid and water have hydrogen-bonding interactions in their pure liquid state. A new H-bond is formed between the acid and water due to the presence of the hydrophilic -COOH group in water-rich regions. The more solubility of formic acid in the aqueous phase is due to the special interactions and the high affinity of formic acid for water. The following equations were applied to calculate the distribution coefficient (D) and the separation factor (S), as a measure of the suitability of the solvent for extraction. The results are shown in Table 3 and graphically in Figs. 4-5.

Table 1. Components, Supplier, CAS Number and Refractive Index n_D^{20} of the Pure Components at 293.15 K along with the Literature Values

Component	Supplier	CAS number	n_D^{20}	
			Expt.	Lit.
2-Methylpropyl ethanoate	Merck	110-19-0	1.3901	1.3905[19]
Formic acid	Merck	64-18-6	1.3712	1.3714[9]
Bidistilled water			1.3330	1.3330[20]

Standard uncertainties u is $u(n_D) = 1 \times 10^{-4}$ and $u(T) = 0.05$ K.
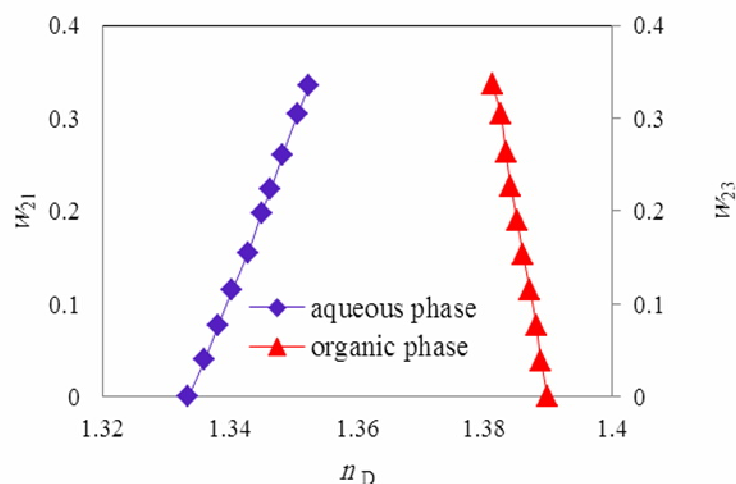

Fig. 1. The concentration of formic acid against the refractive index for cloudy solutions in aqueous (♦) and organic (▲) phases at 293.15 K.

$$S = \frac{D_2}{D_1} \tag{1}$$

$$D_i = \frac{w_{i3}}{w_{i1}} \tag{2}$$

where w_{i1} and w_{i3} are mass fractions of the component i in the aqueous and organic phases, respectively.

It can be seen from Table 3 that all separation factors are higher than one indicating that the extraction of formic acid from the aqueous solutions is possible. The values of the separation factors of 2-methylpropyl ethanoate were compared with the corresponding values for ethyl ethanoate and butyl ethanoate at 291.15 K[15]. The sequence of the separation factors for the solvents is butyl ethanoate > ethyl ethanoate > 2-methylpropyl ethanoate.

Correlations

The Othmer-Tobias, and Hand correlation equations were applied to validate the reliability of the LLE experimental data as following:

$$Ln\left(\frac{1 - w_{33}}{w_{33}}\right) = a_1 + b_1\, Ln\left(\frac{1 - w_{11}}{w_{11}}\right) \tag{3}$$

Table 2. Experimental Tie-line Data for a Ternary Mixture of Water (1) + Formic Acid (2) + 2-Methylpropyl Ethanoate (3) at (293.15 and 323.15) K and Atmospheric Pressure

	Water-rich phase				Solvent-rich phase		
w_{11}	w_{21}	w_{31}		w_{13}	w_{23}	w_{33}
			293.15 K				
0.8924	0.0603	0.0473		0.0219	0.0212	0.9569
0.8332	0.1157	0.0511		0.0253	0.0409	0.9338
0.7854	0.1604	0.0542		0.0286	0.0606	0.9108
0.7434	0.1997	0.0569		0.0319	0.0804	0.8877
0.7052	0.2354	0.0594		0.0353	0.1001	0.8646
0.6727	0.2658	0.0615		0.0386	0.1199	0.8415
0.6116	0.3230	0.0654		0.0452	0.1594	0.7954
			303.15 K				
0.8811	0.0606	0.0583		0.0479	0.0409	0.9112
0.8251	0.1095	0.0654		0.0524	0.0551	0.8925
0.7669	0.1603	0.0728		0.0580	0.0728	0.8692
0.726	0.1961	0.0779		0.0624	0.0870	0.8506
0.6873	0.2299	0.0828		0.0669	0.1011	0.8320
0.6442	0.2675	0.0883		0.0736	0.1224	0.8040
0.5818	0.3221	0.0961		0.0825	0.1507	0.7668
			313.15 K				
0.8795	0.0675	0.0530		0.0284	0.0268	0.9448
0.8265	0.1143	0.0592		0.0314	0.0372	0.9314
0.7734	0.1611	0.0655		0.0364	0.0547	0.9089
0.725	0.2039	0.0711		0.0405	0.0686	0.8909
0.6882	0.2364	0.0754		0.0445	0.0825	0.8730
0.649	0.2711	0.0799		0.0495	0.1000	0.8505
0.5798	0.3321	0.0881		0.0596	0.1348	0.8056
			323.15 K				
0.8772	0.0685	0.0543		0.0612	0.0259	0.9129
0.8162	0.1269	0.0569		0.0670	0.0405	0.8925
0.7645	0.1763	0.0592		0.0714	0.0514	0.8772
0.7246	0.2145	0.0609		0.0758	0.0623	0.8619
0.6823	0.2549	0.0628		0.0802	0.0732	0.8466
0.6471	0.2886	0.0643		0.0861	0.0877	0.8262
0.5837	0.3492	0.0671		0.1022	0.1277	0.7701

