

Effect of Magnetic Field on the Liquid-liquid Equilibria of (Water + Acetic Acid + Organic Solvent) Ternary Systems

Kh. Bahrpaima*, A. R. Bijanzadeh, M. Behzadi

Department of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad, Iran

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The effect of magnetic field on the liquid-liquid equilibrium of two ternary systems (water + acetic acid + butyl acetate and water + acetic acid + dimethyl succinate) at 298.15 K under atmospheric pressure was investigated. The results obtained show that the strength of the magnetic field (0.02 T) affects the solubility of acetic acid in the used organic solvents. Distribution coefficients and separation factors were determined from the experimental LLE tie-line data for these systems. The comparisons indicated that the separation factor for the mixtures with dimethyl succinate is more effective than those with butyl acetate. The reliability of the tie-line data was ascertained through the Othmer-Tobias method. The tie-line data of studied ternary systems were also correlated using NRTL method and the values of the binary interaction parameters were obtained. It was concluded that the NRTL model accurately correlates the experimental data of the mentioned ternary systems.

Keywords: Liquid-liquid equilibria, Magnetic field, Ternary systems, NRTL

INTRODUCTION

The accurate liquid-liquid equilibrium data of multicomponent systems is of great importance in developing thermodynamics in chemical engineering. For many years several works have focused on presenting further information about phase behavior of LLE; such as suitable mixed solvents, ionic liquids, salting effects, etc. [1-10]. In recent years, the influence of the magnetic field on chemical engineering has attracted the interest of many researchers [11-15].

It is anticipated that the magnetic field, as an external factor, can affect LLE data by influencing mass transfer, changing the thermodynamic equilibrium position and possibly improving distribution coefficient of components in both phases [16-19]. Therefore, for this purpose, in this piece of work we investigated the effect of magnetic field on LLE data of two ternary systems (water + acetic acid +

butyl acetate and water + acetic acid + dimethyl succinate) at 298.15 K, and finally compared the results with those which had formerly been obtained on the same systems in the absence of magnetic field [20-23].

Furthermore, the non-random two-liquid model (NRTL) [24] was used to predict the tie-line data for these ternary systems. The data predicted by the proposed model were then compared with the experimental data. The NRTL model was also used to estimate the binary interaction parameters determined by minimizing the differences between the experimental and calculated mass percentages for each of the components over all the tie-lines [24-25].

MATERIAL AND METHODS

Materials

The chemicals acetic acid (0.99), butyl acetate (0.99) and dimethyl succinate (0.95) were obtained from Merck and were used without further purification. The purity of these materials was checked by gas chromatography.

