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# Phase equilibrium data for aqueous solutions of formic acid with 2-ethyl-1-hexanol at *T*=(298.2, 308.2, 318.2, and 328.2) K

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**Abstract**−Liquid-liquid equilibrium (LLE) data for the system of (water+formic acid+2-ethyl-1-hexanol) were experimentally determined at T=(298.2, 308.2, 318.2, and 328.2) K and atmospheric pressure. A type-2 LLE was obtained for this ternary system. The influence of temperature on the equilibrium characteristics was found to be smallat the temperatures studied. Distribution coefficients and separation factors were calculated over the immiscibility regions. The experimental tie-line data were correlated using the UNIQUAC model. The values of the interaction parameters between each pair of the components were obtained for this thermodynamic model. The root mean square deviation (RMSD) between the observed and calculated mass fractions was 0.61%.

Key words: Liquid-liquid Equilibrium, Tie-line Data, Formic Acid, 2-Ethyl-1-hexanol, UNIQUAC Model, Separation Factor, Distribution Coefficient

## INTRODUCTION

Separation of carboxylic acids from water resulting from fermentation processes or synthetic methods is chemically and industrially important [1-4]. Certain carboxylic acids have important applications in chemical, bio-chemical, beverage, food, cosmetic and pharmaceutical industries. Therefore, precise LLE data are needed in design of many chemical processes, and in the fermentation industry. The LLE studies of various ternary systems including carboxylic acids have been the subject of much interest in recent years [5-12].

Formic acid (FA, H-COOH), which is the simplest carboxylic acid, has many chemical and industrial applications [13,14]. Pure FA is a colorless, toxic, corrosive liquid having a highly pungent odor. It is miscible with water and most polar organic solvents. It can be produced by chemical synthetic or fermentation methods. Therefore, the extraction of this acid from water using liquid extraction technique is an important problem [15-19]. In the past, several authors have reported important LLE data for the aqueous solutions of FA with various organic solvents [20,21]. As far we are aware, heavy alcohols [22] and esters [23-25] have mainly been tested for extraction of FA from water and the phase equilibrium data of the related systems are presented in the literature.

In the present work, 2-ethyl-1-hexanol (2EH) was chosen as an organic solvent for the LLE investigation of ternary system consisting of water, FA, and 2EH T=(298.2, 308.2, 318.2, and 328.2) K, where no such data are available in the literature. 2EH is a branched primary alcohol that has a suitable molecular structure, low cost, high boiling point, and very low solubility in water. It is therefore, a good solvent for industrial application. Distribution coefficients and separation factors were calculated from the tie-line data to establish the possibility of the use of this solvent for the separation of FA from water. The experimental LLE data are correlated using the universal quasi chemical (UNIQUAC) method of Abrams and Prausnitz [26]. This model depends on optimized interaction parameters between each pair of components in the system, which can be obtained by experiment. The values for the binary interaction parameters were obtained for this equilibrium model.

## EXPERIMENTAL

### 1. Material

The supplier, purity, and some properties for the organic chemicals used in this study are listed in Table 1. The organic chemicals were dried over molecular sieves (Merck 4 Å. Deionized and redistilled water with an electrical conductivity less than 5 μS/cm was used throughout all experiments. All materials were used as received without any further purification.

### 2. Apparatus and Procedure

The sample weighting was carriedout with an AND electronic analytical balance (model HR-200) with an accuracy of ±0.0001 g. Refractive indices and densities of the pure liquids were measured with an Abbe Refractometer (Model CETI) and a DA210 (Kyoto electronic) density meter, respectively. The uncertainties in the refractive index and density measurements were ±0.0002 and ±0.01 kg $m^{-3}$, respectively.

The binodal curves for the ternary mixtures were determined by the cloud point method. The prepared binary mixtures of known compositions were introduced into the glass cell. The temperature of the cell was controlled by a water jacket and maintained with an accuracy of within ±0.1 K. At each temperature, the third component was progressively added using a Brand Transferpette micropipette (with an accuracy of ±0.001 ml). The end point was determined by observing the transition from a homogeneous to a heterogeneous

