# Liquid+liquid equilibria of ternary water+carboxylic acid+solvent systems at 288.15 K

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**Abstract**−The experimental liquid-liquid equilibrium (LLE) data for six ternary systems containing (chloroform+ propionic acid+water), (chloroform+acetic acid+water), (diethyl ether+propionic acid+water), (diethyl ether+acetic acid+water), (trichloroethylene+propionic acid+water) and (trichloroethylene+acetic acid+water) were measured at 288.15 K and at atmospheric pressure. An accurate and simple titration method was used for determining of the concentration of carboxylic acid in the both liquid phases at equilibrium. The reliability of the experimental tie-line data was confirmed by using the Othmer-Tobias correlation. The distribution coefficients and selectivity factors were presented to evaluate the efficiency of the solvents for extraction of carboxylic acid from water. The results show that chloroform and diethyl ether are satisfactory solvents for extraction of carboxylic acids from water. Trichloroethylene separates propionic acid from water; however, it cannot be used as a solvent for separation of acetic acid.

Key words: Propionic Acid, Acetic Acid, Water, Chloroform, Diethyl Ether, Trichloroethylene, LLE Data

## INTRODUCTION

Separation of carboxylic acids from aqueous solutions resulting from fermentation processes or synthetic methods is an important process that has many applications in the food and pharmaceutical industries. Among the carboxylic acids, applications of acetic acid and propionic acid in various industries are many, and therefore separation of these carboxylic acids from water has been investigated in this study.

Solvent extraction is one of the conventional processes for these separations. Solvents that are used in the liquid-liquid extraction process must have the following properties: 1- High capacity that decreases the amount of solvent required. Capacity determines the conditions and size of the separator. 2- High selectivity that leads to products produced with desirable purity. 3- Capability to form two phases at reasonable temperatures and capability of rapid phase separation. 4- Boiling point temperature of solvent should be as varied as possible from the boiling point temperature of components of mixture. 5- Low toxicity, non- corrosiveness and finally, the use of solvent is desired economic justification.

Many investigators [1-8] have published the liquid-liquid equilibrium (LLE) data of ternary systems containing solvent+carboxylic acid+water. Mohsen-Nia et al. have investigated the binodal curve and tie-line data for ternary systems of (water+propionic acid+dichloromethane) at T=(277.15, 284.15, and 294.15) K by using the cloud point measurement method [9]. The experimental LLE data of the ternary systems containing (water+acetic acid+isobutyl acetate) and (water+acetic acid+isobutyl alcohol) at 283.15 and 323.15 K have been presented by Chafer et al. They used the NRTL and UNIQUAC models to fit the data [10]. Liquid+liquid equilibrium (LLE) data for (water+propionic acid+2-ethyl-1-hexanol) were measured by Ghanadzadeh et al. at atmospheric pressure over the temperature

range of (298.15 to 308.15) K [11]. Kırbaslar et al. reported liquid-liquid equilibrium data for the ternary systems (water+propionic acid+diethyl succinate, or diethyl glutarate, or diethyl adipate) and (water+propionic acid+esters) at T=298.15 K [12,13]. Uslu et al. reported the LLE data for the three ternary systems containing (water+ levulinic acid+dimethyl succinate), (water+levulinic acid+dimethyl glutarate) and (water+levulinic acid+dimethyl adipate) at T=298.15 K [14].

In this study, experimental LLE data for six ternary systems of (chloroform+propionic acid+water), (chloroform+acetic acid+water), (diethyl ether+propionic acid+water), (diethyl ether+acetic acid+ water), (trichloroethylene+propionic acid+water) and (trichloroethylene+acetic acid+water) were measured at 288.15 K. The selectivity factors and distribution coefficients of solvents for separation of carboxylic acids from water are compared.

## EXPERIMENTAL

Acetic acid, propionic acid, chloroform, diethyl ether, trichloroethylene and Sodium sulfate were supplied by Merck Company and were of 0.995, 0.99, 0.992, 0.995, 0.99 and 0.995 mass fraction purity. All the chemicals were used as received without further purification. Deionized and redistilled water was used throughout all experiments.

