Ternary Liquid Equilibria of Ethanol-Water-Oleyl Alcohol and Ethanol-Water-Oleic Acid Systems

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The ternary equilibrium data are presented for the ethanol -water - oleyl alcohol and ethanol- water - oleic acid systems at 30°C. The binodal curves, tie lines, plait points, distribution coefficients and separation factors have been determined to extract ethanol from the aqueous solution. Hand's method has been 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.

Keywords: Ternary equilibrium data, Tie line, Ethanol-water-oleyl alcohol.

Introduction

The production of anhydrous alcohol from lower concentration of aqueous solutions, requires almost complete removal of water. This operation is often complicated by the formation of azeotropes. Typically, azeotropic or extractive distillations are used for such separations. These traditional technology for the separation of alcohol from aqueous solutions are energy intensive and expensive because of the high reflux ratio and large number of stages required for nearly complete separation.

Liquid - liquid extraction is one of the separation process in chemical industries and it requires a reliable knowledge of the liquid -liquid equilibria for the system to be separated. The extraction of alcohol from dilute solutions resulting from fermentation processes and many solvents have been tried to improve such recovery by means of liquid-liquid extraction (Munsan and King 1984; Botto *et al* 1989; Letcher *et al* 1991; Arda and Sayar 1992; Briones *et al* 1994; Maeda *et al* 1997; Gomez Marigliano *et al* 1998; Rahman *et al* 2001). For the design of an extracting device, quantitative representation is required of the liquid - liquid equilibria of the appropriate ternaries.

The purpose of this study is to determine precise binodal curves, tie lines and plait points for ethanol-water -oleyl alcohol and ethanol-water-oleic acid systems at 30°C. The distribution coefficients and separation factors have to be evaluated to investigate the extracting capabilities of the selected solvents.

Experimental

Materials. Ethanol (Merck KGaA, Germany, 99-100%, d = 0.79 g/cm³), oleyl alcohol (BDH, England, d = 0.83 g/cm³) and oleic

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acid (BDH, England, 92%, d=0.888 g/cm³) were used without further purification. Distilled water was used throughout this work.

Solubility data. The solubility data for ethanol-water-oleyl alcohol and ethanol-water-oleic acid systems were determined by the titration method (Feki *et al* 1994). 10 cm³ of water was measured into a 125cm³ closed Erlenmeyer flask and solvent was added from a burette and agitated till the solution started to appear turbid. The amount of solvent added was recorded as the maximum solubility of the solvent in the water and gave the first point of the binodal curve on the base line. The appearance of turbidity indicated the beginning of formation of the second phase, the solvent layer. Therefore, further addition of a small amount of solvent gave a heterogeneous mixture. Then ethanol was added from a burette until the first appearance of distinct clear homogeneity. This gave another point of binodal curve on the aqueous side. Same procedure was applied starting with an initially measured quantity of solvent to construct the binodal curve on the solvent side. The refractive index of each mixture indicated as a point on the binodal curve which was measured by using an "Atago Precision Abbe Refractometer."

Equilibrium data. Equilibrium data were determined for these systems at 30°C. Aliquots of 20 cm³ each of water and solvent were taken in five different 250 cm³ closed Erlenmeyer flask and then various amounts of ethanol were added until the formation of single phases were noticed. These flasks were vigorously shaken by an electric shaker for 30 min and were permitted to settle for 60 min. After settling, two coexisting phases were formed. 1-2 Drops of each equilibrated phase were removed by pipette, and their refractive index was carefully measured. Compositions of the phases were determined from the solubility data using calibration curves for refracto-

Table 1

Solubility data of the ethanol-water-oleyl alcohol system at 30°C.

	Composition, wt%		
	Water	oleyl alcohol	ethanol
Water-rich phase	100.0	0.0	0.0
	40.4	1.3	58.3
	37.5	3.1	59.4
	34.0	5.6	60.4
	31.6	7.9	60.5
	28.6	12.1	59.3
	26.6	15.5	57.9
Oleyl alcohol-rich phase	0.0	100.0	0.0
	3.0	68.1	28.9
	7.0	58.5	34.5
	10.5	50.0	39.5
	13.9	42.4	43.7
	18.2	32.0	49.8
	21.3	25.3	53.4
	24.0	19.6	56.4
Plait point	18.2	32.0	49.8

Table 2

Solubility data of the ethanol-water-oleic acid system at 30°C.

