Rahman, M.A.; Rahman, M.S.; Nabi, M.N.; Rahman M.M. S. and Azad, M.A.K. 2008. Extraction of ethanol from aqueous solution using 1-hexanoic acid and 1-nonanoic acid. *Khulna University Studies*, 9(1): 41-46.

Khulna University Studies, 9(1): 41-46, 2008

RESEARCH ARTICLE **LIFE SCIENCE**

EXTRACTION OF ETHANOL FROM AQUEOUS SOLUTION USING 1-HEXANOIC ACID AND 1-NONANOIC ACID

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KUS–07/25-290707

Manuscript received: July 29, 2007; Accepted: June 28, 2008

Abstract: Ternary phase equilibrium data for ethanol-water-1-hexanoic acid and 1-nonanoic acid were experimentally obtained with a view to evaluate the possibility of separation of ethanol from aqueous solutions by distributing each between water and ethanol phases. The mutual solubility curves, tie lines and plait points were constructed from the experimental results. Distribution coefficients and separation factors were computed for these systems. Hand's method was used to correlate tie lines and to calculate coordinates of plait points. Tie line data were satisfactorily correlated by the Othmer-Tobias method on a mass fraction basis.

Key words: Ternary equilibrium data, tie line, plait point, ethanol-water-1-hexanoic acid

Introduction

The fermentation process and its recent developments have led to the efficient production of dilute alcohol-water mixtures. The conventional method, distillation and azeotropic distillation, for recovering anhydrous ethanol from the fermentation broth consumes 50-80% of the energy used in a typical fermentation ethanol manufacturing process and is frequently cited in criticizing the potential of biomass-derived ethanol as a liquid fuel (Ruiz *et al.*, 1987). However, new technologies for separating alcohol from water solutions soon may lower significantly the cost of producing ethyl alcohol by fermentation.

Liquid-liquid extraction is one possible means of accomplishing this separation. Several investigators have obtained experimental data of distribution coefficients and separation factors at high dilution of ethanol for a wide range of solvents (e.g. Rahman *et al*., 2001; Rahman *et al*., 1995; Munson and King, 1984;). Within the scope of this procedure, several alcohols (Luckman *et al*., 2002; Kirk and Othmer, 1992; Ruiz *et al*., 1987; Lee and Pahl, 1985; Furzer, 1984; Leeper and Wankat, 1982) have been used as solvents to extract ethanol from aqueous solutions. However, the design calculation cannot be done using only these data of one tie line for each system, because they depend on the ethanol concentration.

In this study liquid-liquid equilibrium data covering the whole range of the heterogeneous region of ternary systems comprising of ethanol-water-solvents (1-hexanoic acid and 1-nonanoic acid)

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DOI: https://doi.org/10.53808/KUS.2008.9.1.0725-L

have been determined experimentally at temperature 30±0.5°C, and the tie lines, plait points, distribution coefficients and separation factors of the respective systems have been computed.

Materials and Methods

Materials: Ethanol (Merck KgaA, Germany, 99-100%, d=0.79g.cm^{-3}), 1-hexanoic acid (BDH, England, 98-100%, d=0.92g.cm^{-3}) and 1-nonanoic acid (BDH, England, 99-100%, d=0.907g.cm^{-3}) were used. Single distilled deionised water was used throughout this work.

Mutual solubility data: The mutual solubility data for ethanol-water-1-hexanoic acid and ethanol-water-1-nonanoic acid systems were determined by the titration method (Feki et al., 1994). 10 ml of water was measured into a 125 ml closed Erlenmeyer flask and solvent (1-hexanoic acid or 1-nonanoic acid) was added from a burette and agitated till the solution had started to appear turbid. The amount of each solvent added was recorded as the maximum solubility of the respective solvent in water and gave the first point of the mutual solubility curve on the base line. The turbidity indicated the beginning of formation of second phase of the solvent layer. Then ethanol was added from burette until the first appearance of distinct clear homogeneity. That gave another point of mutual solubility curve on the triangular diagram. The procedure was repeated to construct the mutual solubility curve from the aqueous side. Same procedure was applied starting with an initially measured quantity of solvent to construct the mutual solubility curve on solvent side. The refractive index of each mixture (that indicated as the point on the mutual solubility curve) was measured using an "Atago Precision Abbe Refractometer type-3".