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**Table 1. Supplier, purity, the measured and literature physical properties of the materials at T=298.2 K**

| Component | Supplier | Mass fraction purity | $n_D$ | | $\rho$/(kgm$^{-3}$) | |
|---|---|---|---|---|---|---|
| | | | Exp. | Lit. | Exp. | Lit. |
| Formic acid (FA) | Merck | >0.99 | 1.3712 | 1.3714 [21] | 1219.3 | 1220.0 [21] |
| 2-Ethyl-1-hexanol (2EH) | Merck | >0.99 | 1.4292 | 1.4293 [32] | 830.20 | 830.62 [32] |
| Water | Deionized distilled | >0.999 | 1.3325 | 1.3325 [32] | 997.09 | 997.04 [32] |

**Table 2. Solubility data in mass fractions ($w_i$) for (water+formic acid+2-ethyl-1-hexanol) at T=(298.2, 308.2, 318.2, and 328.2) K[a]**

| *T*=298.2 K | | | *T*=308.2 K | | | *T*=318.2 K | | | *T*=328.2 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $w_1$ (water) | $w_2$ (FA) | $w_3$ (2EH) | $w_1$ (water) | $w_2$ (FA) | $w_3$ (2EH) | $w_1$ (water) | $w_2$ (FA) | $w_3$ (2EH) | $w_1$ (water) | $w_2$ (FA) | $w_3$ (2EH) |
| 1.0000 | 0.0000 | 0.0000 | 0.9999 | 0.0000 | 0.0001 | 0.9995 | 0.0000 | 0.0005 | 0.9992 | 0.0000 | 0.0008 |
| 0.8988 | 0.1010 | 0.0002 | 0.8950 | 0.1000 | 0.0050 | 0.8979 | 0.1013 | 0.0008 | 0.9409 | 0.0569 | 0.0022 |
| 0.7991 | 0.2000 | 0.0009 | 0.7987 | 0.2000 | 0.0013 | 0.7956 | 0.2024 | 0.0020 | 0.8968 | 0.1015 | 0.0017 |
| 0.6995 | 0.2987 | 0.0018 | 0.6923 | 0.3055 | 0.0022 | 0.6910 | 0.3049 | 0.0041 | 0.7961 | 0.2010 | 0.0029 |
| 0.5963 | 0.4007 | 0.0030 | 0.5973 | 0.3986 | 0.0041 | 0.5951 | 0.3987 | 0.0062 | 0.6949 | 0.3009 | 0.0042 |
| 0.4981 | 0.4988 | 0.0031 | 0.4969 | 0.4969 | 0.0062 | 0.4971 | 0.4947 | 0.0082 | 0.5957 | 0.3981 | 0.0062 |
| 0.3980 | 0.5958 | 0.0062 | 0.3961 | 0.5946 | 0.0093 | 0.3975 | 0.5923 | 0.0102 | 0.4942 | 0.4976 | 0.0082 |
| 0.2968 | 0.6938 | 0.0094 | 0.2964 | 0.6893 | 0.0143 | 0.2936 | 0.6886 | 0.0178 | 0.3967 | 0.5931 | 0.0102 |
| 0.2466 | 0.7402 | 0.0132 | 0.2459 | 0.7357 | 0.0184 | 0.1932 | 0.7690 | 0.0378 | 0.2944 | 0.6873 | 0.0183 |
| 0.1930 | 0.7718 | 0.0352 | 0.1936 | 0.7693 | 0.0371 | 0.1000 | 0.7700 | 0.1300 | 0.1918 | 0.7628 | 0.0454 |
| 0.0940 | 0.7800 | 0.1260 | 0.0970 | 0.7760 | 0.1270 | 0.0430 | 0.7350 | 0.2220 | 0.1150 | 0.7620 | 0.1230 |
| 0.0410 | 0.7460 | 0.2130 | 0.0420 | 0.7400 | 0.2180 | 0.0000 | 0.6600 | 0.3400 | 0.0443 | 0.7310 | 0.2247 |
| 0.0000 | 0.6800 | 0.3200 | 0.0000 | 0.6700 | 0.3300 | 0.0060 | 0.0000 | 0.9940 | 0.0000 | 0.6570 | 0.3430 |
| 0.0050 | 0.0000 | 0.9950 | 0.0060 | 0.0000 | 0.9940 | 0.0230 | 0.0400 | 0.9370 | 0.0070 | 0.0000 | 0.9930 |
| 0.0190 | 0.0440 | 0.9370 | 0.0210 | 0.0437 | 0.9353 | 0.0319 | 0.0968 | 0.8713 | 0.0240 | 0.0393 | 0.9367 |
| 0.0282 | 0.0972 | 0.8746 | 0.0301 | 0.0970 | 0.8729 | 0.0329 | 0.1934 | 0.7737 | 0.0319 | 0.0968 | 0.8713 |
| 0.0291 | 0.1942 | 0.7767 | 0.0310 | 0.1938 | 0.7752 | 0.0325 | 0.2424 | 0.7251 | 0.0329 | 0.1934 | 0.7737 |
| 0.0220 | 0.2350 | 0.7430 | 0.0290 | 0.2370 | 0.7340 | 0.0310 | 0.2730 | 0.6960 | 0.0310 | 0.2730 | 0.6960 |
| 0.0000 | 0.2800 | 0.7200 | 0.0000 | 0.3000 | 0.7000 | 0.0000 | 0.3200 | 0.6800 | 0.0000 | 0.3250 | 0.6750 |

