

Liquid-Liquid Equilibrium Data of Ternary Systems of Water, Acetic Acid and Alkanols (1-Butanol, 1-Pentanol and 1-Hexanol)

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Abstract. The liquid-liquid equilibrium data are presented for phase behaviour of ternary system of water, acetic acid and alkanols (1-butanol, 1-pentanol and 1-hexanol) at the temperature of 30 ± 0.1 °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 the separation factor.

Keywords: liquid-liquid equilibrium, tie line, liquid-liquid extraction, phase behaviour, distribution coefficient, acetic acid extraction, binodal curve, equilibrium distribution

Introduction

Liquid-liquid extraction has established itself as a unique unit operation during the last few decades. Nowadays, it finds application in a number of commercial processes, such as separation of organic isomers, isolation of antibiotics, extraction of metals, separation of trace elements, and removal of pollutants for pollution control. Since the system is based on solubility, it has distinct advantage over distillation in which the application of heat is required, so that heat sensitive materials and compounds not differing appreciably in their boiling points can be easily separated.

The extraction of organic acids from aqueous solutions resulting from fermentation processes, and from spent or recycle solutions, is industrially important. Many solvents have been previously tried to improve such extractions using liquid-liquid extraction (Acre *et al.*, 1995; Briones *et al.*, 1994; Dramur and Tatli, 1993). Within the scope of this procedure, several alcohols (Fahim *et al.*, 1997; Kirk and Othmer, 1992) and acetates (Colombo *et al.*, 1999; Correa *et al.*, 1989) have been used as solvents to extract acetic acid from aqueous solutions. Only few of these, however, were noted to have distribution coefficients greater than one.

The present work was undertaken to investigate fundamentals of the process of extraction of acetic acid, using aliphatic alcohols as solvents, by studying the liquid-liquid phase equilibria (LLE) of ternary systems comprising of water, acetic acid and alkanols (1-butanol, 1-pentanol and 1-hexanol). The LLE of these systems was studied by determining their binodal curves and equilibrium distribution diagram experi-

mentally, and computing from these, the tie lines, plait points, distribution coefficients and separation factors of the respective systems.

Materials and Methods

Materials. Acetic acid glacial (E. Merck, Germany, 99.5%), 1-butanol (E. Merck, India, 99%), 1-pentanol (BDH, England, 98%) and 1-hexanol (BDH, England, 98%) were used without further purification. Distilled water was used throughout this work.

Solubility data. The solubility data for the three systems, namely, water + acetic + 1-butanol (WAB), water + acetic acid + 1-pentanol (WAP), and water + acetic acid + 1-hexanol (WAH) were determined by the cloud point method (turbidity method) (Feki *et al.*, 1994; Correa *et al.*, 1989). Ten ml water was measured in a 125 ml closed Erlenmeyer flask and a solvent (alcohol) 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 water and gave the first point on the base line of the binodal curve (mutual solubility curve) plotted on a triangular diagram. The appearance of turbidity indicated the beginning of the formation of the second phase, i.e., the solvent layer. Further addition of a small amount of the solvent gave a heterogeneous mixture. Acetic acid was then added from a burette until the first appearance of distinctly clear homogeneity. This gave another point of the binodal curve. The procedure was repeated to construct the binodal curve from the aqueous side. The same procedure was repeated, but by starting with an initially measured quantity of the solvent (alcohol) and the addition of

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water and acetic acid to construct the binodal curve from the solvent side. Each point on the binodal curve indicated a homogeneous mixture with known compositions, which could be read from the binodal curve (mutual solubility curve).