Equilibrium data: Equilibrium data were determined for those systems at room temperature of 30±0.5 °C. Equal amount of the solvent and water were placed in a 250 ml closed Erlenmeyer flask and a measured amount of ethanol was then added. The flask was then vigorously shaken by electric shaker for one hour and allowed to stay undisturbed for an hour. 1-2 drops of each phase were removed as samples by pipette, and its refractive index were carefully measured (Arce *et al*., 1995). Compositions of the phases were determined from the solubility data in the mutual solubility curve using calibration graphs for refractometric measurements (Hegazi and Salem, 1983; Ananthanarayanan and Rao 1968).

Results

The composition at points of mutual solubility curves for ethanol-water-1-hexanoic acid and ethanol-water-1-nonanoic acid systems were determined experimentally at temperature 30±0.5°C. The mutual solubility data are placed in Table 1 and Table 2. These tables also include the measured refractive indices for the equilibrium mixtures. The ternary diagrams are plotted in Fig. 1 and Fig. 2.

Table 1. Mutual solubility data of the ethanol-water-1-hexanoic acid system at 30±0.5 °C.

	Composition, wt%			Refractive
	1-hexanoic acid	Water	ethanol	index
Water-rich phase	0	100	0	1.3306
	2.7	74.4	22.9	1.3446
	6.2	67.2	26.6	1.3480
	11.1	60.3	28.6	1.3504
	15.2	55.2	29.6	1.3526
	21.7	47.3	31.0	1.3540
	26.8	41.6	31.6	1.3548
	30.9	37.3	31.8	1.3550
1-hexanoic acid –rich	94.8	5.2	0	1.4090
Phase	83.0	9.9	7.1	1.4034
	61.9	16.8	21.3	1.3906
	50.6	22.0	27.4	1.3846

	42.1	27.5	30.4	1.3794
	36.6	31.9	31.5	1.3762
	32.8	35.7	31.5	1.3748
Plait point	19.3	50.6	30.1	-

Table 2. Mutual solubility data of the ethanol-water-1-nonanoic acid system at 30±0.5 °C.

	Composition, wt%			Refractive
	1-nonanoic acid	water	ethanol	index
Water-rich phase	0	100	0	1.3306
	1.2	66.7	32.1	1.3494
	5.4	59.7	34.9	1.3536
	9.9	54.4	35.7	1.3554
	13.7	50.2	36.1	1.3565
	19.9	43.8	36.3	1.3577
	24.6	38.7	36.7	1.3580
	28.5	35.0	36.5	1.3583
1-nonanoic acid-rich	100	0	0	1.4256
Phase	92.9	3.1	4.0	1.4216
	76.8	8.5	14.7	1.4102
	61.3	14.2	24.5	1.3990
	53.4	17.7	28.9	1.3938
	43.1	23.8	33.1	1.3856
	36.7	28.4	34.9	1.3822
	32.3	32.0	35.7	1.3792
	30.4	33.5	36.1	1.3774
Plait point	21.5	42.0	36.5	-

The heterogeneous region of ethanol-water-1-nonanoic acid system is slightly broader than that of ethanol-water-1-hexanoic acid system (Table 1. and Table 2.). It is also found that the binary systems of water-1-hexanoic acid and water-1-nonanoic acid were immiscible and the miscibility of water-solvents binary systems decreased with increasing number of carbon atom in the chain of solvents. Experimental data on compositions of coexisting phases are presented in Table 3 and distribution coefficients and separation factors between the coexisting liquid phases were calculated. The corresponding equilibrium distribution curves (Fig. -3) and equilibrium tie lines (Fig. 1 and Fig. 2) are constructed with these data. Fig. 3 shows that the concentration of ethanol in extract phase increased with increasing concentration of ethanol in raffinate phase.

Table 3. Composition of co-existing phases in the ethanol-water-1-hexanoic acid/1-nonanoic acid systems at 30±0.5 °C.

Composition of initial mixture, wt%			Composition of extract phase, wt%			Composition of raffinate phase, wt%			K_D	α
water	1-hexanoic acid	ethanol	water	1-hexanoic acid	ethanol	water	1-hexanoic acid	ethanol		
47.2	43.4	9.3	11.0	79.0	10.0	90.5	1.0	8.5	1.176	9.639
43.2	39.7	17.1	15.5	65.7	18.8	83.5	1.7	14.8	1.270	6.828
39.8	36.6	23.6	20.0	54.4	25.6	78.2	2.0	19.8	1.293	5.051
36.9	33.9	29.2	28.0	41.3	30.7	72.0	4.0	24.0	1.279	3.288
water	1-nonanoic acid	ethanol	water	1-nonanoic acid	ethanol	water	1-nonanoic acid	ethanol		
47.5	43.1	9.4	4.8	87.6	7.6	88.7	0.3	11.0	0.691	12.796
43.4	39.4	17.2	9.0	75.4	15.6	80.3	0.6	19.1	0.817	7.295
40.0	36.3	23.7	13.2	64.2	22.6	74.4	0.8	24.8	0.911	5.147
34.6	31.3	34.1	26.0	40.0	34.0	63.8	2.0	34.2	0.994	2.436

