

## Separation of Acetic acid from its Aqueous Solution by Solvent Extraction using 1-Heptanol, 1-Octanol and 1-Decanol as Extractants

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**Abstract:** The liquid-liquid equilibrium data are presented for phase behaviour of ternary system of water-acetic acid-alcohols (1-heptanol, 1-octanol and 1-decanol) systems at the temperature of (30±0.5)°C. From the data, binodal curves, tie lines, plait points and equilibrium distribution diagram were determined experimentally, and the distribution coefficients and separation factors were computed, with a view to examine the suitability of alcoholic solvents to extract acetic acid from its aqueous solution. It has been found that the solubility of acetic acid increased with the increasing number of carbon atoms in the chain of the alcohol used as the solvent, giving higher values of distribution coefficients and separation factor.

**Keywords:** *Liquid-liquid extraction; Ternary equilibrium data; Acetic acid; Binodal curve*

**Introduction:** Acetic acid is an important organic compound and it is used as an intermediate for production of host of organic chemicals, acetaldehyde, acetylchloride, acid anhydride and acetoacetic ester are only a few to name. If ethanol is allowed to stand in an open container it undergoes the acetic acid formation. The fermentation broths is therefore, an important source of acetic acid. Another important industrial process is the methanol carbonylation,  $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$ . Since methanol is produced from synthesis gas ( $\text{CO} + \text{H}_2$ ), acetic acid can be manufactured from coal and many other hydrocarbons which, upon gasification give synthesis gas. To day the principal source of synthesis gas is natural gas, which is mostly methane. But with the increasing costs of fossil fuel gasification of biomass, fermentation of cellulosic biomass continue to attract attention. In the fermentation broths acetic acid remain in dilute aqueous solution. Whose extraction by using a number of solvents have been attempted. Isopropyl ether, methyl iso-butyl ketone, benzene [1], methyl iso-propyle ketone [2,3], tertiary [4] and quaternary amines [5], trioctyl phosphine [6], toluene [7] and mesityl oxide [8] are a few to mention.

Recently, Colombo et al. [9] and Fahim et al. [10] have studied water-acetic acid-1-hexanol system. Duarte et al. [11] has pointed out that lower alcohols are good solvent for recovery of maleic acid. In the present work ternary phases equilibria of water-acetic acid-alcohols (1-heptanol, 1-octanol and 1-decanol) have been experimentally determined and from the tie line data and equilibrium distribution curves the feasibility of extraction of acetic acid from its dilute aqueous solution has been studied. Materials & Method: Chemicals: Acetic acid, 1-heptanol, 1-octanol, 1-decanol were procured from BDH Ltd., England.

**Mutual solubility data:** The mutual solubility data for water- acetic acid-1-heptanol, water- acetic acid-1-octanol and water- acetic acid-1-decanol systems were determined by the titration method [12]. 10 mL of water was measured into a 125 mL closed Erlenmeyer flask and solvent was added from a burette first point of the binodal curve on the base line. The turbidity indicates the beginning of formation of second phase, the solvent layer. Therefore, further addition of a small amount of solvent gave a

**Article history:**

Received 30 November 2017,

Received in revised form 20 December 2017

Accepted 30 December 2017,

Available online 30 March 2018

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first point of the binodal curve on the base line. The turbidity indicates the beginning of formation of second phase, the solvent layer. Therefore, further addition of a small amount of solvent gave a heterogeneous mixture. Then ethanol was added from burette until the first appearance of distinct clear homogeneity. This gave another point of binodal curve on the triangular diagram. This procedure was repeated to construct the binodal curve from the aqueous side. Same procedure was applied starting with an initially measured quantity of solvent to construct the binodal curve on solvent side. The refractive index of each mixture indicated as a point on the binodal curve was measured using an “Atago Precision Abbe Refractometer type-3”.