mixture. The uncertainty in the mass fraction of the solubility data was estimated to be better than ±0.0008. Table 2 summarizes the experimental cloud point data for this ternary system at each temperature.

A 250 cm$^3$ glass cell connected to a thermostat was made to measure the LLE data. The equilibrium data were determined by preparing the ternary mixtures of known compositions. The prepared mixtures were introduced into the extraction cell and were stirred for 4 h, and then left to settle for 4 h for phase separation. After being allowed to reach equilibrium, samples were carefully taken from each phase and analyzed. The two phases were analyzed by direct titration of weighted sample against 0.1 N sodium hydroxide with phenolphthalein as the indicator. The uncertainty in the mass fraction of the tie-line data was estimated to be better than ±0.001.

**Table 3. Experimental and UNIQUAC correlated tie-line data for the (water+formic acid+2-ethyl-1-hexanol) ternary system at T=(298.2, 308.2, 318.2, and 328.2) K and atmospheric pressure[a]**

| Aqueous phase | | | | Organic phase | | | |
|---|---|---|---|---|---|---|---|
| $w_1$ (water) | | $w_2$ (FA) | | $w_1$ (water) | | $w_2$ (FA) | |
| Exp | UNIQUAC | Exp | UNIQUAC | Exp | UNIQUAC | Exp | UNIQUAC |
| T=298.2 K | | | | | | | |
| 0.844 | 0.839 | 0.149 | 0.154 | 0.028 | 0.028 | 0.076 | 0.074 |
| 0.727 | 0.733 | 0.265 | 0.259 | 0.029 | 0.029 | 0.129 | 0.125 |
| 0.629 | 0.636 | 0.361 | 0.354 | 0.030 | 0.029 | 0.169 | 0.171 |
| 0.548 | 0.553 | 0.440 | 0.435 | 0.031 | 0.030 | 0.200 | 0.207 |
| 0.485 | 0.487 | 0.502 | 0.499 | 0.029 | 0.030 | 0.228 | 0.232 |
| 0.427 | 0.414 | 0.556 | 0.570 | 0.028 | 0.030 | 0.250 | 0.253 |

