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

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Abstract

(Liquid + liquid) equilibrium (LLE) data for the ternary mixtures of {water (1) + acetic acid (2) + ethyl acetate (3)} were determined at T = 298.2 K and atmospheric pressure. The concentration of each phase was determined by acidimetrictitration, the Karl Fischer technique. The reliability of the experimental data wasdetermined through the Othmer–Tobias and Hand plots. Distribution coefficients and separation factorswere 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 thenumber 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 evaluationof industrial units for solvent extraction processes. The accurate interpretation of phase equilibria and thermodynamicbehaviour for the different ternary mixtures is a fundamental andimportant 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 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 Economic importance in the chemical industry(12-13). The type of

solvent is one of the most important factors, whichinfluence the equilibrium characteristics of extraction of the. Capacity determines theconditions 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 phaseseparation. 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 testedas extractants for the recovery and purification of acetic acidfrom water. Heavy alcohols, ketones and ethers have ainly beenused 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).

2. Experimental
2.1. Materials

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

2.2. Apparatus and procedure

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The water content of theorganic phase was measured by the Karl-Fischer method usingMetrohm-870 KF Titrino plus Karl-Fischer titrator. The titrator wascalibrated with a standard solution of sodium tartrate. The sampleweighing 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 measure-ments 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 glasscell. The temperature was estimated to be accurate to within ±0.1 K.The prepared mixtures were placed in the extraction cell and werevigorously agitated by a magnetic stirrer for 2 h. For all the mixtures,the resting time for phase separation was 4 h.The mass fractions ofthe acid in both the phases were obtained by potentiometric NaOHtitration.The solvent was added by an automated microburetwith an accuracy 5.10⁻³cm³. The concentration of water in the organic-rich phase wasmeasured by the Karl-Fisher method .

3.Results and discussion
3.1. Experimental LLE results

The experimental soloubility 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 thesolvent 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) $S = \dfrac{\text{distribution coefficient of acetic acid}}{\text{distribution coefficient of water}} = \dfrac{\frac{W_{23}}{W_{21}}}{\frac{W_{13}}{W_{11}}}$

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 given in table 3. The effectivenessof extraction of acetic acid by ethyl acetate isgiven by its separation factor, which is an indicationof the ability of ethyl acetate to separate acetic acidfrom water. This quantity is found to be greater than 1(separation factors varying between 2.397 and 6.981) for thesystem reported here, which means that extraction ofacetic acid by ethyl acetate is possible. The separationfactor is not constant over the whole two-phase region.

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

Data	M₃ (gr)	M₂ (gr)	M₁ (gr)	W₃	W₂	W₁
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 298.2k

Data	W_{13}	W_{23}	W_{33}
1	26900.	0.2270	50300.
2	26950.	22200.	50850.
3	26100.	21600.	52100.
4	18100.	20100.	61800.
5	14040.	17600.	68360.
6	12600.	14470.	72930.

Table 3 : Experimental tie-line data in the aqueous phases for (water (1) + Acetic acid (2) + Ethyl acetate (3)) at 298.2 k.

Data	W_{11}	W_{21}	W_{31}
1	570.0	195.0	235.0
2	586.0	196.0	218.0
3	585.0	2019.0	2131.0
4	724.0	1809.0	0951.0
5	7951.0	146.0	0589.0
6	821.0	132.0	047.0

Table 4 :Distribution coefficients of Acetic acid (2) and separation factors(S) for the water (1) + Acetic acid (2) + Ethyl acetate (3) system 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	981.6