To find the experimental points that define the tie-line in the phase diagram, experiments were carried out in equilibrium 250 mL glass cells. The mixture was prepared directly inside the cell, and the components were weighted on an analytical balance (A & D Company, GF-600, Japan) accurate to 0.001 g. The mixture was agitated with a magnetic stirrer (Stuart scientific SM 27, UK) for 45 min and then left to settle for 1 h. Preliminary tests showed that these times are enough to achieve equilibrium. Then the system split in two liquid phases that became clear and transparent at equilibrium, with a well defined interface. After decanting, samples from the two liquid phases were taken for analysis. The analysis was repeated at least three

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times. The average of these readings was taken for the component compositions. The tie-line values were obtained by titration of the samples with a 0.05 M NaOH aqueous solution and determination of water in two phases. Sodium sulfate was used as water absorbent for determination of weight percent of water in solvent-rich phase. By determination of water composition in solvent-rich phase

**Table 1. Experimental data for the ternary system {chloroform (1)+carboxylic acid (2)+water(3)} at T=288.15 K**

| Ternary system | Water rich phase (II) | | | Solvent rich phase (I) | | | S | K |
|---|---|---|---|---|---|---|---|---|
| | $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ | | |
| 1 | 0.008 | 0.050 | 0.942 | 0.947 | 0.050 | 0.003 | 314 | 1.00 |
| | 0.004 | 0.094 | 0.902 | 0.858 | 0.126 | 0.016 | 75.57 | 1.97 |
| | 0.107 | 0.168 | 0.725 | 0.604 | 0.258 | 0.138 | 8.07 | 1.54 |
| | 0.105 | 0.223 | 0.672 | 0.518 | 0.358 | 0.124 | 8.70 | 1.58 |
| 2 | 0.003 | 0.085 | 0.912 | 0.989 | 0.008 | 0.003 | 28.61 | 0.09 |
| | 0.012 | 0.175 | 0.838 | 0.971 | 0.022 | 0.007 | 15.05 | 0.13 |
| | 0.018 | 0.218 | 0.764 | 0.942 | 0.046 | 0.012 | 13.43 | 0.21 |
| | 0.046 | 0.367 | 0.587 | 0.871 | 0.115 | 0.014 | 13.14 | 0.31 |

Ternary system 1: chloroform+propionic acid+water
Ternary system 2: chloroform+acetic acid+water

$S=(w_2/w_3)^I/(w_2/w_3)^{II}$
$K=w_2^I/w_2^{II}$

**Table 2. Experimental data for the ternary system {diethyl ether (1)+carboxylic acid (2)+water(3)} at T=288.15 K**

| Ternary system | Water rich phase (II) | | | Solvent rich phase (I) | | | S | K |
|---|---|---|---|---|---|---|---|---|
| | $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ | | |
| 1 | 0.054 | 0.003 | 0.944 | 0.904 | 0.084 | 0.012 | 2202.67 | 28.00 |
| | 0.027 | 0.078 | 0.895 | 0.701 | 0.238 | 0.061 | 44.79 | 3.05 |
| | 0.042 | 0.101 | 0.858 | 0.582 | 0.284 | 0.134 | 18.00 | 2.81 |
| | 0.057 | 0.140 | 0.803 | 0.465 | 0.385 | 0.150 | 14.72 | 2.75 |
| 2 | 0.045 | 0.065 | 0.890 | 0.935 | 0.050 | 0.015 | 45.64 | 0.78 |
| | 0.056 | 0.116 | 0.828 | 0.860 | 0.094 | 0.046 | 14.59 | 0.81 |
| | 0.069 | 0.186 | 0.745 | 0.759 | 0.151 | 0.090 | 6.72 | 0.81 |
| | 0.161 | 0.235 | 0.604 | 0.624 | 0.213 | 0.163 | 3.36 | 0.91 |