**Table 3. Continued**

| Aqueous phase | | | | Organic phase | | | |
|---|---|---|---|---|---|---|---|
| $w_1$ (water) | | $w_2$ (FA) | | $w_1$ (water) | | $w_2$ (FA) | |
| Exp | UNIQUAC | Exp | UNIQUAC | Exp | UNIQUAC | Exp | UNIQUAC |
| T=308.2 K | | | | | | | |
| 0.849 | 0.845 | 0.143 | 0.147 | 0.029 | 0.029 | 0.083 | 0.078 |
| 0.726 | 0.730 | 0.264 | 0.260 | 0.030 | 0.029 | 0.136 | 0.138 |
| 0.636 | 0.642 | 0.353 | 0.346 | 0.031 | 0.030 | 0.181 | 0.183 |
| 0.559 | 0.555 | 0.426 | 0.430 | 0.032 | 0.031 | 0.218 | 0.226 |
| 0.491 | 0.489 | 0.492 | 0.494 | 0.030 | 0.031 | 0.251 | 0.255 |
| 0.438 | 0.433 | 0.544 | 0.548 | 0.029 | 0.031 | 0.276 | 0.277 |
| T=318.2 K | | | | | | | |
| 0.870 | 0.860 | 0.120 | 0.130 | 0.030 | 0.029 | 0.102 | 0.088 |
| 0.747 | 0.744 | 0.240 | 0.243 | 0.031 | 0.031 | 0.157 | 0.164 |
| 0.667 | 0.675 | 0.319 | 0.310 | 0.032 | 0.032 | 0.200 | 0.206 |
| 0.573 | 0.587 | 0.410 | 0.395 | 0.034 | 0.033 | 0.237 | 0.252 |
| 0.504 | 0.519 | 0.477 | 0.460 | 0.033 | 0.034 | 0.268 | 0.279 |
| 0.441 | 0.428 | 0.532 | 0.547 | 0.031 | 0.034 | 0.294 | 0.294 |
| T=328.2 K | | | | | | | |
| 0.864 | 0.858 | 0.128 | 0.134 | 0.030 | 0.028 | 0.095 | 0.085 |
| 0.739 | 0.744 | 0.250 | 0.245 | 0.031 | 0.030 | 0.148 | 0.154 |
| 0.649 | 0.656 | 0.338 | 0.331 | 0.033 | 0.032 | 0.198 | 0.203 |
| 0.569 | 0.574 | 0.415 | 0.410 | 0.034 | 0.033 | 0.233 | 0.243 |
| 0.499 | 0.496 | 0.482 | 0.485 | 0.032 | 0.034 | 0.266 | 0.274 |
| 0.438 | 0.421 | 0.538 | 0.556 | 0.030 | 0.034 | 0.291 | 0.294 |

The uncertainties u are u(w)=0.001, u(T)=0.1 K

## RESULTS AND DISCUSSION

### 1. LLE Measurements

The LLE measurements for the ternary system of (water+FA+2EH) were made at T=(298.2, 308.2, 318.2, and 328.2) K and atmospheric pressure. Table 3 summarizes the experimental LLE data for this ternary system at each temperature. The LLE diagrams at various temperatures for the investigated system are plotted in Figs. 1 to 4. Since (2EH+water) and (2EH+FA) are two liquid pairs that are partially miscible and the only liquid pair (water+FA) is com-

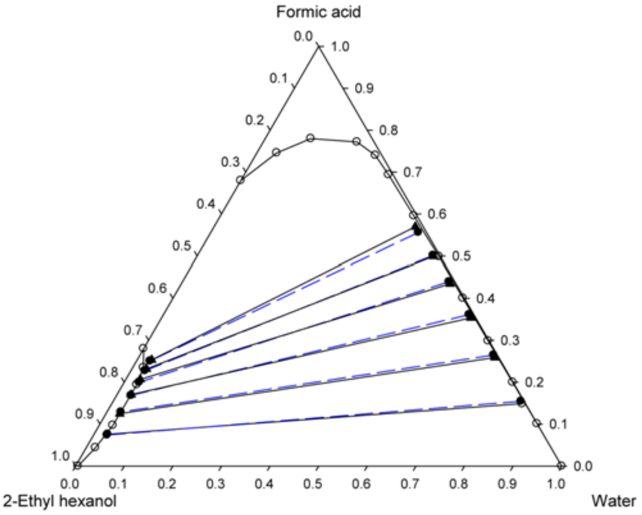

**Fig. 1.** Ternary diagram for LLE of [water (1)+formic acid (2)+2-ethyl-1-hexanol (3)] at T=298.2 K; (-○-) experimental solubility curve, (-●-) experimental tie-line data, (--▲--) calculated UNIQUAC data.

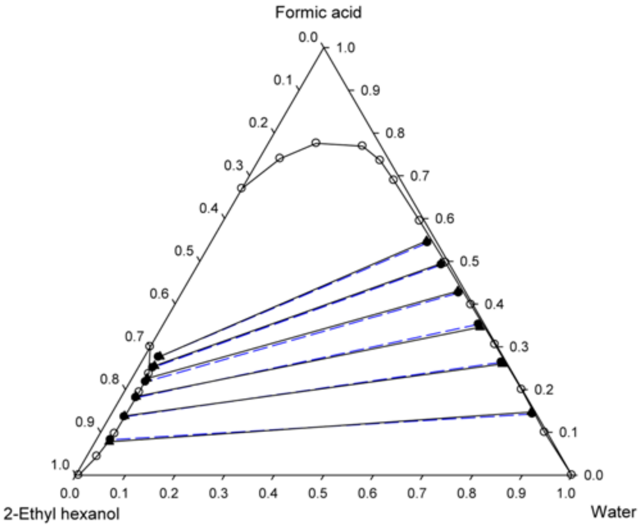

**Fig. 2.** Ternary diagram for LLE of [water (1)+formic acid (2)+2-ethyl-1-hexanol (3)] at T=308.2 K; (-○-) experimental solubility curve, (-●-) experimental tie-line data, (--▲--) calculated UNIQUAC data.