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, thedistribution coefficients in all cases decreased and increased with increasing of the mass fraction of acetic acid in water-rich phase
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The variation of experimental separation factor of the acid as afunction of the mass fraction of the solute in aqueous phase for eachternary system is shown in Fig. 2. As shown in these figures, the selectivity in all cases decreasedwith increasing of the mass fraction of acetic acidin water-rich phase
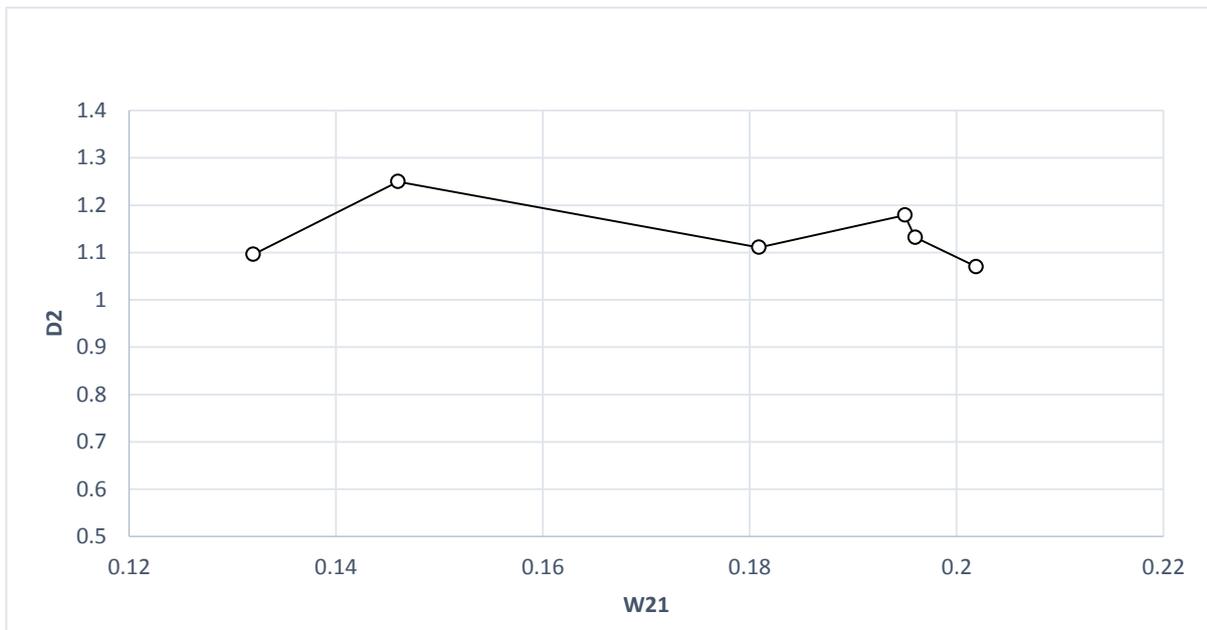
Fig 1 : Distribution coefficient of acetic acid,D2, as a function of the mass fractionof acetyl acetate in the aqueous phase, w21 for the systems of water (1) + acetic acid (2) + ethyl acetate (3)
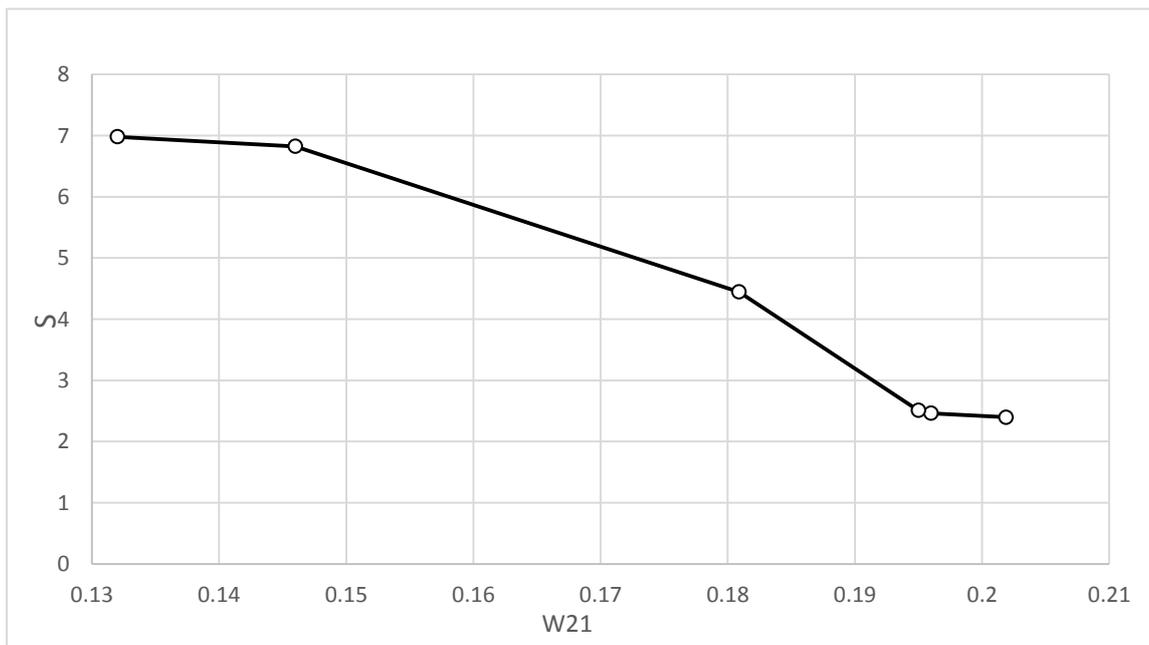
Fig 2:Separation factor, S, as a function of the mass fractionof acetic acid in the aqueous phase, w21 for the systems of water (1) + acetic acid (2) + ethyl acetate (3)