Ternary system 1: diethyl ether+propionic acid+water
Ternary system 2: diethyl ether+acetic acid+water

$S=(w_2/w_3)^I/(w_2/w_3)^{II}$
$K=w_2^I/w_2^{II}$

**Table 3. Experimental data for the ternary system {trichloroethylene (1)+carboxylic acid (2)+water(3)} at T=288.15 K**

| Ternary system | Water rich phase (II) | | | Solvent rich phase (I) | | | S | K |
|---|---|---|---|---|---|---|---|---|
| | $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ | | |
| 1 | 0.060 | 0.096 | 0.844 | 0.912 | 0.048 | 0.040 | 10.55 | 0.50 |
| | 0.078 | 0.150 | 0.772 | 0.849 | 0.098 | 0.053 | 9.52 | 0.65 |
| | 0.081 | 0.385 | 0.534 | 0.597 | 0.322 | 0.081 | 5.51 | 0.84 |
| | 0.090 | 0.491 | 0.419 | 0.485 | 0.430 | 0.085 | 4.32 | 0.88 |
| 2 | 0.057 | 0.283 | 0.660 | 0.917 | 0.026 | 0.057 | 1.064 | 0.09 |
| | 0.058 | 0.388 | 0.553 | 0.895 | 0.042 | 0.064 | 0.94 | 0.11 |
| | 0.057 | 0.535 | 0.408 | 0.859 | 0.083 | 0.058 | 1.09 | 0.16 |
| | 0.085 | 0.619 | 0.295 | 0.815 | 0.120 | 0.065 | 0.88 | 0.19 |

Ternary system 1: trichloroethylene+propionic acid+water
Ternary system 2: trichloroethylene+acetic acid+water

$S=(w_2/w_3)^I/(w_2/w_3)^{II}$
$K=w_2^I/w_2^{II}$

and weights of two phases, the composition of water in the water-rich phase was determined.

## RESULTS AND DISCUSSION

The measured compositions of the equilibrium liquid phases for (chloroform+propionic acid+water), (chloroform+acetic acid+water), (diethyl ether+propionic acid+water), (diethyl ether+acetic acid+water), (trichloroethylene+propionic acid+water) and (trichloroethylene+acetic acid+water) systems are shown in Tables 1-3 and Figs. 1-6, respectively.

Selectivity factor (S) and distribution coefficient (K) are important parameters for evaluation of different solvents which are defined

as follows:

$$S=(w_2/w_3)^{I}/(w_2/w_3)^{II} \qquad (1)$$

$$K=w_2^{I}/w_2^{II} \qquad (2)$$

Where $w_2$ is the mass fraction of carboxylic acid (2) and $w_3$ is the mass fraction of water (3). The superscripts I and II indicate the solvent-rich phase and water-rich phase, respectively. Selectivity factor indicates the ability of solvents for separation of the carboxylic acid from water. If the selectivity factor is greater than one, separation is possible and any amount that is larger than one is more desirable. Distribution coefficient indicates the amount of solvent required in the extraction process. It is not necessary that this par-
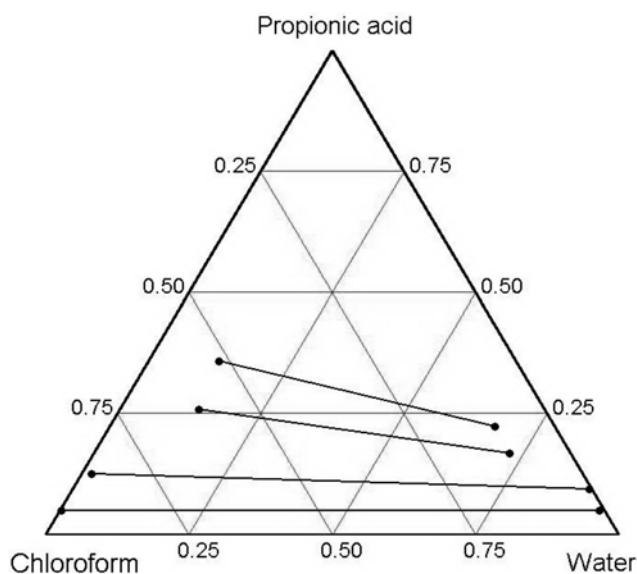