**Equilibrium Data:** Equilibrium data were determined for these systems at room temperature of  $(30 \pm 0.5)^\circ\text{C}$ . Equal amounts of solvent and water placed in a 250 mL closed Erlenmeyer flask and a certain amount of ethanol was then added. The flask was vigorously shaken by electric shaker for 1h and was allowed to settle for 1h. 1-2 drops sample of each phase was removed by pipette, and its refractive index was carefully measured [13]. Compositions of the phases were determined from the solubility data in the binodal curve using calibration graphs for refractometric measurements.

**Results and Discussion:** The composition to points of binodal curves for water-acetic acid-1-heptanol, water-acetic acid-1-octanol and water-acetic acid-1-decanol systems have been experimentally at room temperature  $(30 \pm 0.5)^\circ\text{C}$ . Binodal data are given in Tables I, II and III. These tables also include the measured refractive indices for the equilibrium mixtures.

**Table 1.** Compositions corresponding to points of the bimodal curve and their refractive indices for the water-acetic acid-1-heptanol system at room temperature  $(30 \pm 0.5)^\circ\text{C}$ .

	Composition, wt. %			Refractive Index
	Water	1-heptanol	Acetic acid	
Water-rich-phase	100	0	0	1.3306
	58.0	2.4	39.6	1.3568
	52.9	4.4	42.7	1.3596
	47.7	7.8	44.5	1.3640
	45.0	11.1	43.9	1.3662
	42.4	14.0	43.6	1.3676
	40.3	16.6	43.1	1.3686
	38.2	18.9	42.9	1.3725
	36.5	21.0	42.5	1.3740
	35.0	23.1	41.9	1.3754
	33.6	24.9	41.5	1.3766
	4.6	95.4	0	1.4166
1-heptanol-rich phase	9.3	69.4	21.3	1.4024
	14.1	57.9	28.0	1.3960
	17.9	49.0	33.1	1.3914
	21.1	43.4	35.5	1.3878
	23.7	39.0	37.3	1.3854
	25.8	35.4	38.8	1.3831
	27.9	32.4	39.3	1.3815
	29.5	30.3	40.2	1.3797
	31.0	28.4	40.6	1.3786
	32.3	26.6	41.1	1.3772

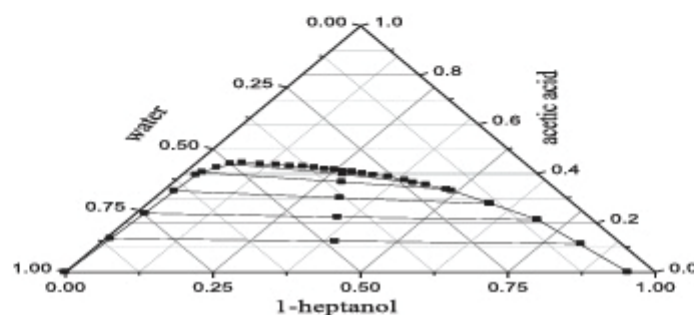
**Table 2.** Compositions corresponding to points of the bimodal curve and their refractive indices for the water-acetic acid-1-octanol system at room temperature (30±0.5)°C.

	Composition, wt. %			Refractive
	Water	1-octanol	Acetic acid	Index
Water-rich-phase	100	0	0	1.3306
	54.6	1.3	44.1	1.3582
	50.9	2.1	47.0	1.3598
	46.5	3.8	49.7	1.3630
	42.3	7.0	50.7	1.3658
	44.3	9.9	49.8	1.3684
	38.2	12.5	49.3	1.3700
	36.3	14.9	48.8	1.3720
	34.6	17.1	48.3	1.3734
	33.4	19.2	47.4	1.3750
	32.1	21.1	46.8	1.3762
	31.0	22.9	46.1	1.3780
1-octanol-rich phase	4.6	95.4	0	1.4192
	6.9	80.7	12.4	1.4114
	8.8	71.9	19.3	1.4064
	13.6	55.8	30.6	1.3978
	16.9	46.4	36.7	1.3924
	19.5	40.1	40.4	1.3892
	22.3	36.6	41.1	1.3862
	24.0	33.0	43.0	1.3841
	25.9	30.5	43.6	1.3822
	27.3	28.0	44.7	1.3810
	28.7	26.2	45.1	1.3794
	29.8	24.5	45.7	1.3784
Plait point	24.8	32.0	43.2	-