3.2. Selectivity

Selectivity diagrams on a solvent-free basis are obtained by 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.
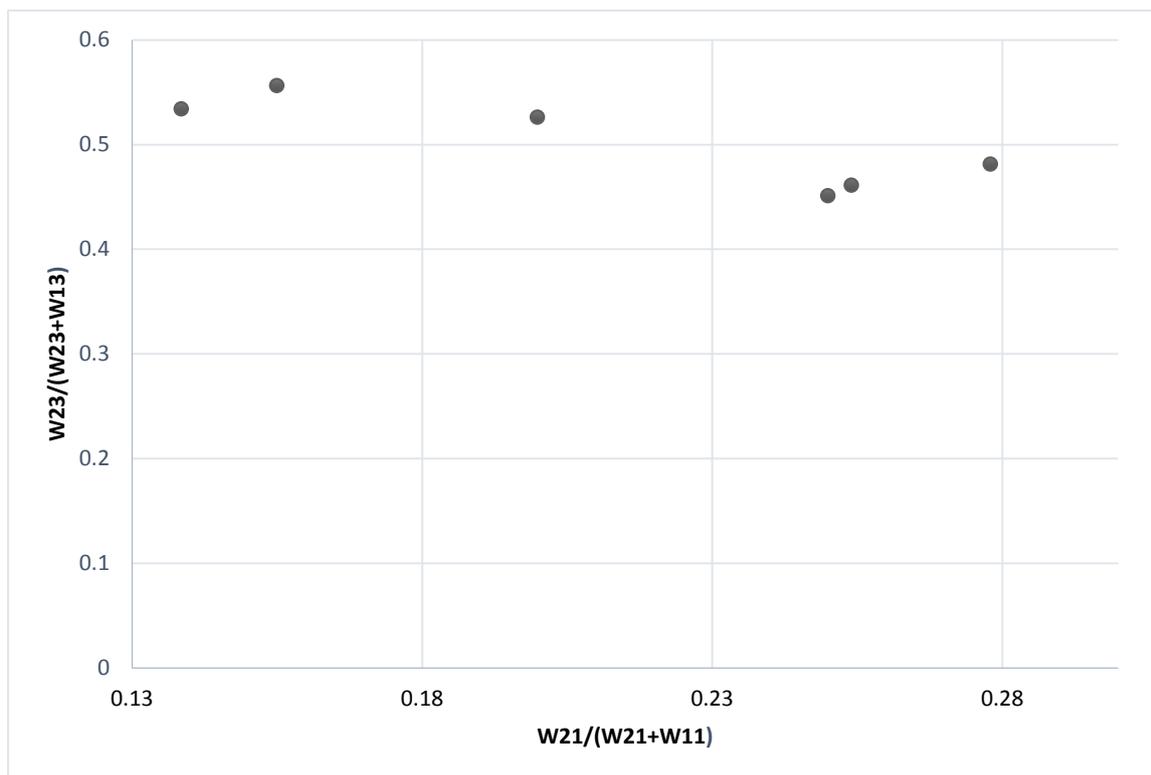
Fig 3 . Selectivity diagram for (water (1) + Acetic acid (2) + Ethyl acetate (3)) at 298.2 k

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

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

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 5 :Experimental data of (water + acetic acid + ethyl acetate) ternary system for tobias Fig