Fig. 1. Experimental LLE data for (chloroform+propionic acid+water) at T=288.15 K.
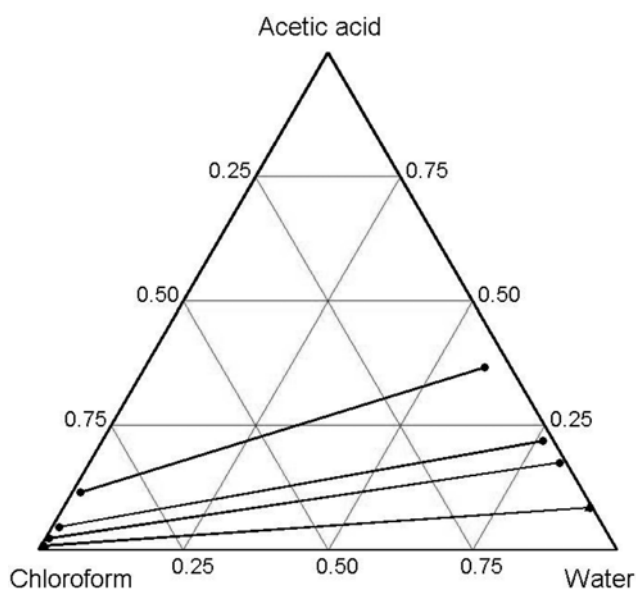


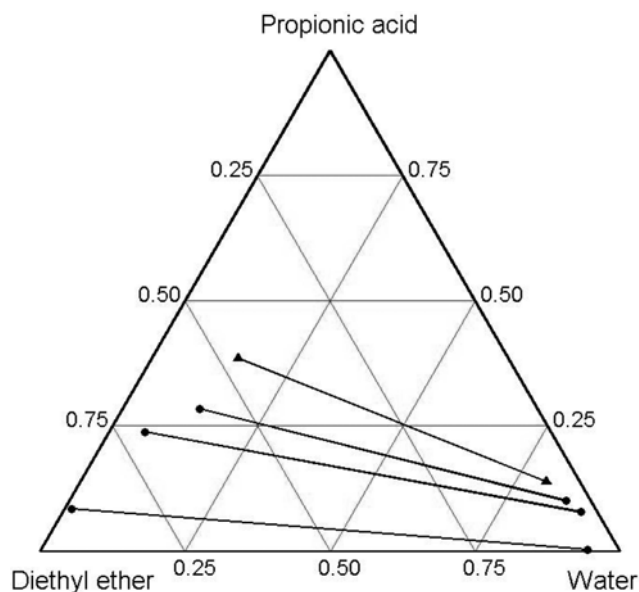Fig. 2. Experimental LLE data for (chloroform+acetic acid+water) at T=288.15 K.



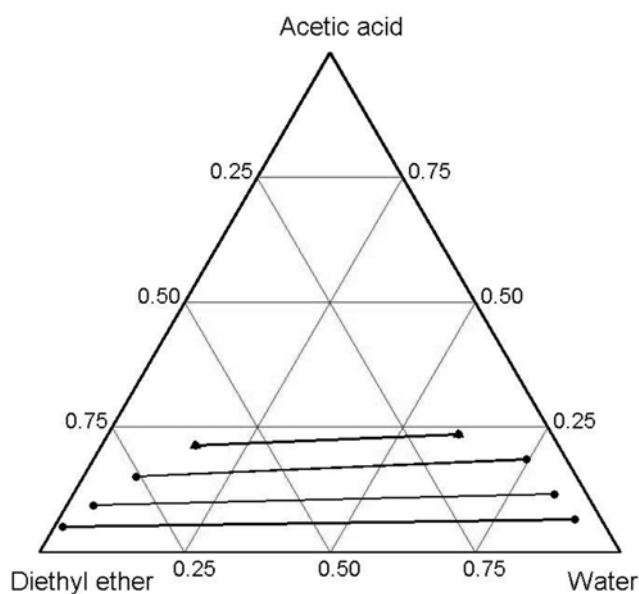Fig. 3. Experimental LLE data for (diethyl ether+propionic acid+water) at T=288.15 K.



