*Bulgarian Chemical Communications, Volume 48, Special Issue D (pp. 84 – 88) 2016*

# Liquid–liquid equilibrium for the ternary systems of water + acetic acid +ethyl acetate at T=298.2 K

M. Manteghian[1], M. Shahbazi[2,*]

*1- Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran*
*2- Department of Chemical Engineering, Separation Processes, Islamic Azad University, North Tehran Branch, Tehran, Iran*

Received June 26, 2016; Revised September 10, 2016

The concentration of each phase was determined by acidimetric titration, the Karl Fischer technique. The reliability of the experimental data was determined through the Othmer–Tobias and Hand plots. Distribution coefficients and separation factors were evaluated over the immiscibility regions. The results show that ethyl acetate is satisfactory solvent for extraction of acetic acid from water.

## INTRODUCTION

Liquid-liquid equilibrium (LLE) data are of interest in extraction operations and recovery of valuable products [1-2]. Nowadays, liquid-liquid extraction has become one of the main separation technologies for separation of complex liquid mixtures.[3]Owing to that, there has been a significant growth in the number of publications devoted to the study on LLE of ternary and quaternary mixtures, including experimental data and correlation parameters.

Studies of phase equilibria of ternary systems are very important in both theoretical and industrial applications [4]. Precise LLE data of aqueous mixtures with organic solvents are needed in the evaluation of industrial units for solvent extraction processes. The accurate interpretation of phase equilibria and thermodynamic behaviour for the different ternary mixtures is a fundamental and important key to improving solvent extraction techniques [4-11].

Acetic acid is one of the most widely used organic acids, which has many industrial applications. The pure acetic acid is extensively used as an additive in the food industry. Therefore, the efficient separation of acetic acid from aqueous solutions, by solvent extraction technique, is of considerable economic importance in the chemical industry [12-13]. The type of solvent is one of the most important factors, which influence the equilibrium characteristics of extraction of the acidfrom aqueous solutions. 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 [14-17].

Many organic solvents have been tested as extractants for the recovery and purification of acetic acid from water. Heavy alcohols, ketones and ethers have been used for extraction of acetic acid from aqueous solutions [18].

As a continuation of that previous work, we present the LLE results for the ternary system (water + acetic acid + ethyl acetate) at T = 298.2 K. The distribution coefficients and separation factors were obtained from experimental results and are also reported. The tie lines were determined and were correlated by the methods of Othmer-Tobias and Hand on a mass-fraction basis. In this work, distribution coefficients (k) and separation factors (S) were determined to establish the possibility of the use of this solvent for the separation process [18-20].

## EXPERIMENTAL

### *Materials*

Analytical grade acetic acid, ethyl acetate (mass fraction purity > 0.99) were supplied by Merck. Bi-distilled water was used throughout all the experiments. The purity of the acid was checked through acidimetric titration with 1 N NaOH.

### *Apparatus and procedure*

---

* To whom all correspondence should be sent:
E-mail: Mehdi.shahbazi72@yahoo.com

The water content of the organic phase was measured by the Karl-Fischer method usingMetrohm-870 KF Titrino plus Karl-Fischer titrator. The titrator was calibrated with a standard solution of sodium tartrate. The sample weighing was carried out with an AND electronic analytical balance (model HR-200) with an accuracy of ±0.0001 g.

Details of the experimental apparatus, procedure and measurements are similar to that of previous work. Solubility or LLE data for the water + acetic acid + ethyl acetate system at T = (298.15) K were determined by the cloud point method.

Tie-line data were determined for the ternary systems atT = 298.2 K. Experiments were carried out in a jacketed 250 ml glass cell. The temperature was estimated to be accurate to within ±0.1 K. The prepared mixtures were placed in the extraction cell and were vigorously agitated by a magnetic stirrer for 2 h. For all the mixtures, the resting time for phase separation was 4 h. The mass fractions of the acid in both the phases were obtained by potentiometric NaOH titration. The solvent was added by an automated microburette with an accuracy $5.10^{-3}$cm$^3$. The concentration of water in the organic-rich phase was measured by the Karl-Fisher method.

(Liquid + liquid) equilibrium (LLE) data for the ternary mixtures of {water (1) + acetic acid and (2) + ethyl acetate (3)} were determined at T = 298.2 K and atmospheric pressure.

## RESULTS AND DISCUSSION

*Experimental LLE results.* The experimental solubility data and experimental LLE data of (water + acetic acid) with ethyl acetate at T = 298.2 K are presented in table 1 and 2[18-20].