Standard uncertainties are $u(w) = 1 \times 10^{-4}$ and $u(T) = 0.1$ K.

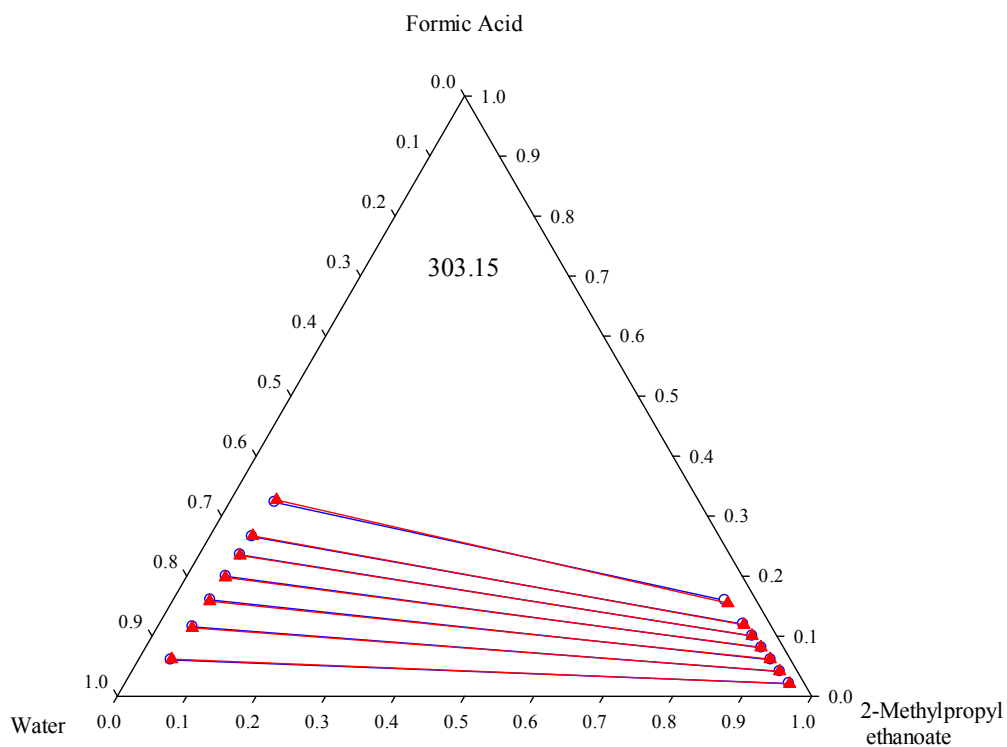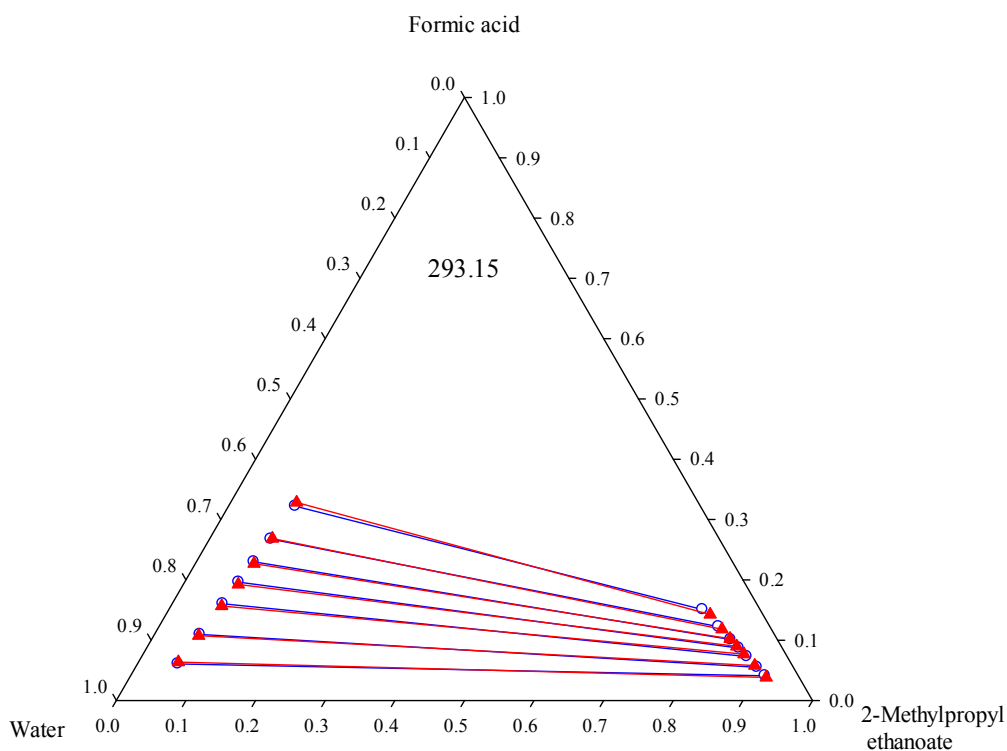**Fig. 2.