*Corresponding author. E-mail: Kh.bahrpyma@iauf.ac.ir

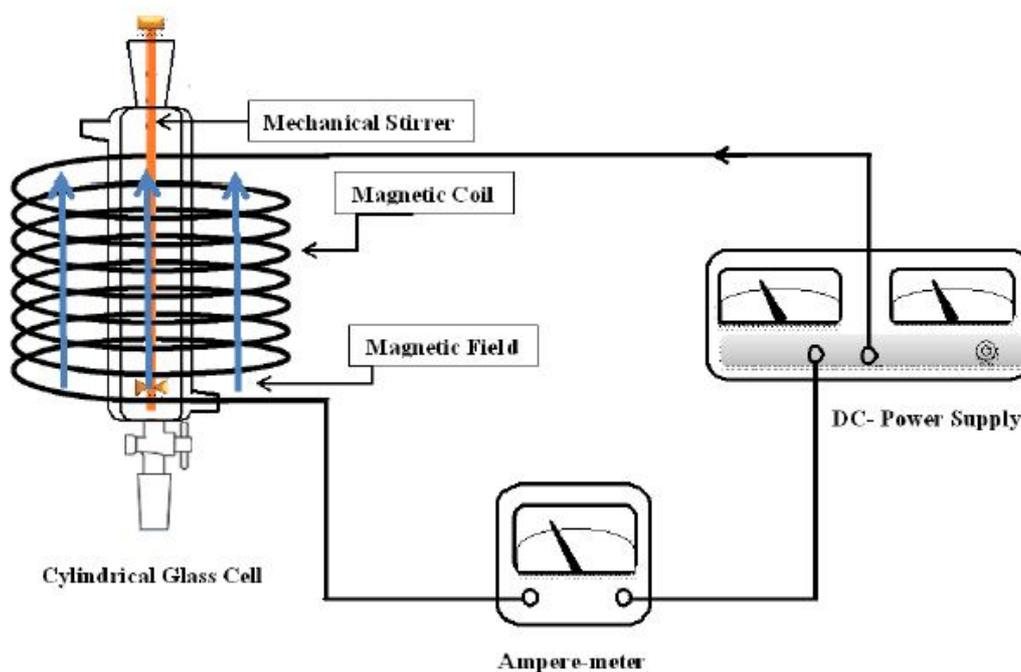


Fig. 1. Schematic diagram of the experimental setup.

Distilled water was prepared in our laboratory and used throughout all experiments.

Apparatus and Procedure

Liquid-liquid measurements at $T = 298.2$ K were performed in a cylindrical glass cell connected to a thermostat (Fig. 1). A water jacket was used to control the temperature of the cell within $\pm 0.1\%$. The heterogeneous mixtures with known masses of (water + acetic acid + solvent) were prepared; the mixtures were placed inside the cell and were vigorously agitated with a mechanical stirrer for 3 h and left to rest for 4 h. A uniform magnetic field of magnitude 0.02 T in the positive y direction was transmitted through the glass cell containing the studied mixture for 2 h. After equilibration and phase settling, samples were taken from both phases; these samples were analyzed using a Varian CP-3800 gas chromatography (GC), equipped with a thermal conductivity detector (TCD) and Star integrator. Chromatography separation of the mixture constituents was achieved by a capillary column $4.0\text{ m} \times 1/4\text{ inch} \times 4.0\text{ mm}$, SS, 7% Carbowax 20M Carbowax 20M on Chromosorb T 40-60 mesh. The flow rate of carrier (helium) gas was $40\text{ cm}^3\text{ min}^{-1}$ and the temperatures of detector and injector were

set at 423.15 K and 523.15 K, respectively. Oven temperature was programmed as follows: the initial temperature was set at 323.15 K for 7 min, followed by a constant heating rate of 10 K min^{-1} until a final temperature of 503.15 K is attained. The TCD's response was calibrated with methanol for both phases as an internal standard.

The schematic diagram of the experimental setup is shown in Fig. 1. According to this figure, the cell has been placed in the center of a solenoid. The constant DC magnetic field was produced by a current in the solenoid; powered by a DC-power supply in the circuit, providing a current measured by an ammeter measures it. The number of windings of the solenoid is 7800/m and the magnitude of the magnetic field generated at the center of solenoid is 0.02 T.

RESULTS AND DISCUSSION

Table 1 reports the mass percentages of each component in the two liquid phases at equilibrium for (water + acetic acid + butyl acetate and water + acetic acid + dimethyl succinate) mixtures in the presence of a magnetic field.

Moreover, the LLE phase diagrams for these systems at

Table 1. Experimental Tie-line Data for {Water (1) + Acetic Acid (2) + Solvent (3)} in the Presence of DC Magnetic Field ($B = 0.02$ T) for Mass Percents W at Temperature $T = 298.15$ K and Pressure $p = 0.1$ MPa^a

W_{13}	W_{23}	W_{33}	W_{11}	W_{21}	W_{31}
Water (1) + Acetic acid (2) + Butyl acetate (3)					
2.3	2.3	95.4	93.2	5.3	1.5
3.2	8.4	88.4	80.6	17.7	1.7
4.2	13.6	82.2	71.8	25.3	2.9
5.4	19.8	74.8	62.0	31.6	6.4
9.6	32.0	58.4	44.7	44.0	11.3
Water (1) + Acetic acid (2) + Dimethyl succinate (3)					
11.8	6.4	81.8	79.3	8.2	12.5
16.9	8.7	74.4	74.8	11.3	13.9
21.6	11.6	66.8	67.9	13.8	18.3
30.1	14.4	55.5	60.2	16.4	23.4
35.5	15.5	49.0	55.0	17.0	28.0