The effectiveness of acetic acid extraction done using the solvent ethyl acetate is given by it separation factor(S), which is a measure of the ability of solvent to separate theacid from water. To show the selectivity and extraction strength of the solvent to extract acetic acid, distribution coefficients, $d_i$, for water (i = 1) and acetic acid (i = 2) and separation factors, s, were calculated as follows:

1) $d_i = w_{i3}/w_{i1}$

2) $S=\frac{distribution\ coefficient\ of\ acetic\ acid}{distribution\ coefficient\ of\ water}=\frac{\frac{W23}{W21}}{\frac{W13}{W11}}$

where $w_{23}$ and $w_{21}$ are the acetic acid concentrations insolvent-rich and water rich phases, respectively, and $w_{13}$and $w_{11}$ are the water concentrations in solvent-rich and water rich phases, respectively. The distribution coefficients and separation factors at T =273 k and atmospheric pressure are shown. The effectiveness of extraction of acetic acid by ethyl acetate is given by its separation factor, which is an indication of the ability of ethyl acetate to separate acetic acid from water. This quantity is found to be greater than 1(separation factors varying between 2.397 and 6.981) for the system reported here, which means that extraction of acetic acid by ethyl acetate is possible. The separation factor is not constant over the whole two-phase region.

The distribution coefficients D2 versus w21 were plotted in Fig1and the separation factors S versus w21 were plotted in Fig2. As shown in fig 1, the distribution coefficients in all cases decreased and increased with increasing of the mass fraction of acetic acid in water-rich phase

The variation of experimental separation factor of the acid as a function of the mass fraction of the solute in aqueous phase for each ternary system is shown in Fig. 2. As shown in these figures, the selectivity in all cases decreased with increasing of the mass fraction of acetic acid in water-rich phase.

*Selectivity.* Selectivity diagrams on a solvent-free basis are obtained y plotting $w_{23}/(w_{23} + w_{13})$ vs. $w_{21}/(w_{21} + w_{11})$for system (water + acetic acid + ethyl acetate ) in figure 3. The effect of a mass fraction of ethyl acetate in the aqueous phase change on the selectivity values was found to be significant.

*Consistency of tie-line data.* The reliability of experimental tie-line data can be determined using the Othmer–Tobias and Hand correlations for each solvent, as shown in the following equations:

3) $Ln ((1-w_{33})/w_{33}) = A + B\ Ln ((1-w_{11})/w_{11})$

4) $Ln (w_{21}/w_{11}) = A^{'}+ B^{'} Ln (w_{23}/w_{33})$

where $w_{23}$ the mole fraction of phosphoric acid in organic phase and $w_{11}$ is the mole fraction of water in aqueous phase; *A, B, A*′, and *B*′ are the parameters of the Othmer–Tobias and the Bachman correlations, respectively.

**Table 1** : LLE Data for (Water + Acetic acid + Ethyl acetate) at T = 298.2 K and atmospheric pressure.

| Data | $M_3$ (gr) | $M_2$ (gr) | $M_1$ (gr) | $W_3$ | $W_2$ | $W_1$ |
|---|---|---|---|---|---|---|
| 1 | 660.6 | 670.5 | 462.15 | 239.0 | 204.0 | 556.0 |
| 2 | 035.8 | 081.4 | 301.7 | 413.0 | 2109.0 | 376.0 |
| 3 | 323.8 | 670.3 | 090.5 | 487.0 | 215.0 | 298.0 |
| 4 | 829.8 | 092.3 | 590.3 | 569.0 | 199.0 | 231.0 |
| 5 | 441.9 | 590.2 | 842.2 | 634.0 | 174.0 | 192.0 |
| 6 | 610.9 | 053.2 | 622.2 | 672.0 | 144.0 | 183.0 |

**Table 2.** Experimental tie-line data in the organic phases for [water (1) + Acetic acid (2) + Ethyl acetate (3)] at 298.2 K

| Data | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $d_1$ | 0.4701 | 0.4598 | 0.4461 | 0.250 | 0.1765 | 0.1534 |
| $d_2$ | 1.179 | 1.132 | 1.070 | 111.1 | 205.1 | 096.1 |
| S | 508.2 | 462.2 | 397.2 | 444.4 | 824.6 | 981. |

**Table 3.** Experimental data of (water + acetic acid + ethyl acetate) ternary system for Tobias Fig

| Data | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Ln((1-$w_{33}$/$w_{33}$)) | -/008 | -/034 | -/088 | -/481 | -/481 | -/991 |
| Ln((1-$w_{11}$/$w_{11}$)) | -/2818 | -/3474 | -/368 | -/964 | -1/355 | -1/553 |