** Ternary phase diagram of LLE for water + formic acid + 2-methylpropyl ethanoate system at $T = 293.15$-323.15 K: (○-○) experimental tie-line data; (▲-▲) calculated NRTL tie-line data.
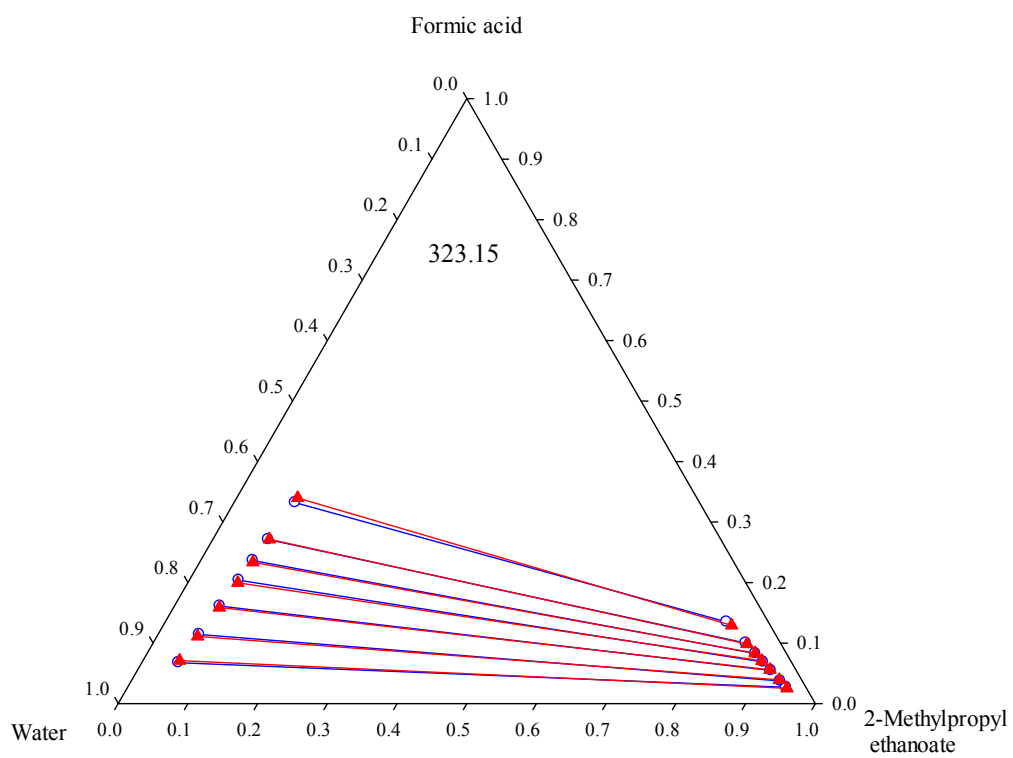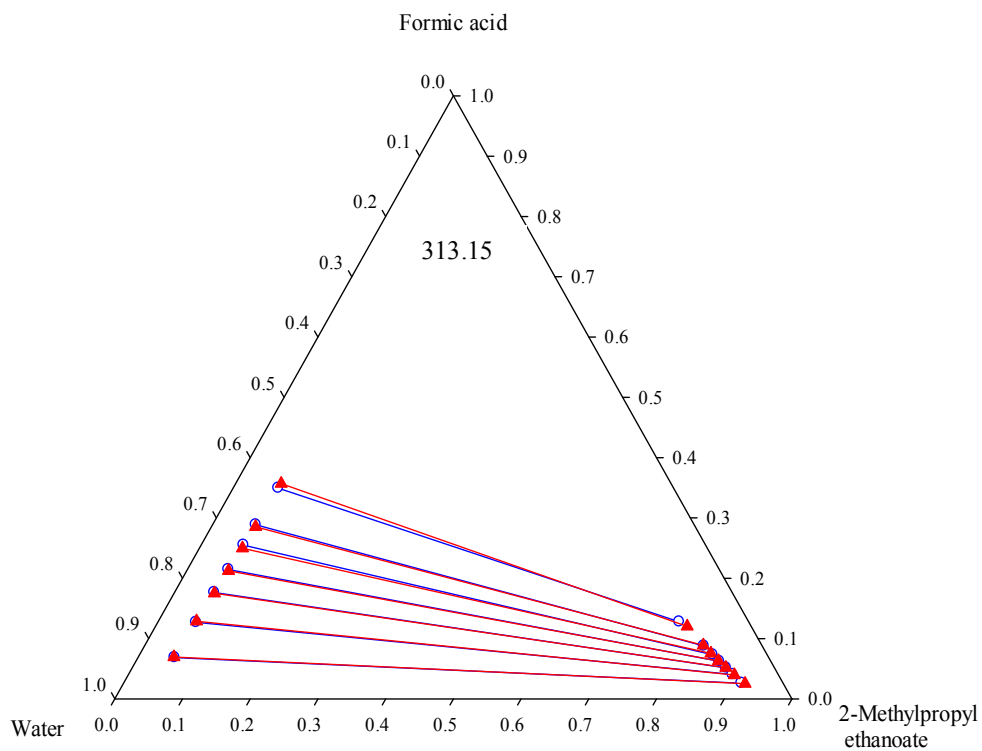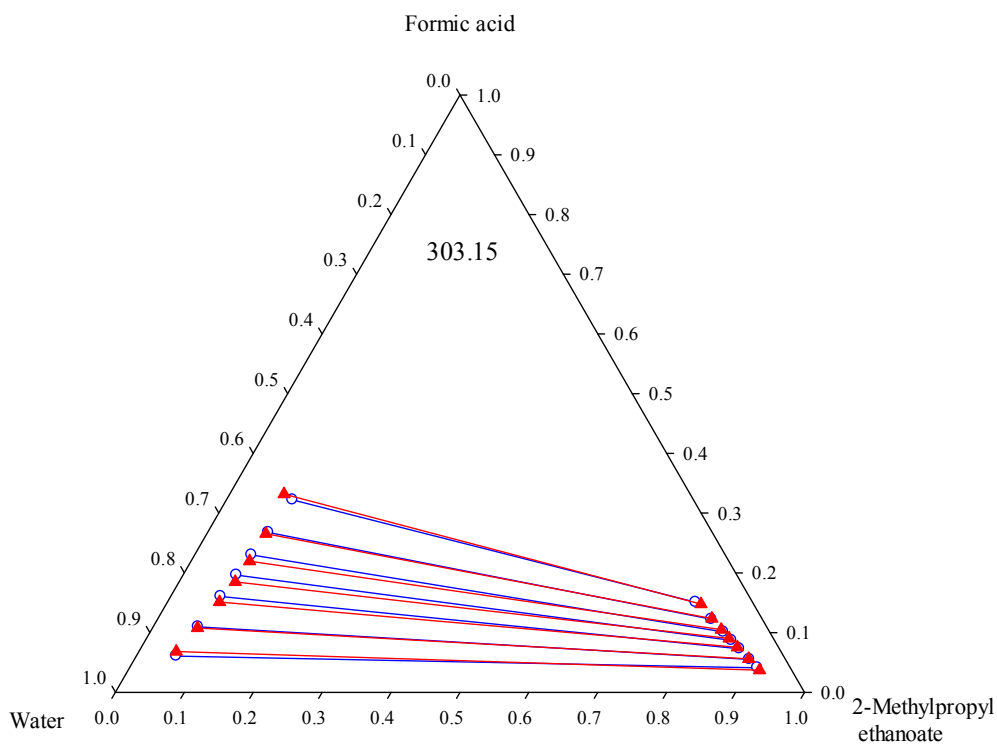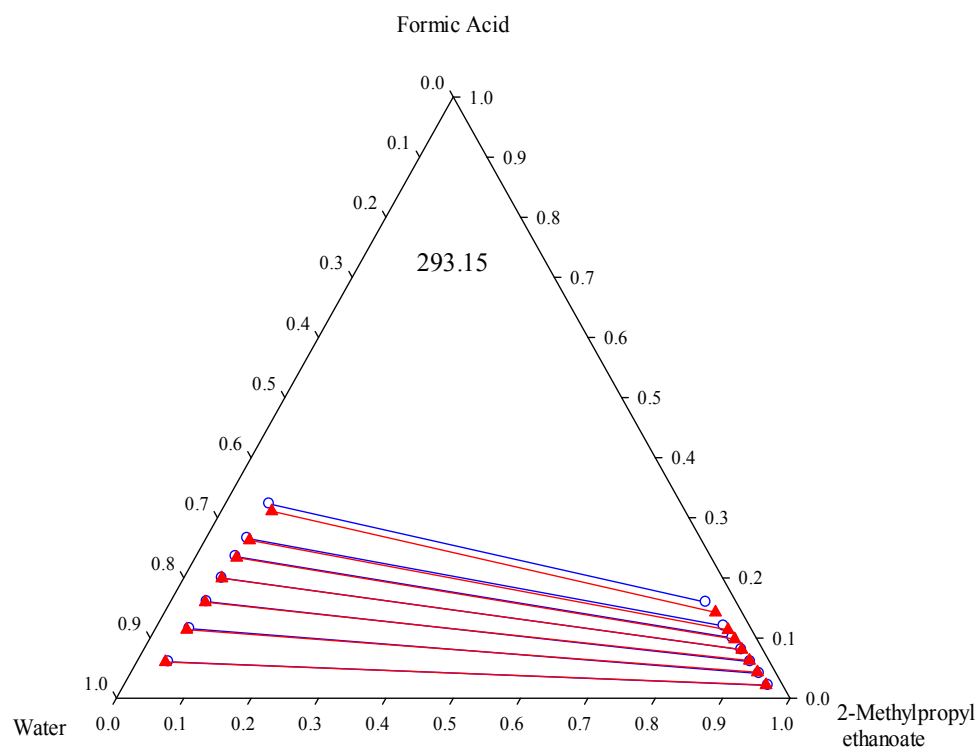
Fig. 2. Continued.