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

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 Handplots are shown in figures 4 and 5, respectively. The correlation factor (R2) isapproximately unity, and the linearity of the plots indicate the degree of consistencythe measured LLE results in this study.
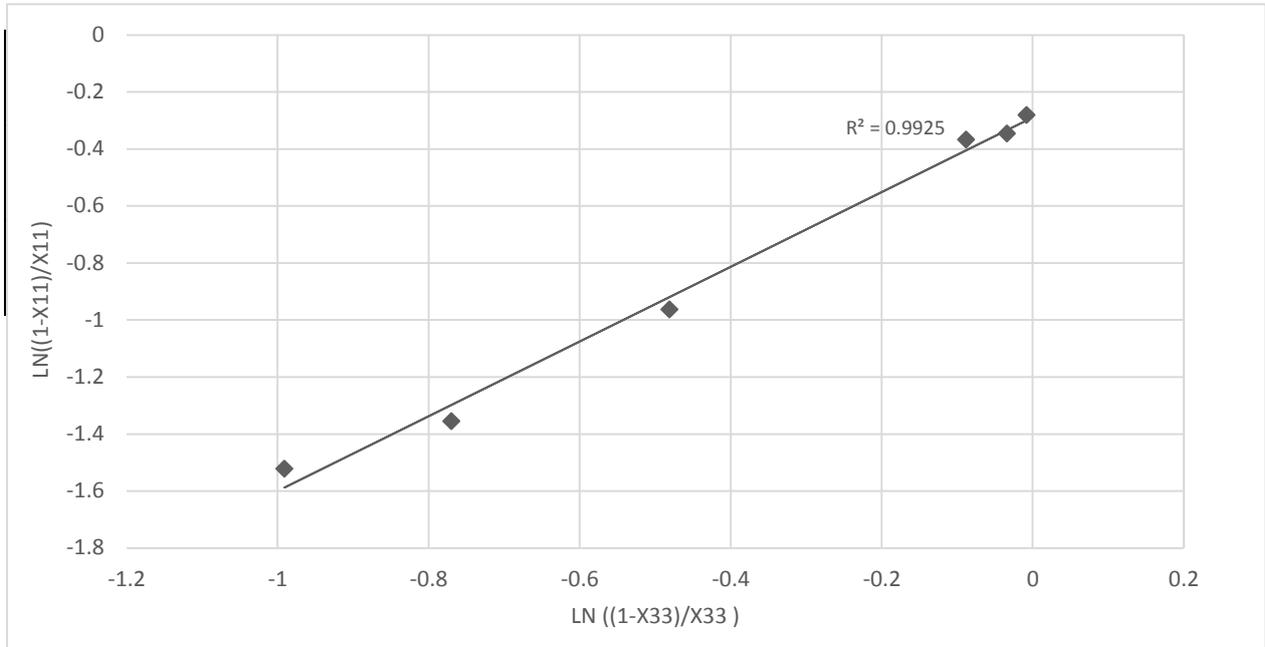
Fig. 4. Othmer–Tobias correlation for the system of water + acetic acid + ethyl acetate at 298.2 k
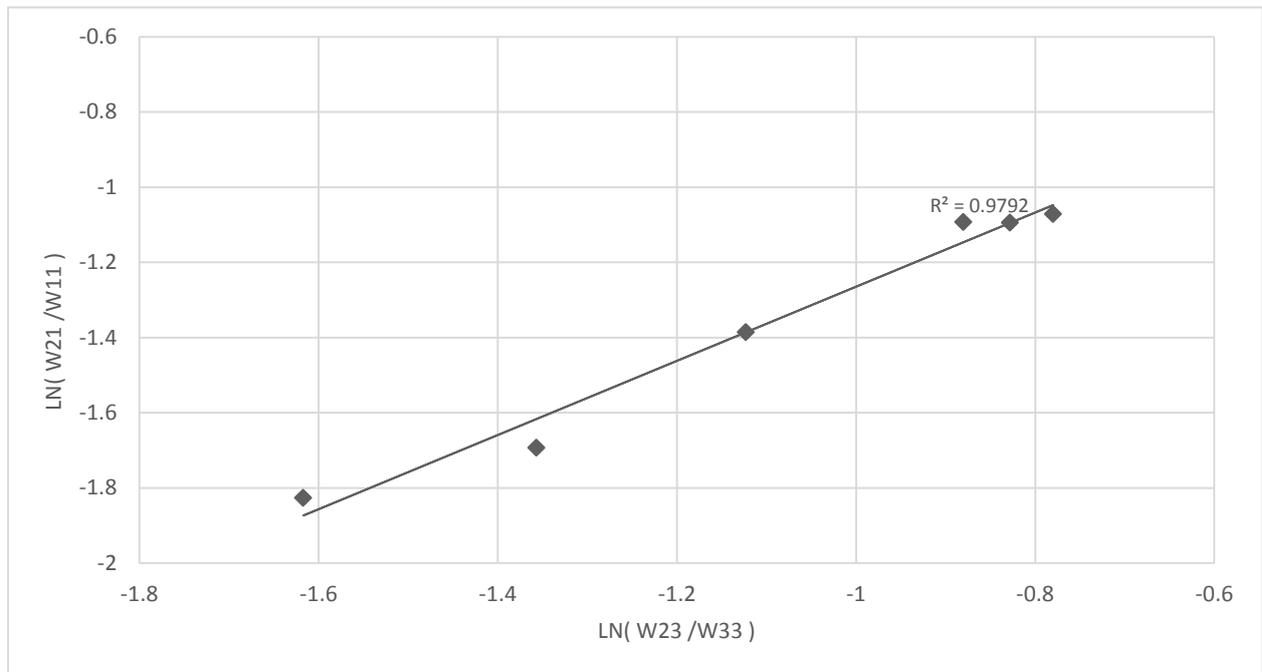
Fig. 5.Hand correlation for the system of water + acetic acid + ethyl acetate at 298.2 k