^aStandard uncertainties u are $u(W) = 0.1$, $u(T) = 0.01$ K, and $u(p) = 10$ kPa.**Table 2.** Distribution Coefficients of Acetic Acid (D_2) and Water (D_1) and Separation Factors (S) in Presence of DC Magnetic Field ($B = 0.02$ T) at Temperature $T = 298.15$ K

D_1	D_2	S
Water (1) + Acetic acid (2) + Butyl acetate (3)		
0.02	0.43	17.58
0.04	0.47	11.95
0.06	0.54	9.19
0.09	0.63	7.19
0.21	0.73	3.39
Water (1) + Acetic acid (2) + Dimethyl succinate (3)		
0.15	0.78	5.25
0.23	0.77	3.41
0.32	0.84	2.64
0.50	0.88	1.76
0.65	0.91	1.41

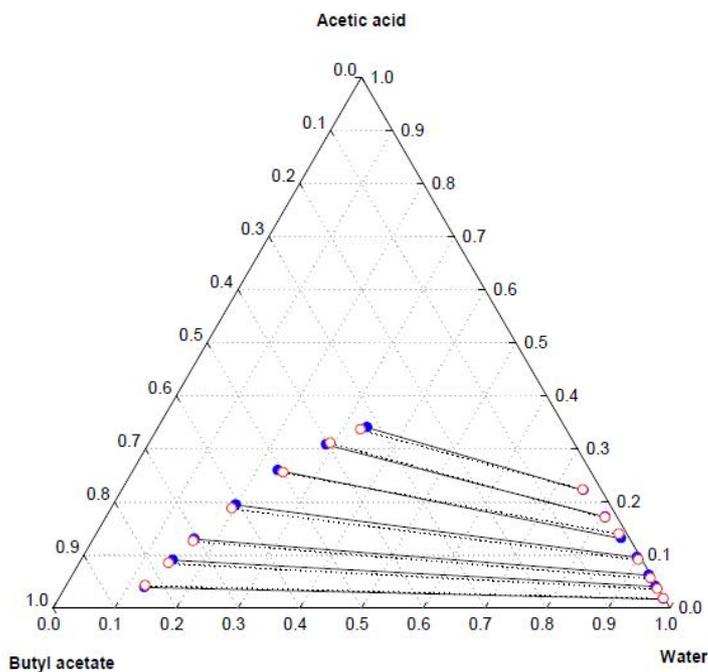


Fig. 2. Correlation of the experimental data for {water + acetic acid + butyl acetate} system in the presence of DC magnetic field ($B = 0.02$ T) at temperature $T = 298.15$ K.; experimental points; —●—, calculated points; --○--.

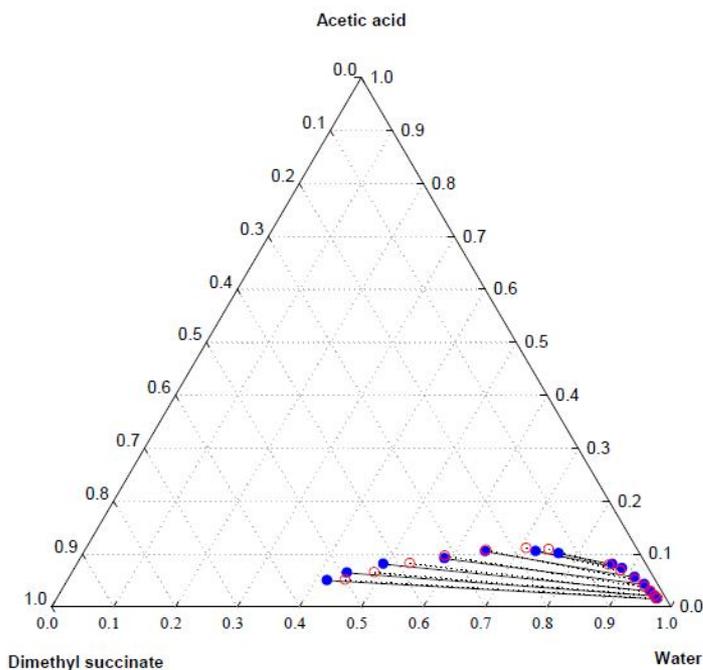


Fig. 3. Correlation of the experimental data for {water + acetic acid + dimethyl succinate} system in the presence of DC magnetic field ($B = 0.02$ T) at temperature $T = 298.15$ K.; experimental points; —●—, calculated points; --○--.