Fig. 3. Ternary phase diagram of LLE for water + formic acid + 2-methylpropyl ethanoate system at T = 293.15-323.15 K: (○-○), experimental tie-line data; (▲-▲) calculated UNIQUAC tie-line data.
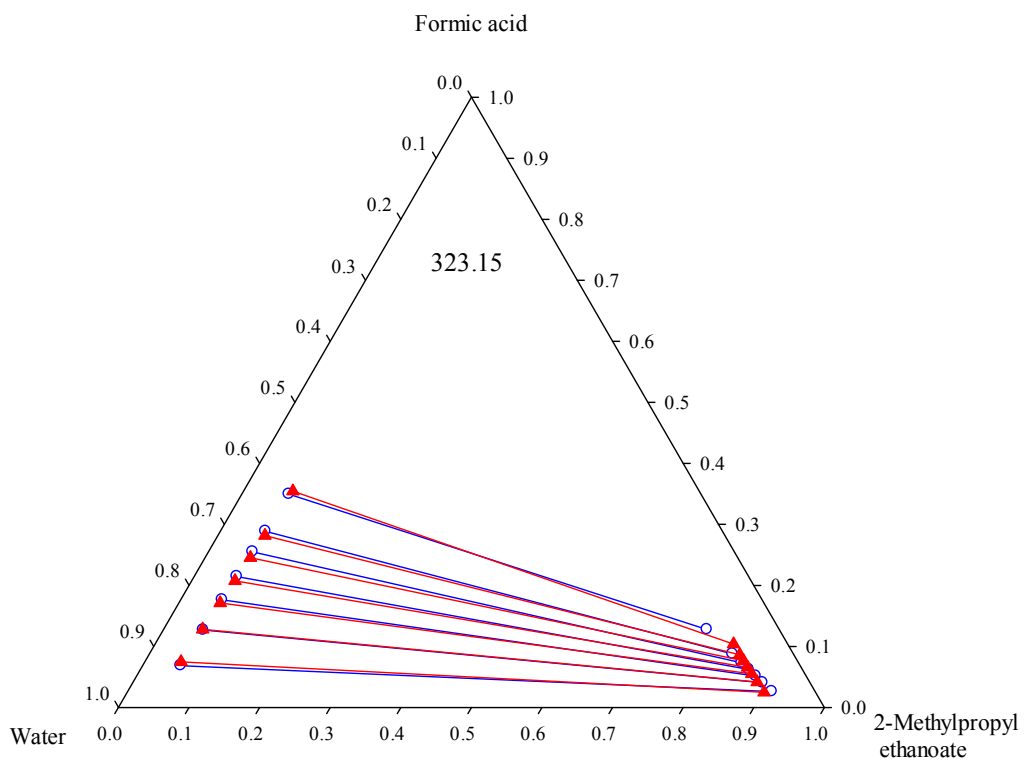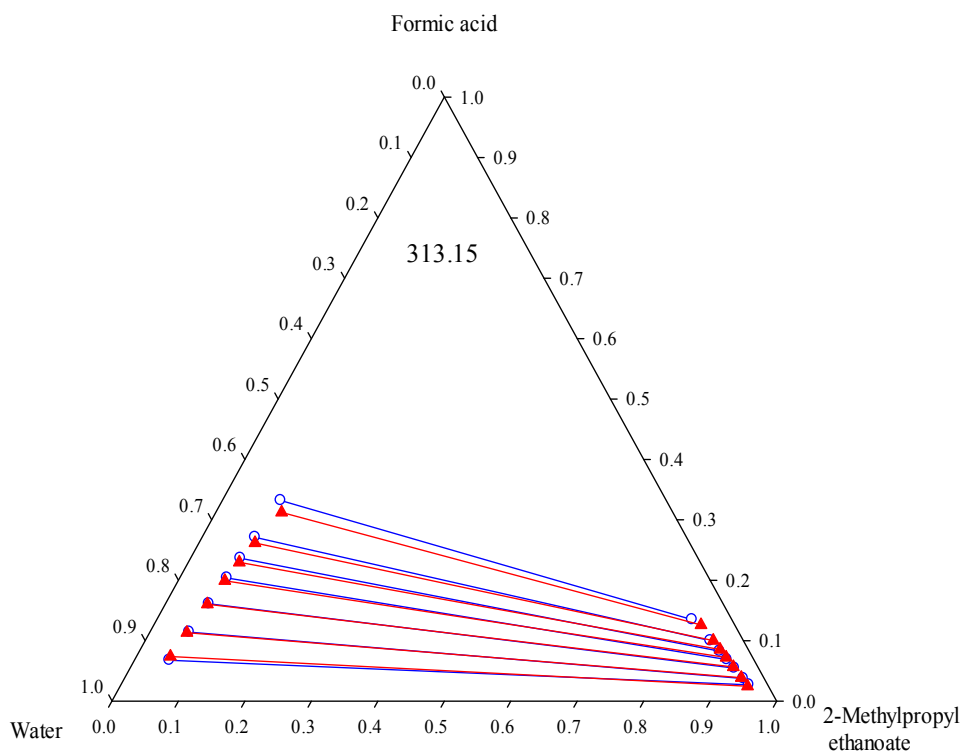
Fig. 3. Continued.