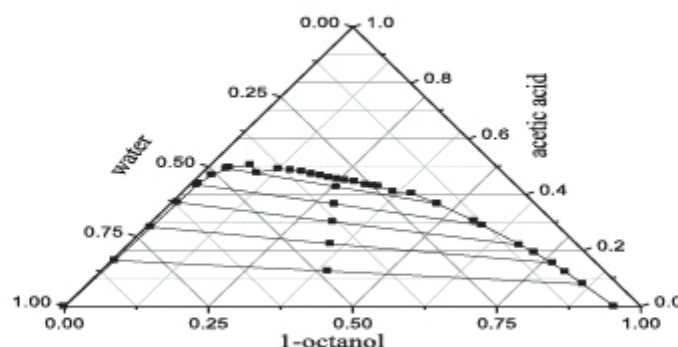
**Table 3.** Compositions corresponding to points of the bimodal curve and their refractive indices for the water-acetic acid-1-decanol system at room temperature (30±0.5)°C.

	Composition, wt. %			Refractive
	Water	1-decanol	Acetic acid	Index
Water-rich-phase	100	0	0	1.3306
	45.4	0.8	53.8	1.3636
	39.0	1.6	59.4	1.3666
	36.3	3.0	60.7	1.3684
	33.3	5.5	61.2	1.3706
	30.3	10.1	59.6	1.3740
	28.0	13.9	58.1	1.3770
	25.4	19.0	55.6	1.3810
1-decanol-rich phase	3.5	96.5	0	1.4286
	4.9	81.7	13.4	1.4198
	8.1	67.2	24.7	1.4112
	15.3	42.1	42.6	1.3958
	19.4	32.0	48.6	1.3892
	22.0	26.1	51.9	1.3852
	24.0	22.2	53.8	1.3820
	24.7	20.5	54.8	1.3814
Plait point	18.4	34.3	47.3	-

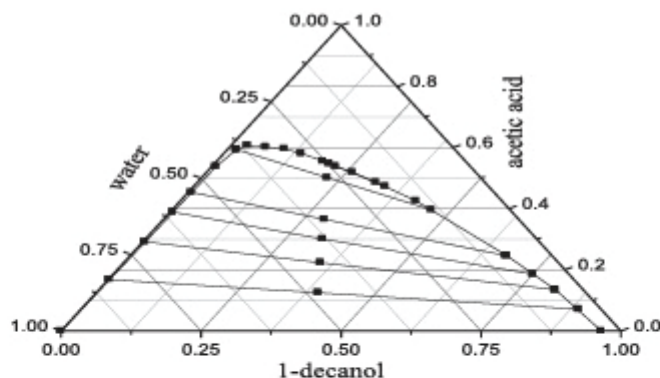
Binodal curves of water-acetic acid-1-heptanol, water-acetic acid-1-octanol and water-acetic acid-1-decanol systems are plotted in Figures 1, 2 and 3. From these Figures it is seen that the binary systems of water-solvents (1-heptanol, 1-octanol and 1-decanol) completely immiscible, and the binary systems of acetic acid-solvents are miscible at temperature,  $(30\pm0.5)^{\circ}\text{C}$  and it is also seen from Figures 1, 2 and 3 that the heterogeneous region of water-acetic acid-1-heptanol, water-acetic acid-1-octanol and water-acetic acid-1-decanol systems increase in the order of 1-heptanol<1-octanol<1-decanol.



**Fig. 1:** Binodal curve and tie lines for the water-acetic acid-1-heptanol system at room temperature  $(30\pm0.5)^{\circ}\text{C}$ .