**Table 4.** Experimental data of (water + acetic acid + ethyl acetate) ternary system for Hand Fig

| Data | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Ln(($w_{23}$/$w_{33}$)) | -0.780 | -0.828 | -0.880 | -1.123 | -1.356 | -1.617 |
| Ln(($w_{21}$/$w_{11}$)) | -1.072 | -1.095 | -1.093 | -1.386 | -1.694 | -1.827 |

**Table 5**. Constants of Othmer–Tobias and Hand equations for the (water + acetic acid ethyl acetate) system (R2: regression coefficient).

| Tobias equatio | | | Hand equation | | |
|---|---|---|---|---|---|
| A | B | $R^2$ | A' | B' | $R^2$ |
| -2886.0 | 2924.1 | 99250. | -0.2788 | 0.9862 | 0.9792 |

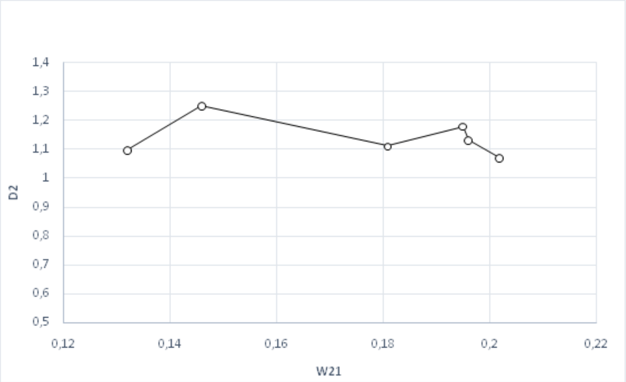

**Fig 1** : Distribution coefficient of acetic acid,D2, as a function of the mass fraction of acetyl acetate in the aqueous phase, w21 for the systems of water (1) + acetic acid (2) + ethyl acetate (3)

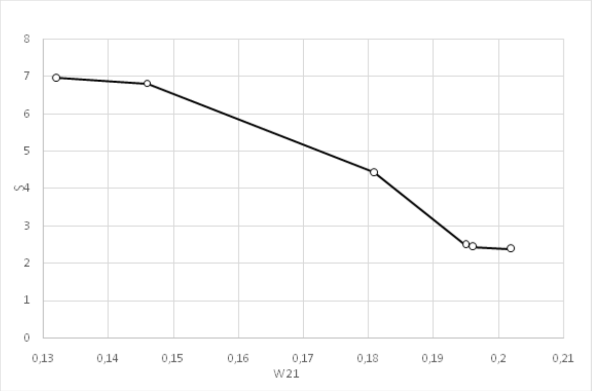

**Fig 2:** Separation factor, S, as a function of the mass fraction of acetic acid in the aqueous phase, w21 for the systems of water (1) + acetic acid (2) + ethyl acetate (3)

The parameters of the Othmer–Tobias and Hand correlations, at T = 298.2 K, are listed in table 7. For these investigated systems, the Othmer–Tobias and Hand plots are shown in figures 4 and 5, respectively. The correlation factor ($R^2$) is approximately unity, and the linearity of the plots indicate the degree of consistency the measured LLE results in this study.