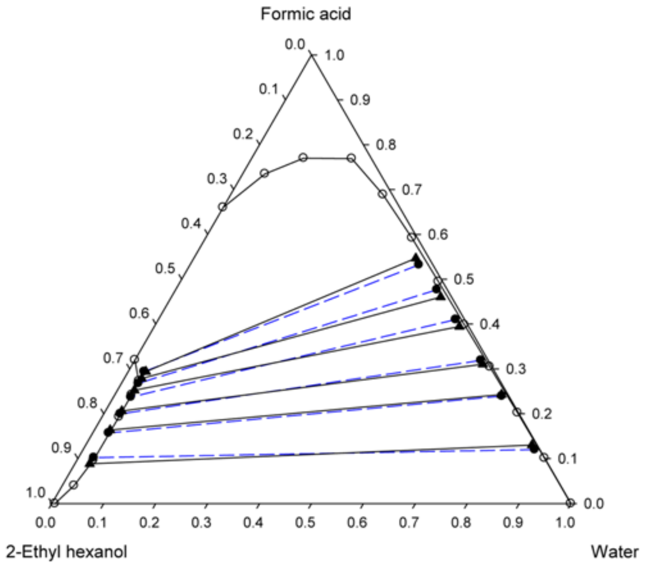

**Fig. 3. Ternary diagram for LLE of [water (1)+formic acid (2)+ 2-ethyl-1-hexanol (3)] at T=318.2 K; (-○-) experimental solubility curve, (-●-) experimental tie-line data, (--▲--) calculated UNIQUAC data.**

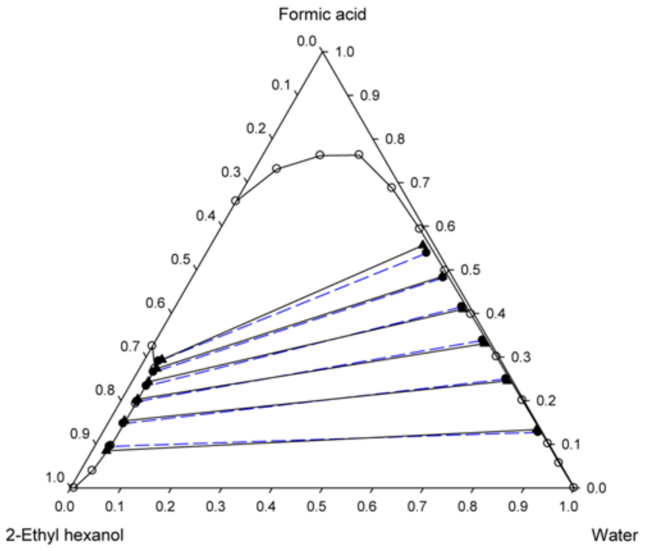

**Fig. 4. Ternary diagram for LLE of [water (1)+formic acid (2)+ 2-ethyl-1-hexanol (3)] at T=328.2 K; (-○-) experimental solubility curve, (-●-) experimental tie-line data, (--▲--) calculated UNIQUAC data.**

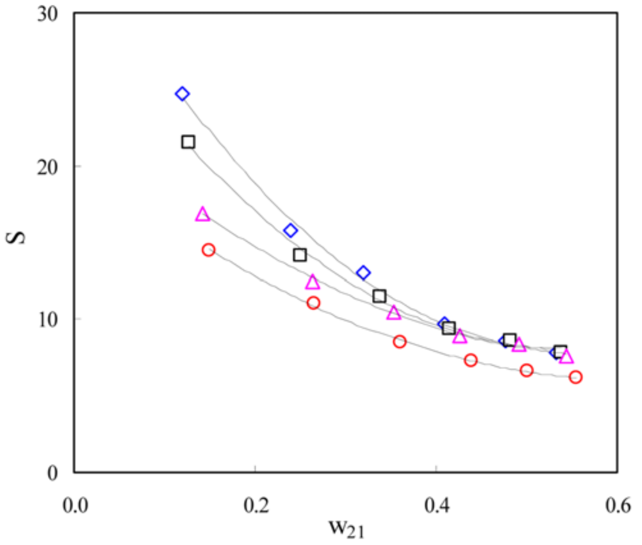

**Fig. 5. Separation factor (S) plotted against the mass fraction of the acid in the aqueous phase (◇) T=298.2 K, (□) T=308.2 K, (△) T=318.2 K, (○) T=328.2 K.**

pletely miscible, the ternary system behaves as a type-2 LLE [27].