	Composition, wt%		
	Water	oleic acid	ethanol
Water-rich phase	100.0	0.0	0.0
	44.4	1.7	54.3
	41.0	4.0	55.0
	38.2	9.6	54.9
	36.2	9.6	54.2
	32.5	14.5	53.0
	29.7	18.4	51.9
Oleyl alcohol-rich phase	0.0	100.0	0.0
	3.4	78.6	18.0
	6.0	67.4	26.6
	10.3	53.7	36.0
	14.5	44.0	41.5
	19.0	35.5	45.5
	22.1	30.0	48.9
	26.4	23.3	50.3
Plait point	22.5	28.7	48.8

metric measurements (Ananthanarayanan and Rao 1968; Hegazi and Salem 1983).

Results and Discussion

The composition to points of binodal curves for ethanol-water-oleyl alcohol and ethanol-water-oleic acid systems have been experimentally determined at 30°C. Binodal data are given in Table 1 and 2 and the ternary diagrams are plotted in Fig. 1 and 2. It is seen that the binodal region of ethanol-water-oleyl
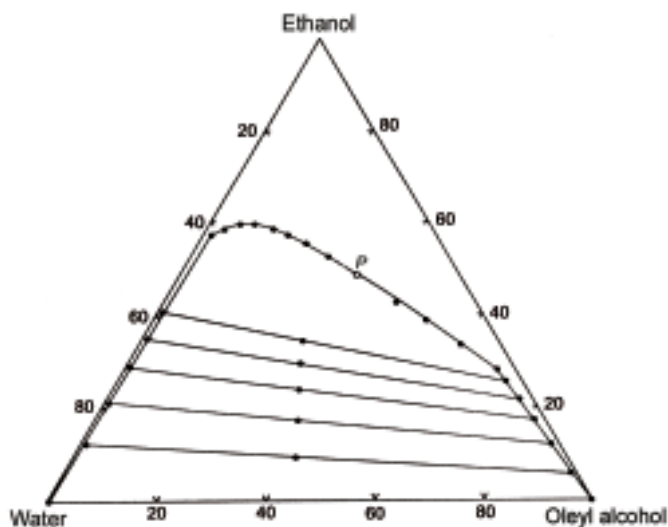

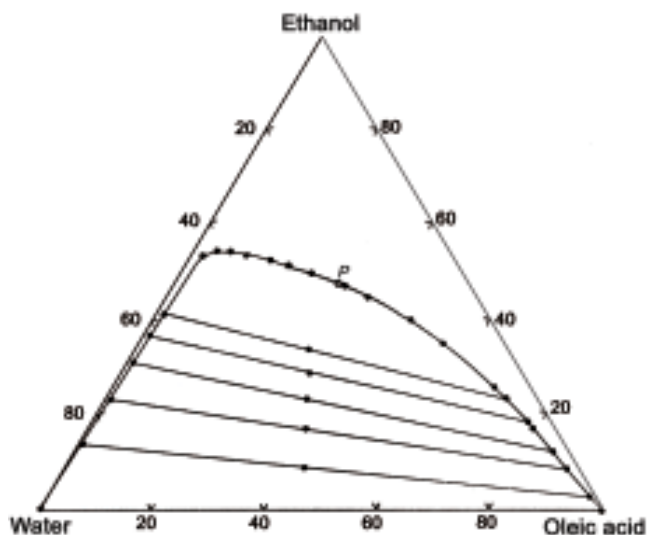**Fig 1.** Binodal curve for the ethanol - water - oleyl alcohol system at 30°C

Fig 2. Binodal curve for the ethanol - water - oleic acid system at 30°C.

alcohol system is slightly broader than that of ethanol-water-oleic acid system. It is also found that the binary systems of water-oleyl alcohol and water-oleic acid are immiscible.

Experimental data on compositions of coexisting phases are presented in Table 3 and distribution coefficients and separation factors between the coexisting liquid phases have been calculated. These data allowed to draw the corresponding equilibrium distribution curves in Fig 3 and equilibrium tie lines in Fig 1 and 2. Fig 3 shows that the concentration of ethanol in organic phase increases with increasing concentration of ethanol in aqueous phase. Ethanol containing one methyl group ($-CH_3$) and one methylene group ($=CH_2$) in the

Table 3

Composition of co-existing phases in the ethanol- water - oleyl alcohol/oleic acid systems at 30°C.