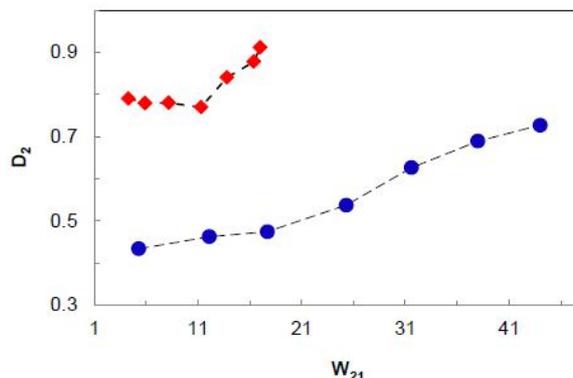


Fig. 4. Experimental distribution coefficients D_2 of acetic acid as a function of the mass percentages W_{21} of acid in aqueous phase in the presence of DC magnetic field ($B = 0.02$ T) at temperature $T = 298.15$ K; $\text{---}\blacklozenge\text{---}$, butyl acetate mixtures; $\text{---}\bullet\text{---}$, dimethyl succinate mixtures; $\text{---}\blacklozenge\text{---}$.

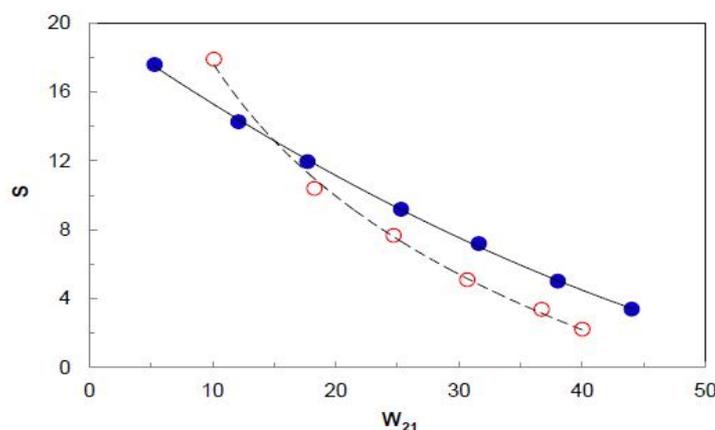


Fig. 5. Experimental separation factors S of acetic acid as a function of the mass percentages W_{21} of acid in aqueous phase for butyl acetate solutions at $T = 298.15$ K; $\text{---}\bullet\text{---}$, Separation factor calculated from Eq. (1); $\text{---}\circ\text{---}$, in the presence of DC magnetic field ($B = 0.02$ T); $\text{---}\circ\text{---}$, without a magnetic field which were directly obtained from reference [20]; $\text{---}\circ\text{---}$.

298.15 K were plotted and shown in Figs. 2 and 3.

The separation factor S and distribution coefficient D for the studied ternary systems in the presence of a magnetic field are reported in Table 2 and Figs. 4-6. The separation factor is defined as [26]:

$$S = \frac{D_2}{D_1} \quad (1)$$

where D_2 (distribution coefficient of acetic acid) is the

(mass percentage of acetic acid in organic phase/mass percentage of acetic acid in aqueous phase) and D_1 is the (mass percentage of water in organic phase/mass percentage of water in aqueous phase) [27].