The area of the two-phase region depends on the mutual solubilities of water and the organic solvent. The water solubility in 2EH is very low and the slope of the tie lines obtained in this work shows that FA is more soluble in water than 2EH. As can be seen, the temperature effect on the binodal curves and biphasic region of the ternary system is small at the temperatures studied. It is a consequence of strong intermolecular interactions and high boiling point of formic acid due to the aggregation in these systems.

## 2. Distribution Coefficient and Separation Factor

To indicate the ability of the solvent in the recovery of the acid, separation factors ($S=D_2/D_1$) were calculated from the experimental data. Here ($D_1=w_{13}/w_{11}$) and ($D_2=w_{23}/w_{21}$) are the distribution coefficients of water and FA, respectively. $w_{11}$ and $w_{21}$ arethe mass fractions of water and FA in the aqueous phase, respectively. $w_{13}$ and $w_{23}$ are the mass fractions of water and the acid in the organic-rich phase, respectively. The distribution coefficients and separation factors for each temperature are given in Table 4.

Variation of the experimental separation factor as a function of the mass fraction of the acid in aqueous phase for the ternary system at various temperatures is shown in Fig. 5. As can be seen, the separation factor values decrease with increasing FA mass fraction in aqueous phase. Also, for the investigated temperature range, the

**Table 4. Distribution coefficients for water ($D_1$) and Formic acid ($D_2$), and separation factors (S) at T=(298.2, 308.2, 318.2, and 328.2) K**

| *T*=298.2 K | | | *T*=308.2 K | | | *T*=318.2 K | | | *T*=328.2 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $D_1$ | $D_2$ | S | $D_1$ | $D_2$ | S | $D_1$ | $D_2$ | S | $D_1$ | $D_2$ | S |
| 0.04 | 0.51 | 14.5 | 0.03 | 0.58 | 16.9 | 0.03 | 0.85 | 24.7 | 0.04 | 0.75 | 21.5 |
| 0.04 | 0.49 | 11.0 | 0.04 | 0.52 | 12.5 | 0.04 | 0.66 | 15.8 | 0.04 | 0.59 | 14.1 |
| 0.06 | 0.47 | 8.5 | 0.05 | 0.51 | 10.5 | 0.05 | 0.63 | 13.1 | 0.05 | 0.59 | 11.5 |
| 0.06 | 0.46 | 7.3 | 0.06 | 0.51 | 8.9 | 0.06 | 0.58 | 9.7 | 0.06 | 0.56 | 9.4 |
| 0.07 | 0.45 | 6.6 | 0.06 | 0.51 | 8.4 | 0.07 | 0.56 | 8.6 | 0.06 | 0.55 | 8.6 |
| 0.07 | 0.45 | 6.2 | 0.07 | 0.51 | 7.7 | 0.07 | 0.55 | 7.9 | 0.07 | 0.54 | 7.9 |

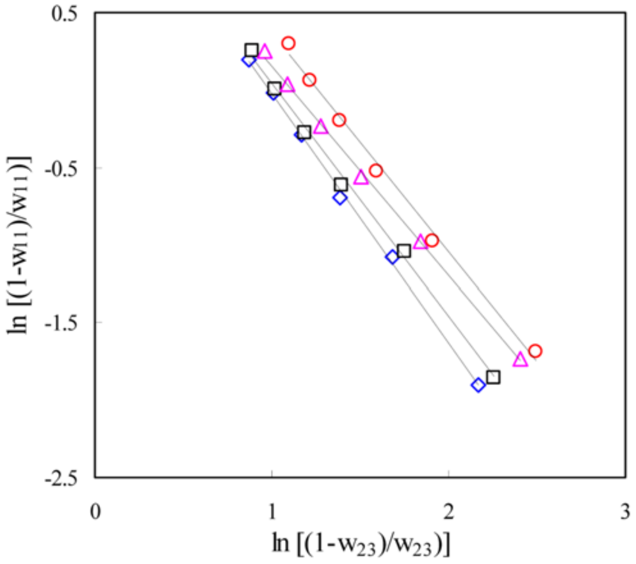

**Fig. 6. Othmer-Tobias plot for (water+formic acid+2-ethyl-1-hexanol) system at various temperatures (◇) T=298.2 K, (□) T=308.2 K, (△) T=318.2 K, (○) T=328.2 K.**