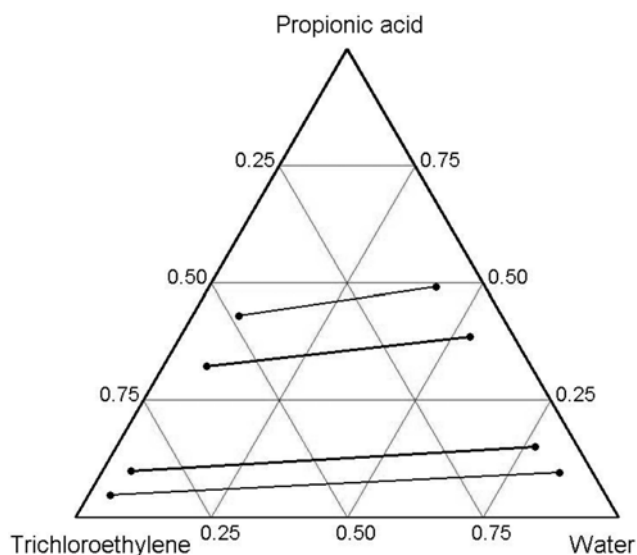Fig. 4. Experimental LLE data for (diethyl ether+acetic acid+water) at T=288.15 K.

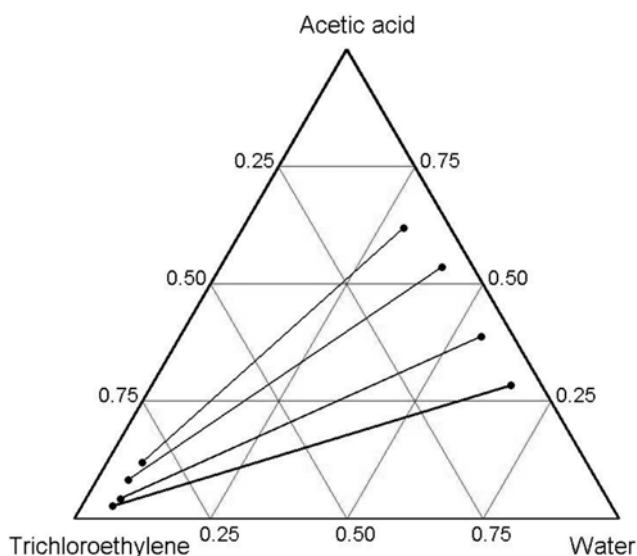Fig. 5. Experimental LLE data for (trichloroethylene+propionic acid+water) at T=288.15 K.



Fig. 6. Experimental LLE data for (trichloroethylene+acetic acid+water) at T=288.15 K.

ameter is more than one, but if the distribution coefficient of solvent is large, the amount of required solvent in the process, the size of equipment and solvent recovery costs decrease.

The experimental values of the S and K in this research are shown in Tables 1-3. According to the results in Tables 1-3, for chloroform and diethyl ether, selectivity factor s in all cases is greater than one, and this means that for these two solvents extraction is possible. But the results show that trichloroethylene is a satisfactory solvent for separation of propionic acid from water; however, it cannot be used as a solvent for separation of acetic acid. Based on the data in Table 3, the selectivity factor for a ternary system (trichloroethylene+acetic acid+water) in all cases is nearly unity, and this means that extraction is impossible.