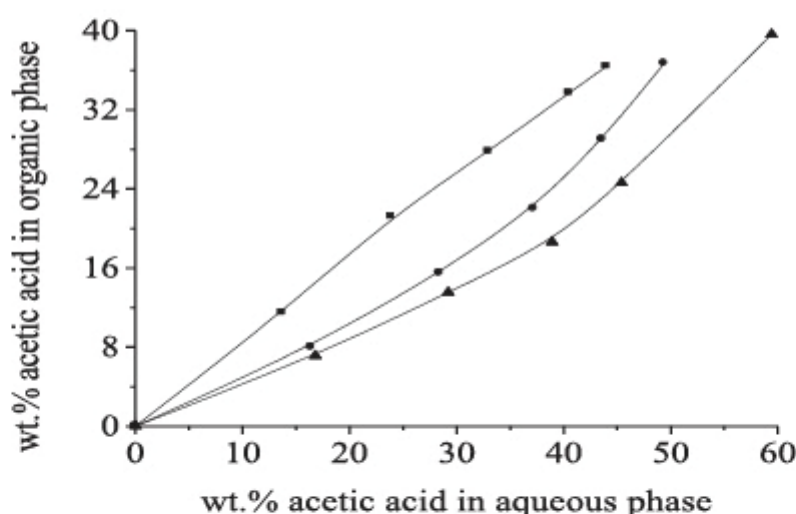


**Fig. 2:** Binodal curve and lines for the water-acetic acid-1-octanol system at room temperature  $(30)^{\circ}\text{C}$ .



**Fig. 3:** Binodal curve and tie lines for the water-acetic acid-1-decanol system at room temperature  $(30\pm0.5)^{\circ}\text{C}$ .

**Tie line and solubility:** The tie line data of the water-acetic acid-1-heptanol, water-acetic acid-1-octanol and water-acetic acid-1-decanol systems are determined at room temperature,  $(30 \pm 0.5)^\circ\text{C}$ . Experimental data on compositions of coexisting phases are presented in Table 4 and distribution coefficients and separation factors between the coexisting liquid phases have been calculated. The data allowed to draw the corresponding equilibrium distribution curves in Figure 4 and equilibrium tie lines in Figures 1, 2 and 3.



**Fig. 4:** Equilibrium distribution curve for water-acetic acid-alcohol type solvent systems. (■) 1-heptanol, (●) 1-octanol and (▲) 1-decanol.

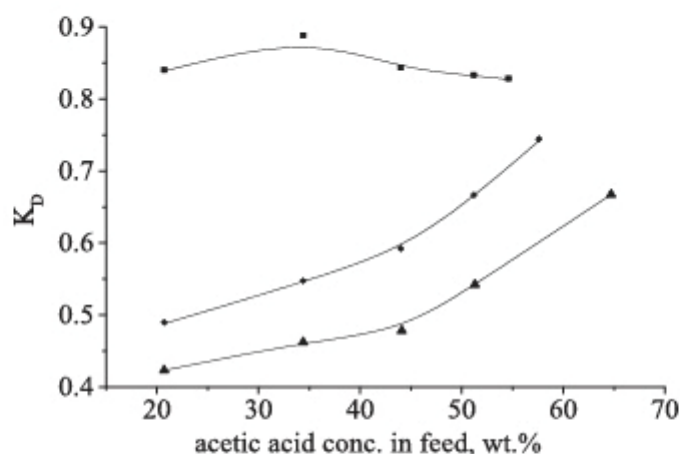
Figure 4 show that the concentration of acetic acid in organic phase increases with increasing concentration of acetic acid in aqueous phase. Acetic acid containing one methyl group ( $-\text{CH}_3$ ) in the molecule, with a ratio of ( $\text{COOH} : \text{C}$ ) 1:1, has far stronger polarity than higher carboxylic acids. Figures 1, 2, 3 and 4 show that the concentration of acetic acid in 1-heptanol, 1-octanol and 1-decanol type solvents-rich phase is lower than that in water-rich phase. Therefore, 1-heptanol, 1-octanol and 1-decanol have lower affinity for acetic acid than water. It is found that an increase in the number of carbon atoms in the chain of solvents (1-heptanol, 1-octanol and 1-decanol) results in a wider heterogeneous zone and in a decreasing solubility of the acetic acid into the organic phase. The solubility of acetic acid in 1-heptanol, 1-octanol and 1-decanol type solvents is found in the following order: 1-heptanol > 1-octanol > 1-decanol.