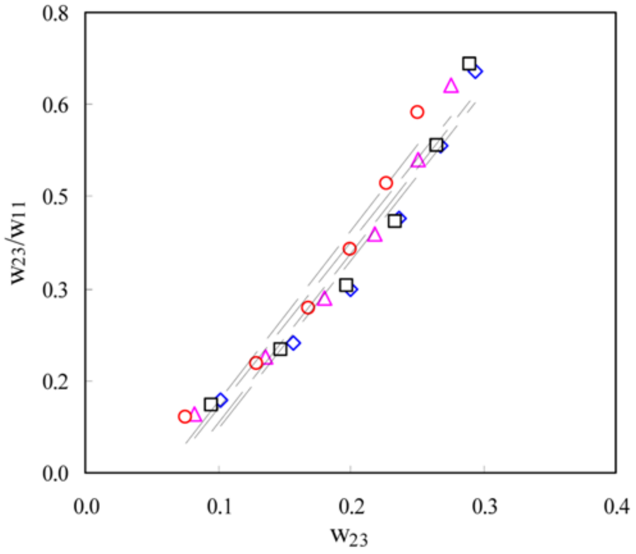

**Fig. 7. Bachman plot for (water+formic acid+2-ethyl-1-hexanol) system at various temperatures (◇) T=298.2 K, (□) T=308.2 K, (△) T=318.2 K, (○) T=328.2 K.**

separation factor changed little with temperature. For the system reported in this work, the experimental results confirm that the organic solvent has relatively high separation factor, indicating ability of the solvent to extract the acid from water.

**Table 6. Values of the UNIQUAC structural parameters r and q**

| Components | r | q |
|---|---|---|
| Water | 0.9200 | 1.4000 |
| Formic acid | 1.5280 | 1.5320 |
| 2-Ethyl-1-hexanol | 6.1500 | 5.0200 |

## 3. Consistency of Tie-line Data

The consistency of experimentally determined tie-line data can be determined by using the Othmer-Tobias [28] (Eq. (1)) and Bachman [29] (Eq. (2)) for the ternary system at each temperature:

$$\ln[(1-w_{33}/w_{33})]=A+B\ln[(1-w_{11}/w_{11})] \tag{1}$$

$$w_{23}=A'+B'(w_{23}/w_{11}) \tag{2}$$

where $w_{11}$, is mass fraction of water in the aqueous phase; $w_{23}$ and $w_{21}$, are mass fractions of the acid in organic and aqueous phases, respectively; $w_{33}$ is mass fraction of the solvent in organic phase; A, B, A′, and B′ are the parameters of the Othmer-Tobias correlation and the Bachman correlation, respectively. The Othmer-Tobias and Bachman plots for the system at each temperature are presented in Figs. 6 and 7. The linearity of the plots indicates the degree of reliability of the related data. The parameters of the correlations, at different temperatures, are listed in Table 5.

## 4. LLE Correlation

The experimental LLE data were correlated using the UNIQUAC model [22]. Values of the UNIQUAC structural parameters r and q used in the UNIQUAC equation are presented in Table 6. An objective function was used to optimize the equilibrium model [30]. The binary interaction parameters were obtained by minimizing the composition-based objective function [31]. The iterative optimization procedure based on the average minimizes the difference between measured and calculated values. The optimization results were judged by calculating the corresponding rmsd (root-mean-square deviation) data. The correlated results together with the experimental data for this ternary system were plotted and shown in Figs. 1 to 4. The UNIQUAC interaction parameters ($a_{ij}$ and $a_{ji}$) are usually assumed independent of temperature and are expressed in Kelvin (K). These parameters represent the energy interactions between an i-j pair of molecules. The UNIQUAC binary interaction parameters are presented in Table 7. Table 8 shows the values obtained for the interaction parameters, assuming that there is a linear relation with temperature. These values were obtained from fitting to the values in Table 7.