Table 3. Distribution Coefficients for Water (D_1), Formic Acid (D_2)
and Separation Factor (S) in a Ternary System of Water (1)
+ Formic Acid (2) + 2-Methylpropyl Ethanoate (3)

D_1	D_2	S
	293.15 K	
0.0245	0.3516	14.33
0.0304	0.3535	11.64
0.0364	0.3778	10.38
0.0429	0.4026	9.38
0.0501	0.4252	8.50
0.0574	0.4511	7.86
0.0739	0.4935	6.68
	303.15 K	
0.0544	0.6749	12.41
0.0635	0.5032	7.92
0.0756	0.4541	6.00
0.0860	0.4437	5.16
0.0973	0.4398	4.52
0.1143	0.4576	4.00
0.1418	0.4679	3.30
	313.15 K	
0.0323	0.3970	12.30
0.0380	0.3255	8.57
0.0471	0.3395	7.21
0.0559	0.3364	6.02
0.0647	0.3490	5.40
0.0763	0.3689	4.84
0.1028	0.4059	3.95
	323.15 K	
0.0698	0.3781	5.42
0.0821	0.3191	3.89
0.0934	0.2915	3.12
0.1046	0.2904	2.78
0.1175	0.2872	2.44
0.1331	0.3039	2.28
0.1751	0.3657	2.09