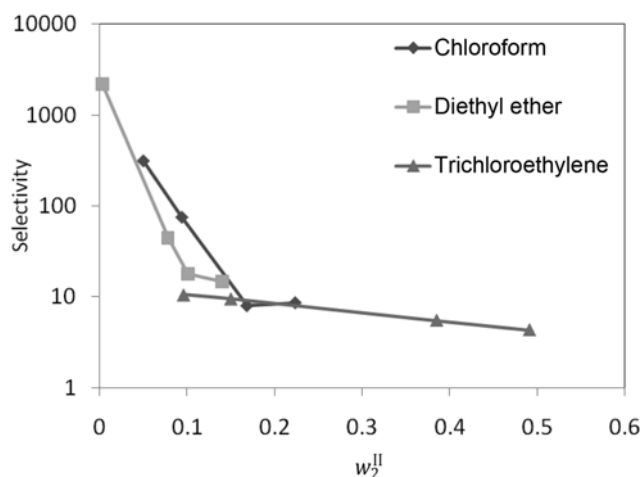Based on the data in Tables 1 to 3, it is clear that for chloroform,

Fig. 7. Selectivity of solvents as a function of the mass fraction of propionic acid in water-rich phase; chloroform, ◆; diethyl ether, ■; trichloroethylene, ▲.
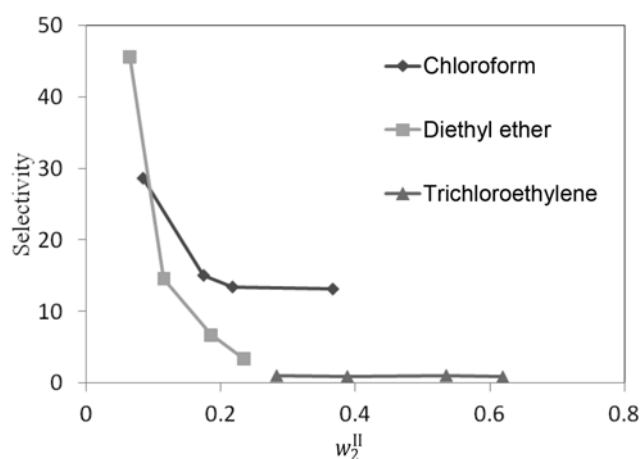


Fig. 8. Selectivity of solvents as a function of the mass fraction of acetic acid in water-rich phase; chloroform, ◆; diethyl ether, ■; trichloroethylene, ▲.

diethyl ether and trichloroethylene the selectivity factor and distribution coefficient of these solvents for separation of propionic acid from water have the order (diethyl ether>chloroform>trichloroethylene). For acetic acid, the selectivity factor and distribution coefficient of chloroform and diethyl ether have the order (chloroform>diethyl ether) for selectivity factor and (diethyl ether>chloroform) for distribution coefficient.

The phase diagrams for the studied ternary systems are presented in Figs. 1-6.

The selectivity factor against mass fraction of propionic acid or acetic acid in water-rich phase, for studied ternary systems, is shown in Figs. 7 and 8.