**Table 4.** Composition of co-existing phases for distribution co-efficient and separation factor in the acetic acid- Water-alcohols (1-heptanol, 1-octanol and 1-decanol) systems at room temperature (30±0.5)°C.

Composition of initial mixtures, wt. %			Composition of organic phase, wt. %			Composition of aqueous phase, wt. %			Distribution co-efficient of acetic acid, $K_D$	Separation factor, $\alpha$
water	1 heptanol	acetic acid	water, $Y_1$	1 heptanol, $Y_2$	acetic acid, $Y_3$	water, $X_1$	1 heptanol, $X_2$	acetic acid, $X_3$		
47.9	39.5	12.6	6.8	81.7	11.5	85.5	0.8	13.7	0.839	10.488
42.6	35.0	22.4	9.3	69.5	21.2	74.5	1.6	23.9	0.887	7.096
38.3	31.5	30.2	14.0	58.2	27.8	65.0	2.0	33.0	0.842	3.916
34.8	28.6	36.6	18.5	47.8	33.7	56.5	3.0	40.5	0.832	2.544
33.0	27.2	39.8	22.8	40.8	36.4	50.0	6.0	44.0	0.827	1.814
water	1-octanol	acetic acid	water, $Y_1$	1-octanol, $Y_2$	acetic acid, $Y_3$	water, $X_1$	1-octanol, $X_2$	acetic acid, $X_3$		
48.0	39.4	12.6	6.0	86.0	8.0	83.0	0.6	16.4	0.488	6.778
42.6	35.0	22.4	7.5	77.0	15.5	70.8	0.8	28.4	0.546	5.151
38.3	31.5	30.2	10.0	68.0	22.0	61.8	1.0	37.2	0.591	3.648
34.8	28.6	36.6	13.0	58.0	29.0	55.2	1.2	43.6	0.665	2.818
31.4	25.8	42.8	16.0	46.4	36.7	47.2	3.4	49.4	0.743	2.075
water	1-decanol	acetic acid	water, $Y_1$	1-decanol, $Y_2$	acetic acid, $Y_3$	water, $X_1$	1-decanol, $X_2$	acetic acid, $X_3$		
47.8	39.7	12.5	4.0	88.9	7.1	83.0	0.2	16.8	0.423	8.813
42.5	35.2	22.3	5.0	81.5	13.5	70.4	0.4	29.2	0.462	6.507
38.2	31.7	30.1	6.4	75.0	18.6	60.6	0.5	38.9	0.478	4.509
34.7	28.8	36.5	8.1	67.3	24.6	54.0	0.6	45.4	0.542	3.613
27.3	22.6	50.1	14.0	46.4	39.6	39.0	1.6	59.4	0.667	1.858

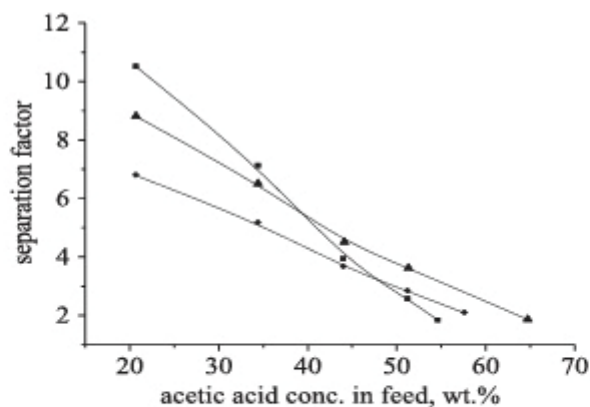
#### Distribution coefficient and separation factor:

The separation factor ( $\alpha$ ) is determined numerically from the tie line data because, it is the ratio of distribution coefficient of acetic acid to the distribution coefficient of water. The distribution coefficient of acetic acid (KD) is the ratio of concentration of acetic acid in organic phase and aqueous phase respectively. Similarly, the distribution coefficient of water is the ratio of concentration of water in organic and aqueous phases, respectively. The distribution coefficient of acetic acid (KD) and separation factor ( $\alpha$ ) have been measured for extraction of acetic acid with weight percent feed (AcOH-H<sub>2</sub>O) concentration. These results are in Tables IV and graphically shown in Figures 5 and 6. From Figure 5, it is found that the distribution coefficient of acetic acid (KD) increases with increasing concentration of acetic acid in the feed solution. In the present study it has been found that the distribution coefficient of acetic acid (KD) is lower than 1 for 1-heptanol, 1-octanol and 1-



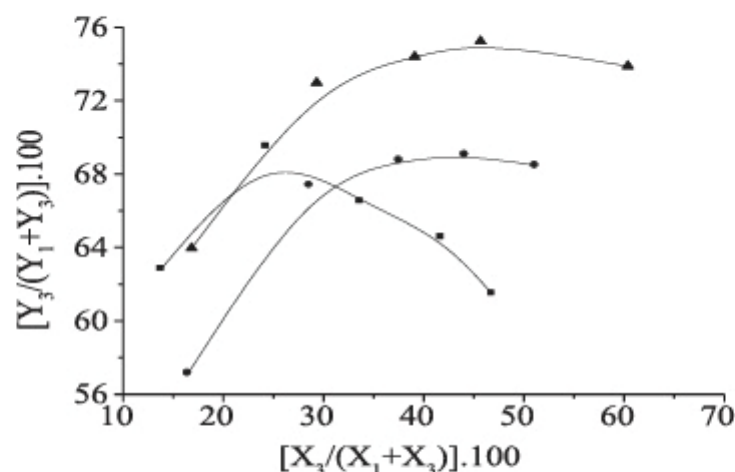
**Fig. 5:** Distribution coefficient for extraction of acetic acid from water by alcohol type solvent systems. (■) 1-heptanol, (●) 1-octanol and (▲) 1-decanol.

Selectivity diagrams are constructed by plotting weight percent of acetic acid in the organic phase against that in the aqueous phase both on solvent-free basis.



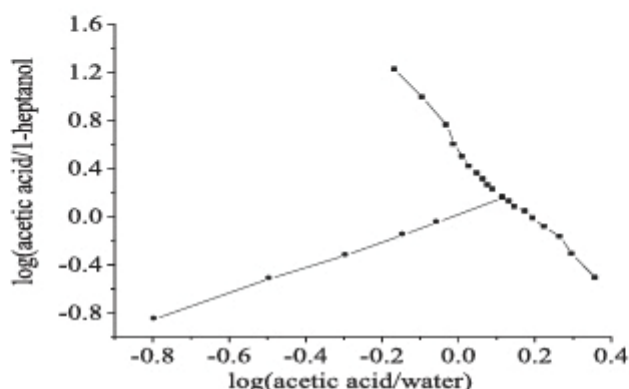
**Fig. 6:** Separation factor for extraction of acetic acid from water by alcohol type solvent systems. (■) 1-heptanol, (●) 1-octanol and (▲) 1-decanol.

decanol investigated. It is also seen that the order of distribution coefficients of acetic acid ( $K_D$ ) with weight percent feed (AcOH-H<sub>2</sub>O) concentration are 1-heptanol>1-octanol>1-decanol for and from Figure 6, it is seen that the separation factor decreases with increasing concentration of acetic acid in the feed solution. The separation factors are considerably greater than 2 for all the solvents studied. The order of separation factors with weight percent feed (AcOH-H<sub>2</sub>O) concentration are 1-octanol<1-heptanol<1-decanol for alcohol type solvents.