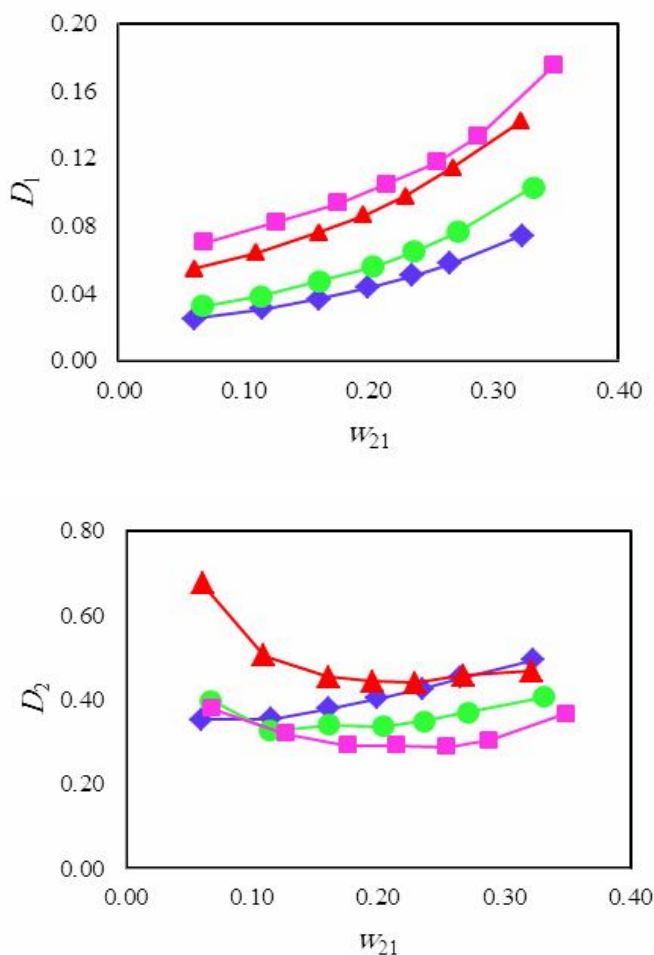Standard uncertainties u are $u(w) = 1 \times 10^{-4}$ and $u(T) = 0.1$ K.

Fig. 4. Distribution coefficients of water (D_1) and formic acid (D_2) against the concentration of formic acid in aqueous phase (w_{21}) at 293.15 K (♦), 303.15 K (▲), 313.15 K (●) and 323.15 K (■).

$$Ln\left(\frac{w_{23}}{w_{33}}\right) = a_2 + b_2\, Ln\left(\frac{w_{21}}{w_{11}}\right) \tag{4}$$

where w_{11} is the mass fraction of water in the water-rich phase, and w_{33} is the mass fraction of 2-methylpropyl ethanoate in solvent-rich phase.

Table 4 reports the parameters of Othmer-Tobias and Hand equations, (a_1, b_1) and (a_2, b_2), respectively. Figure 6 represents the correlations. The values of linear correlation coefficients, R^2, display good consistency of the LLE data.

Furthermore, the NRTL[22] and UNIQUAC[23] models (local composition models) were used to correlate the

experimental LLE data. The binary interaction parameters of the models were obtained by Aspen Plus simulator and are collected in Table 5 together with the root-mean-square deviation (RMSD), as a measure of the quality of the correlations. The graphical representation of the correlations is given in Figs. 2-3.

$$\text{RMSD} = \sqrt{\frac{\sum_i \sum_m \sum_n (w_{imn}^{\exp} - w_{imn}^{cal})^2}{6N}} \tag{5}$$

Where, w is mass fraction of the tie line, the subscripts i, m and n index the numbe of components (i = 1, 2, 3),
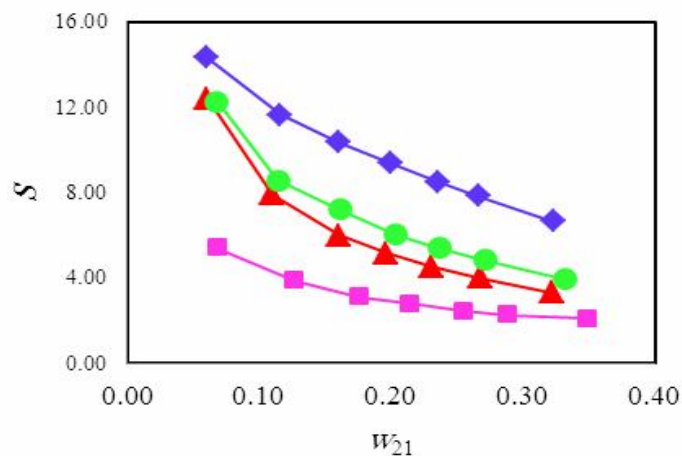
Fig. 5. Separation factor, S, as a function of concentration of formic acid in aqueous phase (w_{21}) at 293.15 K (♦), 303.15 K (▲), 313.15 K (●) and 323.15 K (■).

Table 4. The Parameters of Othmer-Tobias and Hand Equations

T (K)	a_1	b_1	R^2
	Othmer-Tobias		
293.15	-0.922	1.052	0.996
303.15	-1.028	0.683	0.983
313.15	-1.219	0.856	0.986
323.15	-1.130	0.660	0.951
	Hand		

T (K)	a_2	b_2	R^2
293.15	0.893	0.928	0.997
303.15	1.756	1.379	0.980
313.15	1.511	1.109	0.986
323.15	1.789	1.178	0.970

phases (m = I, II) and tie-lines (n = 1, 2,….., N), respectively, and the superscript *exp* and *cal* index the experimental and calculated data.