Composition of initial mixtures, wt%			Composition of organic phase, wt%			Composition of aqueous phase, wt%			K_D	α
Water	Oleyl alcohol	Ethanol	Water	Oleyl alcohol	Ethanol	Water	Oleyl alcohol	Ethanol		
49.3	40.9	9.8	0.8	92.5	6.7	87.2	0.2	12.6	0.532	57.82
44.9	37.3	17.8	1.2	86.0	12.8	78.2	0.3	21.5	0.595	39.67
41.3	34.3	24.4	1.6	80.4	18.0	70.1	0.4	29.5	0.610	26.52
38.2	31.7	30.1	2.1	75.5	22.4	63.9	0.6	35.5	0.631	19.12
35.5	29.5	35.0	2.6	71.0	26.4	58.2	0.8	41.0	0.644	14.31
Water	Oleic acid	Ethanol	Water	Oleic acid	Ethanol	Water	Oleic acid	Ethanol		
47.9	42.6	9.5	0.8	95.9	3.3	85.5	0.4	14.1	0.234	26.00
43.8	38.9	17.3	1.7	89.0	9.3	75.8	0.7	23.5	0.396	18.00
40.3	35.8	23.9	2.3	84.8	12.9	67.7	1.0	31.3	0.412	12.12
37.3	33.2	29.5	3.8	77.0	19.2	61.7	1.1	37.2	0.516	8.32
34.8	30.9	34.3	5.2	70.6	24.2	56.9	1.2	41.9	0.578	6.35

K_D, Distribution coefficient of ethanol; α, Separation factor,
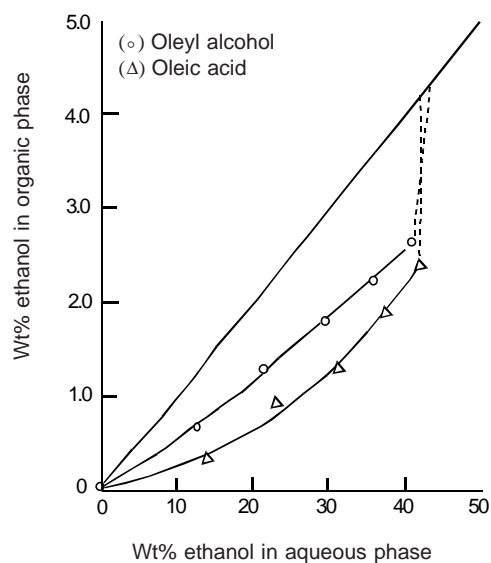
Fig 3. Equilibrium distribution curve for the ethanol - water - solvent systems.

Fig 4. Hand type ternary diagram for plait point determination of the ethanol - water - oleyl alcohol system.

molecule, with a ratio of (OH:C) 1:2, has for stronger polarity (Katayama *et al* 1998) than oleyl alcohol and oleic acid. Oleyl alcohol has a considerably higher dielectric constant (Weast and Astle 1982-1983) that can both donate and accept hydrogen bonds (Loudon 1995), it is a better polar molecule than oleic acid. Fig 1 and 2 show that the concentration of ethanol in oleyl alcohol or oleic acid-richer phase is lower than that in water-richer phase; water has stronger affinity for ethanol than oleyl alcohol and oleic acid.

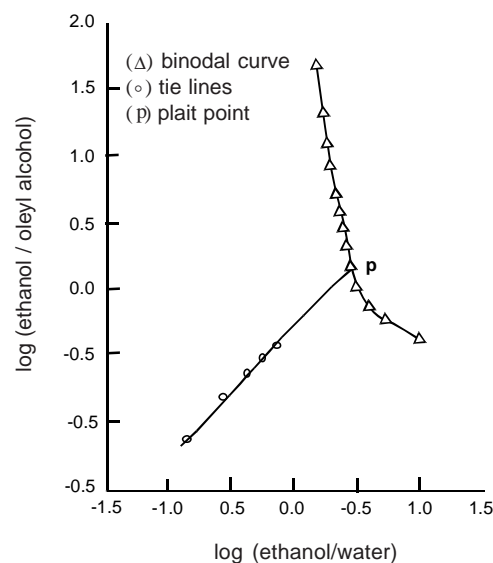The separation factor (α) is determined numerically from the