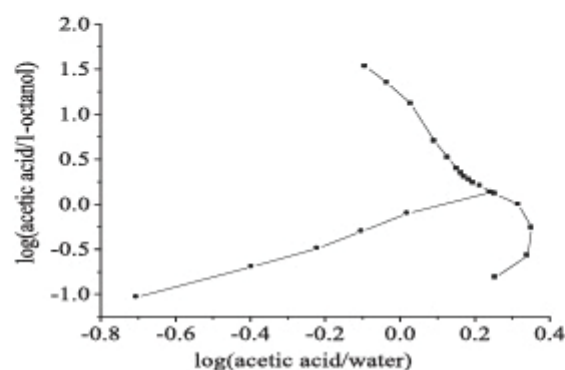


**Fig. 7:** Selectivity diagram on solvent-free basis for water-acetic acid-alcohol type solvent systems. (■) 1-heptanol, (●) 1-octanol and (▲) 1-decanol

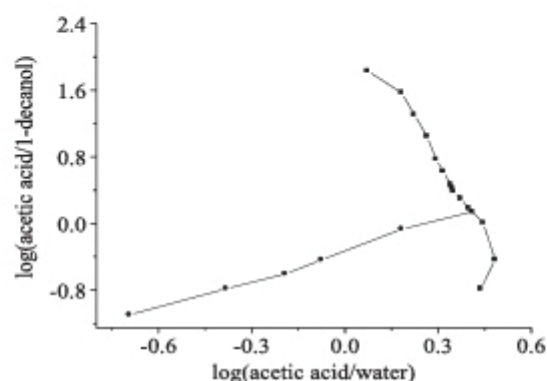
It is shown in Figure 7, it is found that acetic acid concentration in organic phase increases with increasing acetic acid concentration in aqueous phase and attains the maximum value when the feed solution is completely free from water. Figures 5, 6 and 7 also show that an increase in the number of carbon atoms in the chain results in a decrease in solubility of the acetic acid into the organic phase. The increase of carbon chain length has a significant effect on the decrease of distribution coefficients and consequent increase in separation factors. On the other hand, when considering the values of distribution coefficients of acetic acid (KD) involving higher alcohol and carboxylic acid type solvents, it may be assumed that the low molecular weight of solvents lead to a better compatibility of the solvents with acetic acid [14].



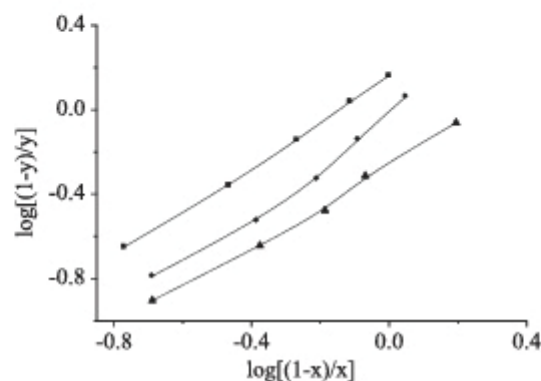
**Fig. 8:** Hand type ternary diagram for plait point determination of the water-acetic acid-1-heptanol system. (■) binodal curve, (●) tie line and λ plait point.



**Fig. 9:** Hand type ternary diagram for plait point determination of the water-acetic acid-1-octanol system. (■) binodal curve, (●) tie line and  $\lambda$  plait point.



**Fig. 10:** Hand type ternary diagram for plait point determination of the water-acetic acid-1-decanol system. (■) binodal curve, (●) tie line and  $\lambda$  plait point.



**Fig. 11:** Othmer-Tobias plot of tie lines data for water-acetic acid-alcohol type solvent systems. (■) 1-heptanol, (●) 1-octanol and (▲) 1-decanol.