Also, in Figs. 5 and 6, the separation factors of these solutions in the absence [20,22-23] and presence of the uniform magnetic field ($B = 0.02$ T) were compared. According to the results in these Figs, the separation factors for (water + acetic acid + dimethyl succinate) system are

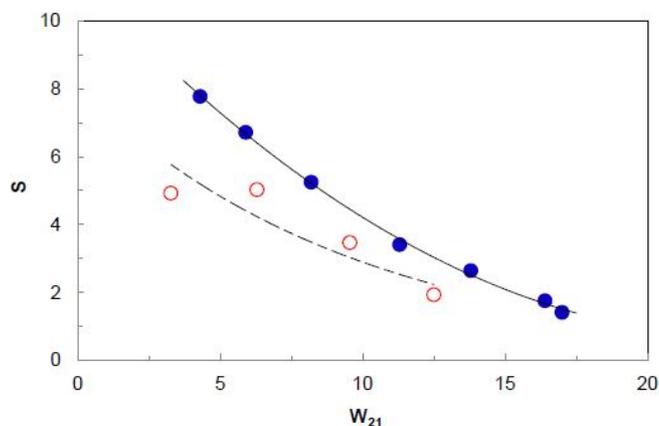


Fig. 6. Experimental separation factors S of acetic acid as a function of the mass percentages W_{21} of acid in aqueous phase for dimethyl succinate solutions at $T = 298.15$ K., without a magnetic field which were directly obtained from reference [22,23]; --○--, in the presence of DC magnetic field ($B = 0.02$ T); —●—.

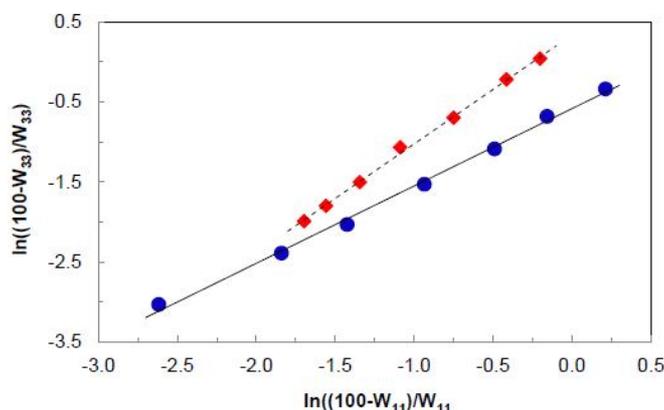


Fig. 7. Othmer-Tobias plots for the experimental data of {water (1) + acetic acid (2) + solvent (3)} systems in the presence of DC magnetic field ($B = 0.02$ T) at $T = 298.15$ K., butyl acetate mixtures; —●—, dimethyl succinate mixtures; --◆--, Othmer-Tobias data calculates from Eq. (3).

varying and climbing between 3.03 and 8.57 in the presence of the magnetic field, whilst these values in the same percentages of acid in aqueous phase are increasing from 1.93 to 4.92 in the absence of field [22,23] (Fig. 6). In addition, the ranges of variations of this quantity for the systems with butyl acetate are (5.49 to 11.49) and (2.23 to 10.39) [20] in the presence and absence of the magnetic field, respectively, when acetic acid percentage varies between 18.26 and 40.01 (Fig. 5). It means that extraction of acetic acid from aqueous solutions by the reported

solvents can be impressive in the presence of the magnetic field ($B = 0.02$ T).

The NRTL tie-line data and optimized interaction parameters were predicted using the NRTL activity coefficient model for the studied mixtures at $T = 298.15$ K, presenting in Tables 3 and 4.

Furthermore, the root-mean-square deviation (*RMSD*) was calculated from the difference between the experimental and calculated mass percentages according to the following equation:

Table 3. NRTL Tie-line Data for {Water (1) + Acetic Acid (2) + Solvent (3)} for Mass Percents W at Temperature $T = 298.15$ K and Pressure $p = 0.1$ MPa^a