CONCLUSIONS

The LLE data for a ternary system (water + formic acid + 2-methylpropyl ethanoate) were determined at (293.15-
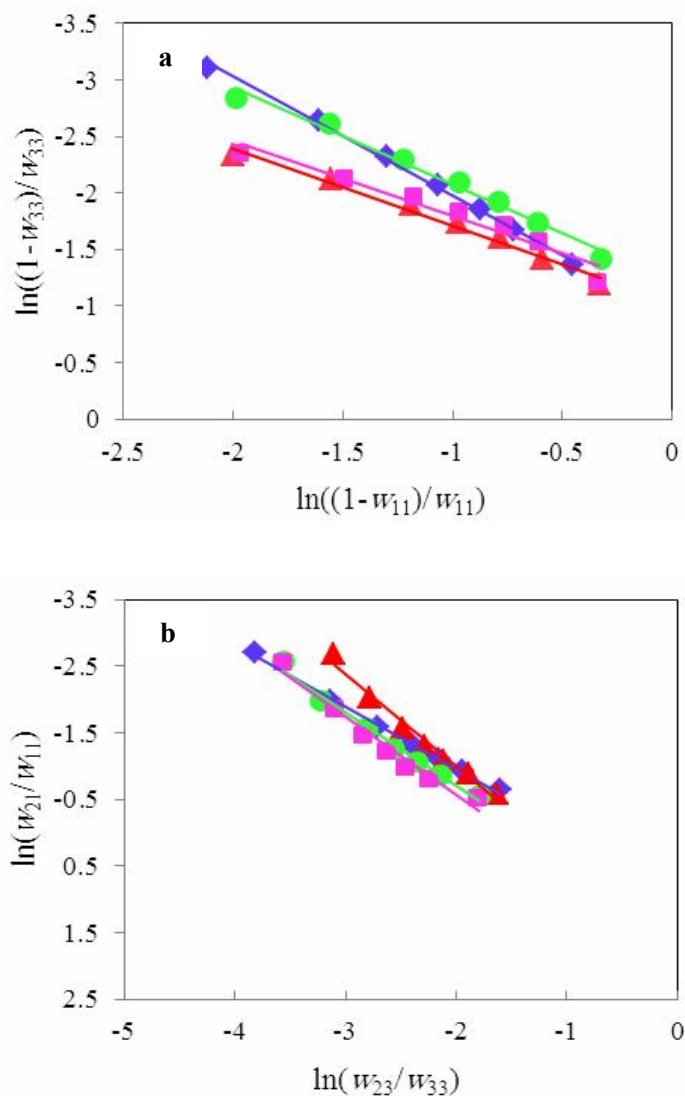
Fig. 6. Graphical representation of the correlation equations for LLE data of the ternary system of water + formic acid + 2-methylpropyl ethanoate at 293.15 K (♦), 303.15 K (▲), 313.15 K (●) and 323.15 K (■), (a) Othmer-Tobias (b) Hand.

323.15) K temperature range. The results show that the effect of temperature on the equilibrium data is negligible. The experimental data were correlated using two local composition models (NRTL and UNIQUAC). The RMSD values for the models are 0.0123 and 0.0144, respectively. The mixture has only one partially miscible pair, so it is classified as Treybal type I. It is found that the solubility of formic acid in the water-rich phase is more than that in the solvent-rich phase. The separation factors (*S*) and

distribution coefficients (*D*) were calculated. The separation factor values show that 2-methylpropyl ethanoate can extract formic acid from aqueous solutions.

ACKNOWLEDGMENTS

Table 5. The Binary Interaction Parameters of NRTL and UNIQUAC Models along with the RMSD Values for a Ternary System Consisting Water (1) + Formic Acid (2) + 2-Methylpropyl Ethanoate (3)

T (K)	i-j	NRTL ($\alpha = 0.2$) b_{ij}	b_{ji}	RMSD	UNIQUAC b_{ij}	b_{ji}	RMSD
293.15	1-2	77.145	-1077.631	0.0018	2564.970	-192.282	0.0058
	1-3	-2143.32	-5695.386		-47.867	-866.595	
	2-3	7800.339	-2066.116		-866.904	2621.053	
303.15	1-2	2512.853	-1437.094	0.0041	-18.832	-115.345	0.0057
	1-3	-2029.057	-5961.394		189.8686	-1746.48	
	2-3	18000	-442.354		-1421.88	-279.535	
313.15	1-2	2349.377	-1535.585	0.0031	49.858	18.911	0.006
	1-3	-2219.698	-5656.634		-46.378	-866.975	
	2-3	18000	-481.618		-595.377	135.731	
323.15	1-2	1446.208	-1881.516	0.0039	-220.097	-227.177	0.0108
	1-3	-2094.790	18000		-154.418	-465.859	
	2-3	18000	-548.4		-14546.487	-138.883	

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