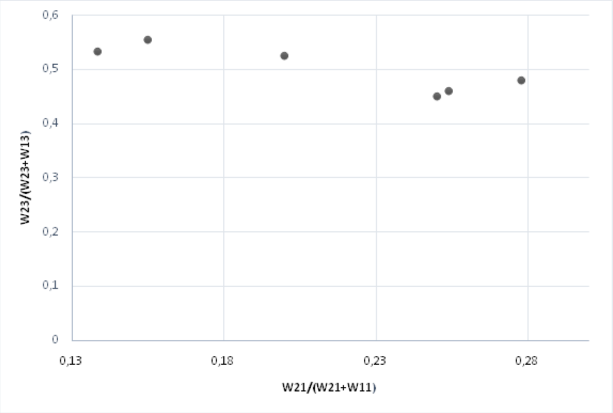

**Fig 3** . Selectivity diagram for [water (1) + Acetic acid (2) + Ethyl acetate (3)] at 298.2 k

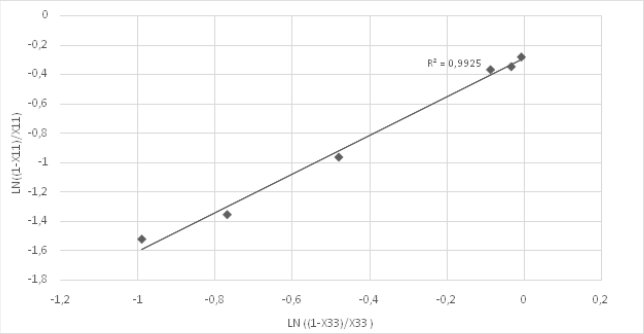

**Fig. 4.** Othmer–Tobias correlation for the system of water + acetic acid + ethyl acetate at 298.2 K.

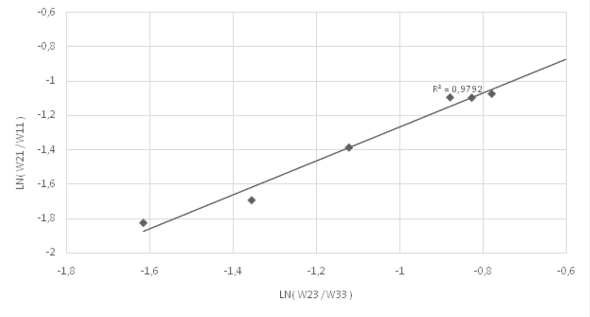

**Fig. 5.** Hand correlation for the system of water + acetic acid + ethyl acetate at 298.2 K.

## CONCLUSION

LLE data for acetic acid + water +ethyl acetate systems were obtained at 298.2 K. Experimental results showed that ethyl acetate havel ow solubility in water and high solubility for acetic acid. Thus, they can serve as extractors to extract acetic acid from the mixture of acetic acid and water and can serve as an entrainer to separate acetic acid and water via heterogeneous azeotropic distillation. The tie-line data of the system were satisfactorily ascertained by the Othmer–Tobias and Hand correlating equations. The separation factors and distribution coefficients for the solvents used in this work were calculated. The obtained separation factors confirm the ability of these solvents

for extraction of acetic acid from water. As well as the selectivity in all cases decreased with increasing of the mass fraction of acetic acid in water-rich phase.

## REFERENCES

1. S. de Moura, J. dos Santos, F. da Silva**,** *Amer. J. Phys. Chem.,* **2**, 117 (2013).
2. J.C. Upchurch, M. Van Winkle, *Ind. Eng. Chem*., **44**, 618 (1952).
3. H. Ghanadzadeh , A. Ghanadzadeh , Z. Aghajani , S. Abbasnejad, S. Shekarsaraee, *J. Chem. Thermodyn.*, **42,** 695 (2010).
4. A. Senol, *Fluid Phase Equilibria*, **227,** 87 (2005).
5. A. Arce, A. Blanco, P. Souza, I.J. Vidal, J. *Chem. Eng. Data*, **40,** 225 (1995).
6. S.Ismail Kırbaslar, S. Sahin, M. Bilgin, *J. Chem. Thermodyn,* **38,** 1503 (2006).
7. D. Ozmen, S. Cehreli, U. Dramur, *J. Chem. Thermodyn,*. **37**, 837 (2005).
8. H. Ghanadzadeh, A. Ghanadzadeh, *J. Chem. Eng. Data,* **49,** 783 (2004).
9. H. Ghanadzadeh, A. Ghanadzadeh, R. Sariri, *J. Chem. Thermodyn.* 36 (2004)1001.
10. H. Ghanadzadeh, A.K. Haghi, *Fluid Phase Equilibri*a, **45**, 243 (2006).
11. C. Hanson, Recent Advances in Liquid-Liquid Extraction, Pergamon, New York, 1971.
12. R. Blumberg, *Solvent Extr. Rev.*, **1**, 93 (1971).
13. J.F. McCullough, L.L. Frederick, *J. Agric. Food Chem.*, **24**, 180 (1976).
14. A. Arabi, J. Mahmoudi , H. Saradar, A. Jafarzade, *Korean J. Chem. Eng*., **28**, 917 (2011).
15. C.-T. Hsieh, W.-Y. Ji, H.-M. Lin, M.-J. Lee, *Fluid Phase* Equilibria, **271**, 69 (2008).
16. A. Orjuela, A. J. Yanez, P. K. Rossman, D.T. Vuc, D. Bernard-Brunel,D. J. Miller, C. T. Lira, *Fluid Phase Equilibria*, **290**, 68 (2010).
17. C.R. Bhupesh, M. R. Awual, M. Goto, *Applied Sciences*, **7**, 1053 (2007).
18. T. Afolabi, A. Alao , *Fluid Phase Equilibria,* **379,** 19 (2014).
19. E. Ince, Y. Selim, *Fluid Phase Equilibria,* **370,** 19 (2014).
20. H. Ghanadzadeh Gilani, A. Ghanadzadeh Gilani, M. Sangashekan, *J. Chem. Thermodyn.,* **58,** 142 (2013).