W_{13}	W_{23}	W_{33}	W_{11}	W_{21}	W_{31}
Water (1) + Acetic acid (2) + Butyl acetate (3)					
2.3	2.5	95.2	93.5	5.3	1.2
3.1	7.9	89.0	82.4	15.4	2.2
4.1	13.0	82.9	72.8	23.7	3.5
5.7	19.7	74.6	60.8	33.2	6.0
9.7	32.0	58.3	40.6	45.0	14.4
Water (1) + Acetic acid (2) + Dimethyl succinate (3)					
13.0	6.6	80.4	79.6	8.6	11.8
16.5	8.8	74.7	74.7	10.9	14.4
21.8	11.8	66.4	68.0	13.5	18.5
29.7	14.8	55.5	60.1	15.7	24.2
35.4	16.2	48.4	55.1	16.6	28.3

^aStandard uncertainties u are $u(W) = 0.1$, $u(T) = 0.01$ K, and $u(p) = 10$ kPa.**Table 4.** NRTL Binary Interaction Parameters (Δu_{ij} and Δu_{ji}) and Root-mean Square Deviation ($RMSD$) Values for LLE Data of Studied Systems in Presence of Magnetic Field at Temperature $T = 298.15$ K

α_{ij}	$i-j$	Δu_{ij} (J mol ⁻¹)	Δu_{ji} (J mol ⁻¹)	$RMSD$
Water (1) + Acetic acid (2) + Butyl acetate (3)				
0.3	1-2	-45.7709	1.2826	
	1-3	44.7851	14.9749	1.13
	2-3	4.6343	-53.5610	
Water (1) + Acetic acid (2) + Dimethyl succinate (3)				
0.3	1-2	41.3542	-17.7521	
	1-3	38.5769	2.6855	0.48
	2-3	-1.1871	10.2888	

Table 5. Othmer-Tobias Equation Constants for Studied Systems in Presence of Magnetic Field at Temperature $T = 298.15$ K

	Othmer-Tobias correlation		
	A	B	R^2
Water (1) + Acetic acid (2) + Butyl acetate (3)			
Exp.	-0.606	0.950	0.996
NRTL	-0.694	0.880	0.999
Water (1) + Acetic acid (2) + Dimethyl succinate (3)			
Exp.	0.317	1.327	0.996
NRTL	0.309	1.279	0.999

$$RMSD = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 (W_{ijk} - \hat{W}_{ijk})^2}{6n}} \quad (2)$$

where n is the number of the tie-lines, W indicates the experimental mass percentage, \hat{W} is the calculated mass percentage, subscripts i and j are respectively index components and phases and $k = 1, 2, \dots, n$ (tie-lines). The results of $RMSD$ calculations by using the model NRTL indicate a good agreement with experimental data, which are shown in Table 4.

The consistency of the experimental tie-line data can likewise be determined using the Othmer and Tobias correlation [28] for the ternary systems:

$$\ln\left(\frac{100 - W_{33}}{W_{33}}\right) = A + B \ln\left(\frac{100 - W_{11}}{W_{11}}\right) \quad (3)$$

where A and B are constants, W_{33} is mass percentage of solvent in organic phase and W_{11} is the mass percentage of water in aqueous phase. The Othmer-Tobias plots are presented in Fig. 7, and the correlation parameters are also listed in Table 5 for these systems at 298.15 K. As it is seen, the plots are linear for each acid solution, indicating a high degree of consistency for the related data.

CONCLUSIONS

In this study LLE data of (water + acetic acid + butyl acetate and water + acetic acid + dimethyl succinate) ternary systems under the influence of a uniform magnetic field (0.02 T) at $T = 298.15$ K were obtained. Experimental LLE data for the reported systems were predicted using NRTL model and then the average $RMSD$ values were measured. The calculated overall $RMSD$ indicated a good agreement with experimental data and the calculated values. The results also showed that the magnetic field ($B = 0.02$ T) is, on the whole, effective on LLE data and separation factors of the studied systems. The separation factor values for the mixtures with dimethyl succinate and butyl acetate additionally increased in the presence of a magnetic field. It can be also seen that the influence of magnetic field on systems with dimethyl succinate is a bit higher than those with butyl acetate. The comparison of our results with those obtained without a magnetic field concludes that extraction of acetic acid from aqueous solutions by dimethyl succinate and butyl acetate under magnetic field is more preferable.

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