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 organic and aqueous phases, respectively. Similarly, the distribution coefficient of water is the ratio of concentration of water in organic and aqueous phases, respectively. Table 3 shows value of distribution coefficient (K_D) and separation factor (α) have been measured for extraction of ethanol with weight percent feed (EtOH-H_2O) concentration. It is seen from Table 3 that oleyl alcohol gives
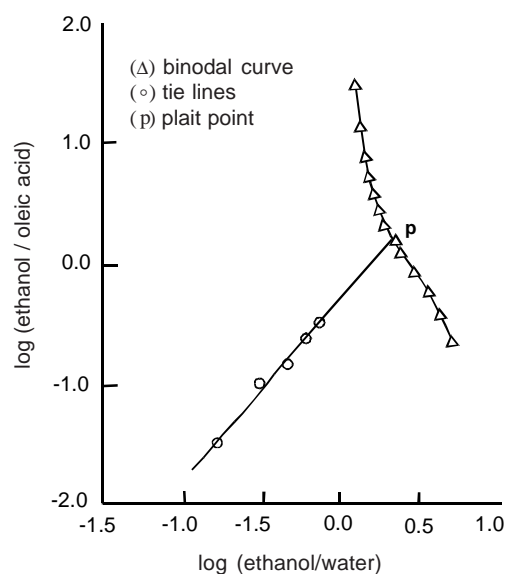
Fig 5 Hand type ternary diagram for plait point determination of the ethanol-water-oleic acid system.

Fig 6 Othmer-Tobias plot of tie lines data for ethanol-water-solvent systems.

K_D values ranging from 0.5 - 0.6 and for oleic acid, it ranges from 0.2 - 0.6 for various ethanol concentration in feed. The separation factors for ethanol-water-oleyl alcohol and ethanol-water-oleic acid systems are considerably greater than 6. Oleyl alcohol and oleic acid give the separation factors (α) ranging from 14.3 - 57.8 and 6.3 - 26.0, respectively, for various ethanol concentration in feed. This indicates that ethanol has preferential solubility in solvents as 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 solubility curves at the plait points, as shown in Fig 4 and 5. The plait point compositions for ethanol-water-oleyl alcohol and ethanol-water - oleic acid systems are obtained graphically by means of Hand's plot which are mentioned in Table 1 and 2.

The tie lines were satisfactorily correlated by the Othmer-Tobias method on a mass fraction basis, and their coordinates for ethanol-water-oleyl alcohol and ethanol-water-oleic acid systems are presented in Fig 6. This figure shows log [(1-y)/y] plotted against log [(1-x)/x], where y is the weight fraction solvent in the organic phase and x is the weight fraction water in the aqueous phase. From this figure it is seen that the relation indeed results in the straight lines. It is expected that both Othmer-Tobias plot and Hand's correlation would yield tie lines as straight lines (Hand 1930).

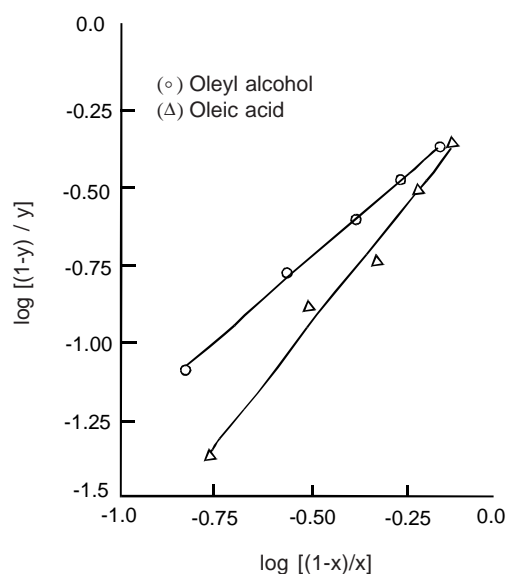Selection of solvents for extraction of ethanol from dilute aqueous solution should be guided by considerations of selectivity with respect to water (separation factor), as well as equilibrium distribution coefficient for ethanol. It can be observed from Table 3, that oleyl alcohol is the better of the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

Conclusion

Liquid-liquid phase equilibrium data have been measured for ethanol-water-oleyl alcohol and ethanol-water-oleic acid ternary systems. The binodal curves, tie lines, distribution coefficients and separation factors have been determined. Hand's method has been 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, and their plot would yield tie lines as straight lines. The binodal region of oleyl alcohol system has appeared to be slightly broader than that of oleic acid system. The distribution coefficients of ethanol for oleyl alcohol and oleic acid systems are greater than 0.5 and 0.2, respectively and the separation factors of oleyl alcohol and oleic acid systems are greater than 14 and 6, respectively. It is concluded that oleyl alcohol may be considered a separating agent for dilute aqueous ethanol solutions.