Conclusion

LLE data for acetic acid + water +ethyl acetate systems were obtainedat 298.2 K. Experimental resultsshowed that ethyl acetate havelow solubility in water and high solubility for acetic acid. Thus,they can serve as extractors to extract acetic acid from themixture 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 systemwere satisfactorily ascertained by the Othmer–Tobias and Handcorrelating equations. The separation factors and distributioncoefficients 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 asthe selectivity in all cases decreasedwith increasing of the mass fraction of acetic acidin water-rich phase.

Refrences

S.de Moura, J.dos Santos, F.da Silva, American Journal of Physical Chemistry 2013; 2(6): 117-121.

Upchurch, J.C. and Van Winkle, M., Industrial and EngineeringChemistry, 44, 618, 1952.

H. Ghanadzadeh , A. Ghanadzadeh , Z. Aghajani , S. Abbasnejad , S. Shekarsaraee,J. Chem. Thermodynamics 42 (2010) 695–699.

A. Senol, Fluid Phase Equilibr. 227 2005 87.

A. Arce, A. Blanco, P. Souza, I.J. Vidal, J. Chem. Eng. Data 40 (1995) 225.

S.Ismail Kırbas_lar, S. Sahin, M. Bilgin, J. Chem. Thermodyn. 38 (2006) 1503.

D. Ozmen, S. Cehreli, U. Dramur, J. Chem. Thermodyn. 37 (2005) 837.

H. Ghanadzadeh, A. Ghanadzadeh, J. Chem. Eng. Data 49 (2004) 783.

H. Ghanadzadeh, A. Ghanadzadeh, R. Sariri, J. Chem. Thermodyn. 36 (2004)1001.

H. Ghanadzadeh, A.K. Haghi, Fluid Phase Equilibr. 243 (2006) 45.

C. Hanson, Recent Advances in Liquid-Liquid Extraction, Pergamon, New York,1971.

R. Blumberg, Solvent Extr. Rev. 1 1971 93.

J.F. McCullough, L.L. Frederick, J. Agric. Food Chem. 24 (1) 1976 180–187.

A. Arabi, J. Mahmoudi , H. Saradar, A. Jafarzade, Korean J. Chem. Eng., 28(3),2011 917-922

C.-T. Hsieh, W.-Y. Ji, H.-M. Lin and M.-J. Lee, Fluid Phase Equilibria,271, 69 2008.

A. Orjuela, A. J. Yanez, P. K. Rossman, D.T. Vuc, D. Bernard-Brunel,D. J. Miller and C. T. Lira, Fluid Phase Equilibria, 290, 68 2010.

C.R. Bhupesh, M. R. Awual and M. Goto, Applied Sciences, 7, 1053 2007.

T. Afolabi, A. Alao , Fluid Phase Equilibria 379 2014 19–25

H. Ghanadzadeh Gilani, A. Ghanadzadeh Gilani, M. Sangashekan , J. Chem. Thermodynamics 58 2013 142–148