As shown in these figures, the selectivity in all cases decreased with increasing of the mass fraction of propionic acid or acetic acid in water-rich phase. Based on these figures and Tables 1 to 3, the selectivity of chloroform, diethyl ether and trichloroethylene for separation of propionic acid from water was greater than the selectivity of these solvents for separation of acetic acid from water.
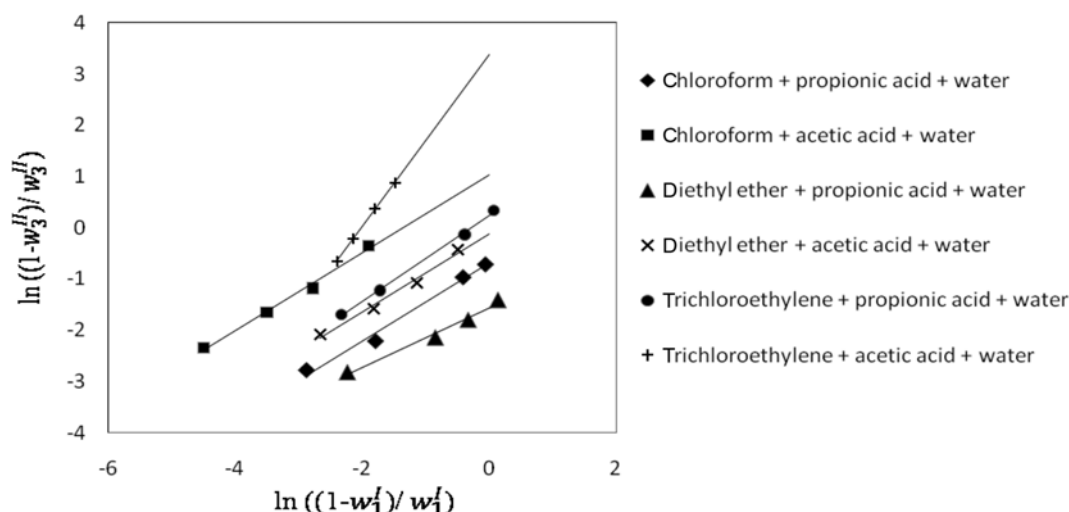
**Fig. 9. Othmer-Tobias plots of six ternary systems (solvent+carboxylic acid+water) at T=288.15 K; (chloroform+propionic acid+water), ◆; (chloroform+acetic acid+water), ■; (diethyl ether+propionic acid+water), ▲; (diethyl ether+acetic acid+water), ●; (trichloroethylene+propionic acid+water), ; (trichloroethylene+acetic acid+water), +.**

**Table 4. Othmer-Tobias equation constants for the ternary system {solvent (1)+carboxylic acid (2)+water (3)} at T=288.15 K**

| Ternary system | A | B | $R^2$ |
|---|---|---|---|
| 1 | −0.6892 | 0.7606 | 0.9872 |
| 2 | 1.0282 | 0.7571 | 0.993 |
| 3 | −1.5666 | 0.5798 | 0.9847 |
| 4 | −0.1166 | 0.7644 | 0.9859 |
| 5 | 0.2358 | 0.8323 | 0.9983 |
| 6 | 3.3738 | 1.6755 | 0.9991 |

Ternary system 1: chloroform+propionic acid+water
Ternary system 2: chloroform+acetic acid+water
Ternary system 3: diethyl ether+propionic acid+water
Ternary system 4: diethyl ether+acetic acid+water
Ternary system 5: trichloroethylene+propionic acid+water
Ternary system 6: trichloroethylene+acetic acid+water

The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer-Tobias correlation [15] for each solvent as shown in the following equation:

$$\ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right) = A + B\ln\left(\frac{1-w_1^{I}}{w_1^{I}}\right) \tag{3}$$

Where $w_3^{II}$ is mass fraction of water in the water-rich phase; $w_1^{I}$ is mass fraction of solvent in the solvent-rich phase; A and B are constants of Eq. (3).

The Othmer-Tobias plots for the correlations of experimental tie-line data are shown in Fig. 9. The correlation parameters also are given in Table 4. As shown in Table 4, the correlation factor ($R^2$) close to unity in all cases, which indicates a high degree of consistency of related data.

## CONCLUSION

The experimental LLE data for six ternary systems containing (chloroform+propionic acid+water), (chloroform+acetic acid+water), (diethyl ether+propionic acid+water), (diethyl ether+acetic acid+water), (trichloroethylene+propionic acid+water) and (trichloroethylene+acetic acid+water) were presented at T=288.15 K and at atmospheric pressure. By comparison of the selectivity factors and distribution coefficients, data for three solvents are used in this research, for separation of propionic acid from water; all solvents have good results and among these solvents, diethyl ether was better than other solvents. For acetic acid separation, diethyl ether and chloroform are appropriate solvents that selectivity in all cases greater than one but trichloroethylene cannot separate of acetic acid from water. Among diethyl ether and chloroform, chloroform was better than diethyl ether for separation of acetic acid from water.

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