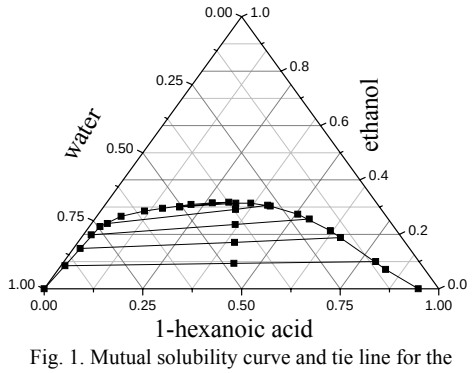

Fig. 1. Mutual solubility curve and tie line for the ethanol-water-1-hexanoic acid system at 30±0.5°C.

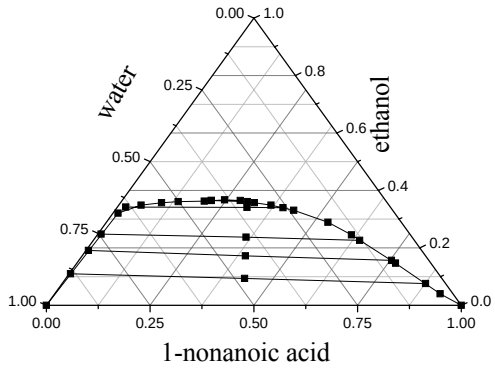

Fig. 2. Mutual solubility curve and tie line for the ethanol-water-1-nonanoic acid system at 30±0.5°C.

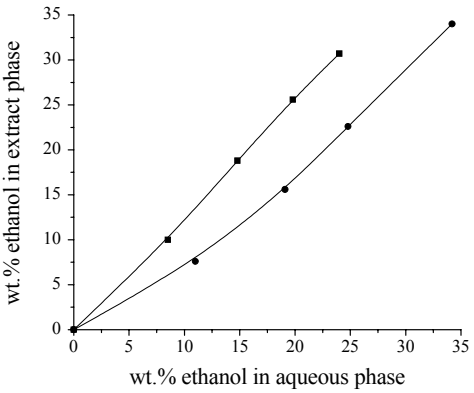

Fig. 3. Equilibrium distribution curve for the ethanol-water-solvent systems. ■-1-hexanoic acid and ●-1-nonanoic acid.

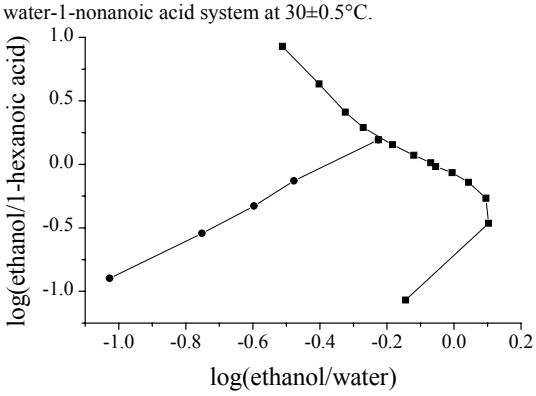

Fig. 4. Hand type ternary diagram for plait point (λ) determination of the ethanol-water-1-hexanoic acid system.

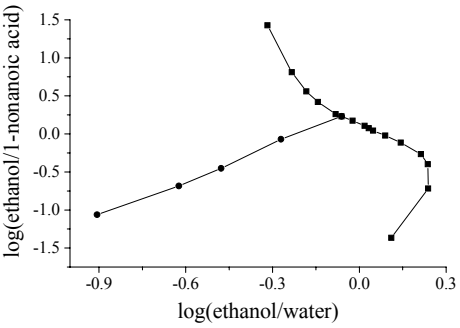

Fig. 5. Hand type ternary diagram for plait point (λ) determination of the ethanol-water-1-nonanoic acid system.