Acknowledgement

References

Ananthanarayanan P, Rao P B 1968 Ternary liquid equilibria of the water-phosphoric acid-isoamyl alcohol, cyclohexanol, or methyl isobutyl ketone systems at 35°C. *J Chem Eng Data* **13** 194-196.

Arda N, Sayar A A 1992 Liquid-liquid equilibria of water-tetrahydrofuran-1-methylcyclohexanol and of water tetrahydrofuran-2-methylbutylethanoate at the temperature (293.16 ± 0.30) K and pressure (101.325 ± 0.070) k Pa. *J Chem Thermodynamics* **24** 145-149.

Botto G J, Agaras H H, Marschoff C M 1989 Liquid-liquid equilibrium data for the system water-benzonitrile-methanol. *J Chem Eng Data* **34** 382-384.

Briones J A, Mullins J C, Thies M C 1994 Liquid-liquid equilibria for the oleic acid-β-sististerol-water system at elevated temperatures and pressures. *Ind Eng Chem Res* **33** 151-156.

Feki M, Fourati M, Chaabouni M M, Ayedi H F 1994 Purification of wet process phosphoric acid by solvent extraction liquid-liquid equilibrium at 25 and 40°C of the system water-phosphoric acid-methylisobutylketone. *Can J Chem Eng* **72** 939-944.

Gomez Marigliano A C, Gramajo De Doz M B, Solimo H N 1998 Influence of temperature on the liquid-liquid equilbria containing two pairs of partially miscible liquids water-furfural-1-butanol ternary system. *Fluid Phase Equilibria* **153** 279-292.

Hand D B 1930 Dineric distribution. *J Phys Chem* **34** 1961-2000.

Hegazi M F, Salem A B 1983 Ternary data for the acetic acid-water-mesityl oxide system. *J Chem Tech Biotechnol* **33A** 145-150.

Katayama H, Hayakawa T, Kobayashi T 1998 Liquid-liquid equilibria of three ternary systems: 2-propanone-glycerol-methanol, 2-butanone-glycerol-ethanol, and 2-butanone-glycerol -2-propanol in the range of 283.15 to 303.15 K. *Fluid Phase Equilibria* **144** 157-167.

Letcher T M, Ravindran S, Radloff S E 1991 Liquid-liquid equilibria for mixtures of an alkanol-methyl tert-butyl ether-water at 25°C. *Fluid Phase Equilibria* **69** 251-260.

Loudon G M 1995 *Organic Chemistry.* The Benjamin Cummings Publishing Company, Inc, California, USA, 3rd ed, pp 346-358

Maeda K, Yamada S, Hirota S 1997 Binodal Curve of two liquid phases and solid-liquid equilibrium for water-fatty acid-ethanol systems and water-fatty acid-acetone systems. *Fluid Phase Equilibria* **130** 281-194.

Munson C L, King C J 1984 Factors influencing solvent selection for extraction of ethanol from aqueous solutions. *Ind Eng Chem Process Des Dev* **23** 109-115.

Othmer D F, Tobias P E 1942 Tie line correlation. *Ind Eng Chem* **34** 693-696.

Perry R H, Green D W, Maloney J O 1984 *Perry's Chemical Engineers' Hand Book.* Mc Graw-Hill International Editions, New York, USA, 6th ed, p 15-25.

Rahman M A, Rahman M S, Nabi M N 2001 Extraction of ethanol from aqueous solution by solvent extraction-liquid-liquid equilibrium of ethanol-water-1-butanol, ethanol-water-1-pentanol and ethanol-water-1-hexanol systems. *Indian J Chem Technol* **8** 385-389.

Weast R C, Astle M J 1982-83 *CRC Handbook of Chemistry and Physics.* CRC Press, Inc, Boca Raton, Florida, USA, 63rd ed, pp E50-53.