#### Determination of plait point:

Distribution of acetic acid between solvent and water may be correlated graphically procedure according to Hand's plot. 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 binodal curves at the plait points, as shown in Figures 8, 9 and 10. The plait point compositions for water-acetic acid-1-heptanol, water-acetic acid-1-octanol and water-acetic acid-1-decanol systems are obtained graphically by means of Hand's method, which are mentioned in Table I, II and III. The tie lines were satisfactorily correlated by the Othmer-Tobias method [15] on a mass fraction basis and their coordinates for the water-acetic acid-1-heptanol, water-acetic acid-1-octanol and water-acetic acid-1-decanol systems are presented in Figure 11. This Figure show  $\log[(1-y)/y]$  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. It is found that the relation indeed results in the straight lines [16-18].

**Conclusion:** Liquid-liquid phase equilibrium data have been measured for acetic acid-water-alcohols (1-heptanol, 1-octanol and 1-decanol) ternary systems. Binodal curves were drawn on a triangular diagram, tie line data were obtained from the binodal curves and the distribution co-efficients and separation factors were computed, plait points were obtained from the Hand's plot. 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 increases with the increase of carbon chain lengths of alcohols used as extractant. water-acetic acid-1-heptanol, water-acetic acid-1-octanol and water-acetic acid-1-decanol systems, The distribution coefficients for solvent were found to be in the range of 0.827 - 0.887, 0.488 - 0.743 and 0.423 - 0.667 respectively, while the separation factors were found to be in the range of 1.814 - 10.488, 2.075 - 6.778 and 1.858 - 8.813 respectively.

## References:

- [1] Perry R H, Green D W and Maloney J O, Perry's Chemical Engineers Hand Book, McGraw-Hill International Editions, New York. 6th ed. p.15 (1984).
- [2] Correa J M, Blanco A and Arce A, J Chem Eng Data, 34, 415 (1989).
- [3] Chai J, Huanjing Huaxue, 17(3), 264 (1998).
- [4] Poole L J & King C J, Ind Eng Chem Res, 30, 923 (1991).
- [5] Yang S T, White S A & Hsu S T, Ind Eng Chem Res, 30, 1335 (1991).
- [6] Golob J, Grilc V & Zadnik B, Ind Eng Chem Process Des Dev, 20, 433 (1981).
- [7] Yang Y, Shao H, Chen C, Jiang X & Sun X, Shandong Daxue Xuebao, Ziran Kexueban, 32(4), 437 (1997).
- [8] Hegazi, M. F. and Salem A B, J. Chem. Tech. Biotechnol, 33A, 145 (1983).
- [9] Colombo A, Battilana P, Ragaini V & Bianchi C L, J Chem Eng Data, 44, 35 (1999).
- [10] Fahim M A, Al-Muhtaseb S A & Al-Nashef I M, J Chem Eng Data, 42, 183 (1997).
- [11] Duarte M M L, Lozer J, Malmay G & Molinier J, J. Chem Eng Data, 34(1), 43 (1989).
- [12] Feki, M., Fourati, M. Chaabouni, M M and Ayedi H F, The Canad. J. Chem. Eng, 72, 939 (1994).
- [13] Salem A B S, Ind. Eng. Chem. Res, 30, 1582 (1991).
- [14] Rahman M A, Rahman M S, Nabi M N & Azad M A K, Pak J Sci Ind Res, 48(5), 312 (2005).
- [15] Othmer D F, Tobias P E, Ind Eng Chem 34, 693 (1942).
- [16] Hand, D. B, J. Phys. Chem, 34, 1961 (1930).
- [17] Rahman, M. A., Rahman, M. S. and Nabi, M. N., Indian Journal of Chemical Technology, 8, 385 (2001).
- [18] M. A. Rahman, M. S. Rahman, M. A. K. Azad and M. N. Nabi, "Drying of Ethanol by solvent extraction using higher alcohols as extractants". Accepted in Rajshahi University Journal of Science and Engineering, Vol. 25.