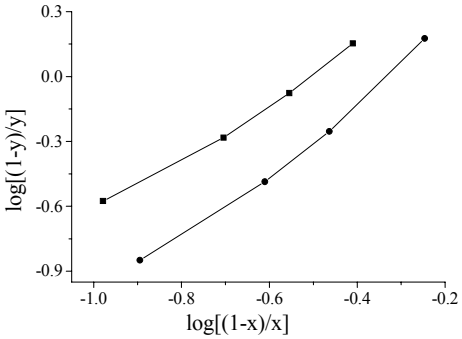

Fig. 6. Othmer-Tobias plot of tie lines data for ethanol-water-solvent systems. ■-1-hexanoic acid and ●-1-nonanoic acid.

Discussion

Ethanol is soluble in water because its –OH group can both donate and accept hydrogen bonds (Loudon, 1995). Acetic acid containing one methyl group (-CH_3) and one methylene group (=CH_2) in the molecule, with a ratio of (OH **:** C) 1**:**2, has far stronger polarity (Katayama *et al.*, 1998) than 1-hexanoic acid and 1-nonanoic acid. Fig. 1 shows that since the concentration of ethanol in 1-hexanoic acid-richer phase was higher than that in water-richer phase, the 1-hexanoic

acid had stronger affinity for ethanol than water. Fig. 2 shows that the concentration of ethanol in 1-nonanoic acid-phase was lower than that of the water-phase. Water had stronger affinity for ethanol than 1-nonanoic acid.

The separation factor (α) is determined numerically from the tie line data because, it is the ratio of distribution coefficient of ethanol to the distribution coefficient of water. The distribution coefficient of ethanol (K_D) is the ratio of concentration of ethanol in extract phase to that of raffinate phase. Similarly, the distribution coefficient of water is the ratio of concentration of water in extract to that of in raffinate phases, respectively. Table 3 shows the value of distribution coefficient of ethanol (K_D) and separation factor (α) that were measured for extraction of ethanol with weight percent feed (EtOH-H_2O) concentration. It may be found from Table 3 that 1-hexanoic acid gave K_D values ranging from 1.176 – 1.279 and 1-nonanoic acid, which range from 0.691 – 0.994 for various ethanol concentrations in the feed. The separation factors for ethanol-water-1-hexanoic acid and ethanol-water-1-nonanoic acid systems were considerably greater than 3 and 2. 1-hexanoic acid and 1-nonanoic acid gave the separation factors (α) ranging from 3.288 – 9.639 and 2.436 – 12.796, respectively for various ethanol concentrations in the feed. It indicates that ethanol had the preferential solubility in the solvents as it was desired in the extraction process.

Distribution of ethanol between solvent and water may be correlated graphically according to Hand's plot (Perry *et al*., 1984). This reduces the number of experimental data required; moreover, it allows a graphical determination of the plait points. Extrapolation of the tie line curves crosses the mutual solubility curves at the plait points (Fig. 4 and Fig. 5). The plait point compositions for ethanol-water-1-hexanoic acid and ethanol-water-1-nonanoic acid systems were obtained graphically by means of Hand's plot which is placed in Table 1 and 2.

The tie lines were satisfactorily correlated by the Othmer-Tobias method (Maeda *et al*., 1997 in Othmer and Tobias, 1942) and are presented in Fig. 6 where log[(1-y)/y] is plotted against log[(1-x)/x] (where y is the weight fraction solvent in the extract phase and x is the weight fraction water in the raffinate phase) and the relation indeed resulted in straight lines. It is expected that both Othmer-Tobias plot and Hand's correlation would yield tie lines as straight lines (Hand, 1930).

Selection of solvents for extraction of ethanol from dilute aqueous solution should be guided by considerations of selectivity with respect to water (separation factor), as well as equilibrium distribution coefficient for ethanol. It can be observed from Table 3, that 1-hexanoic acid was the better among the two solvents and may be regarded as a separating agent for dilute aqueous ethanol solutions.

Conclusion

Liquid-liquid phase equilibrium data were measured for ethanol-water-1-hexanoic acid and ethanol-water-1-nonanoic acid ternary systems. The mutual solubility curves, tie lines, distribution co-efficients and separation factors were determined. Hand's method was used to correlate tie lines and to calculate coordinates of plait points. Tie line data were satisfactorily correlated with the Othmer-Tobias method on a mass fraction basis, and their plot would yield tie lines as straight lines. The distribution coefficients of ethanol for 1-hexanoic acid and 1-nonanoic acid systems were found greater than 1.0 and 0.6, respectively and the separation factors of 1-hexanoic acid and 1-nonanoic acid systems were greater than 3 and 2 respectively. It may be concluded that 1-hexanoic acid would be considered a separating agent for dilute aqueous ethanol solutions.

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