The root-mean-square deviation (RMSD) can be taken as a meas-

**Table 5. Othmer-Tobias and Bachman equations constants (A, B, A′ and B′) and the correlation factor ($R^2$) for ternary system (water+formic acid+2-ethyl-1-hexanol) at T=(298.2, 308.2, 318.2 and 328.2) K**

| T/K | Othmer-Tobias correlation | | | Bachman correlation | | |
|---|---|---|---|---|---|---|
| | A | B | $R^2$ | A′ | B′ | $R^2$ |
| 298.2 | −0.7059 | 1.2613 | 0.9945 | 2.7908 | −0.1630 | 0.9585 |
| 308.2 | −0.7362 | 1.1228 | 0.9979 | 2.7055 | −0.1660 | 0.9640 |
| 318.2 | −0.6129 | 0.9987 | 0.9980 | 2.8026 | −0.2144 | 0.9570 |
| 328.2 | −0.6625 | 1.0280 | 0.9970 | 2.7526 | −0.1940 | 0.9588 |

**Table 7. UNIQUAC binary interaction parameters and RMSD values for the ternary system**

| i-j | $b_{ij}$/K | $b_{ji}$/K | RMSD (%) |
|---|---|---|---|
| | *T*=298.2 | | |
| 1-2 | −16.8405 | −552.8175 | |
| 1-3 | −103.6047 | −366.1332 | 0.488 |
| 2-3 | −384.6675 | −91.9059 | |
| | *T*=308.2 | | |
| 1-2 | 5.6855 | −577.5516 | |
| 1-3 | −89.0255 | −391.1058 | 0.366 |
| 2-3 | −447.2808 | −36.7691 | |
| | *T*=318.2 | | |
| 1-2 | −115.9370 | −521.7477 | |
| 1-3 | −71.2472 | −427.2619 | 0.912 |
| 2-3 | −512.6100 | −77.6289 | |
| | *T*=328.2 | | |
| 1-2 | −65.5699 | −455.2749 | |
| 1-3 | −88.3720 | −431.2761 | 0.686 |
| 2-3 | −559.8137 | −14.8391 | |

**Table 8. Optimized UNIQUAC binary interaction parameter $a_{ij}$ (K) with dependence of temperature (T in K)**

| $a_{ij}$/K | $a_{ji}$/K |
|---|---|
| $a_{12}=-0.1526\ T+305.85$ | $a_{21}=-0.2075\ T+422.55$ |
| $a_{13}=0.6042\ T+366.4$ | $a_{31}=-0.4013\ T+151.09$ |
| $a_{23}=-0.1685\ T+232.98$ | $a_{32}=0.2492\ T+326.98$ |

ure of precision of the correlations. The RMSD value was calculated from the difference between the experimental and calculated massfractions according to the following equation:

$$\mathrm{RMSD}=\sqrt{\frac{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}(\mathrm{w}_{ijk}^{exp}-\mathrm{w}_{ijk}^{cal})^2}{6\mathrm{n}}} \quad (3)$$

where n is the number of tie-lines, $\mathrm{w}^{exp}$ indicates the experimental mass fraction, $\mathrm{w}^{cal}$ the calculated mass fraction, and subscript i indexes components, j indexes phases and k=1, 2, …, n (tie-lines). The RMSD is a measure of the agreement between the experimental and calculated data. The average root-mean-square deviation for the ternary system was 0.61%.

## CONCLUSIONS

Solubility and tie line data for the (water+formic acid+2-ethyl-1-hexanol) ternary system were experimentally determined at four different temperatures ranging from 298.2 K to 328.2 K at regular intervals of 10 K and atmospheric pressure. Those are important and fundamental data for the LLE and separation of formic acid by the new organic solvent, 2-ethyl-1-hexanol (2EH), from the water resulting from chemical synthetic or fermentation processes. This solventhas low cost, high boiling point and very low solubility in water, and is, therefore, a good solvent for industrial applications. The ternary system exhibited type-2 behavior of LLE. The UNIQUAC model was used to correlate and analyze the experimental LLE data. The optimum UNIQUAC interaction parameters between water, FA, and 2EH were determined from the experimental tie-line data. The average RMSD value between the observed and calculated mass fractions was 0.61% for the UNIQUAC model. In general, the LLE data of this ternary system correlate fairly well with this equilibrium model.

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