Equilibrium data. The equilibrium data for the three systems were obtained experimentally at 30 ± 0.1 °C in a thermostatically controlled waterbath (SB-3, Grant Instruments Ltd., England). Twenty ml each of water and the solvents were taken in four different 250 ml closed Erlenmeyer flasks and then various amounts of acetic acid were added. The flasks were vigorously shaken on an electric shaker (Model-1866, Jencons Scientific Ltd., England) for 3 h and the Erlenmeyer flasks were then immersed in a thermostatically controlled waterbath and allowed to settle for 3 h. It was ensured that longer stirring and settling times did not exhibit any change in the phase composition. After the settling period was over, the samples were pipetted out first from the upper phase and then from the lower phase. Concentrations of acetic acid in each phase were determined by potentiometric titration using OSK-8022 potentiometric automatic titrator, (Ogawa Seiki Co., Ltd., Japan) with 0.1 N NaOH. Replicate titrations of a standard mixture gave an error of 0.21%. Water contents of each phase were measured by OSK 8023 Karl Fischer tritator (Ogawa Seiki Co., Ltd., Japan) using the Karl Fischer reagent. In this case, the replicate titrations of a standard sample gave an error of 0.27%. Concentrations of alcohols in each phase were computed by difference.

Results and Discussion

The solubility data (composition defining the binodal curves) for water + acetic acid + 1-butanol (WAB); water + acetic acid + 1-pentanol (WAP); and water + acetic acid + 1-hexanol (WAH) systems, obtained experimentally, are given respectively in Tables 1, 2, and 3. These results were plotted as triangular diagrams to give ternary diagrams (binodal curve) of the above three systems, as shown respectively in Fig. 1, 2, and 3. A close examination of the curves in these figures revealed that the heterogeneous region involving the 1-hexanol system was greater than that of the 1-pentanol and 1-butanol systems. Binary mixtures in both the ends of the ternary diagram, at the base line, revealed that mutual solubility of water and solvent (alcohols) was greater in the organic-rich phase than in the aqueous-rich phase. The mutual solubility in both the phases decreased as the number of carbon in the alcohol molecule, as $=CH_2$ increased. This may be attributed to the fact that the polarity of alcohols decreases in the order of 1-butanol > 1-pentanol > 1-hexanol (Katayama *et al.*, 1998).

The experimental equilibrium data indicating the compositions of the coexisting phases are presented in Table 4. The

corresponding equilibrium distribution diagram, based on these data was drawn (Fig. 4), while the separation factor for different systems was also drawn from the obtained solubility data (Fig. 5). The distribution coefficient and separation factors for the respective systems were computed from the equilibrium data. The distribution coefficient is defined as the ratio of concentration of the solute (acetic acid) in the extract phase (organic phase) to that in the raffinate phase (aqueous phase), while the separation factor is defined as the ratio of the distribution coefficient of the solute (acetic acid) to that of water. Both the distribution coefficient and separation factor are the measures of the ability of the solvent to separate the solute (acetic acid) from water. Greater values of the distribution coefficient are desirable, since less solvent is then required for the extraction. A separation factor greater than one would indicate that the solute is preferentially more soluble in the solvent (alcohol) than in water to facilitate its extraction. Values of distribution coefficients and separation factors, for the respective systems, are incorporated in Table 4 indicating that all the solvents studied were suitable for separating acetic acid from its aqueous solution. It may be noted from Table 4 that the distribution coefficients were always greater than unity. The previously reported distribution coefficient of 1.613 at 26.7 °C for water + acetic acid + 1-butanol system (Perry *et al.*, 1984) is comparable with the present results. For

Table 1. Solubility data of the water + acetic acid + 1-butanol system at 30 ± 0.1 °C

	Weight (%)		
	water	1-butanol	acetic acid
Water-rich phase	96.1	3.9	0
	86.6	7.0	6.4
	79.0	1.06	10.4
	72.4	14.7	12.9
	67.0	19.0	14.0
	62.9	23.0	14.1
	58.9	26.2	14.9
	55.6	29.3	15.1
	50.4	34.5	15.1
	46.8	37.9	15.2
1-Butanol-rich phase	19.8	80.2	0
	21.5	75.6	2.9
	26.5	65.1	8.4
	30.5	57.5	11.9
	34.2	52.3	13.5
	37.4	48.2	14.4
	40.5	44.8	14.7
	42.9	41.9	15.2
45.3	39.4	15.3	
Plait point	54.2	30.7	15.1

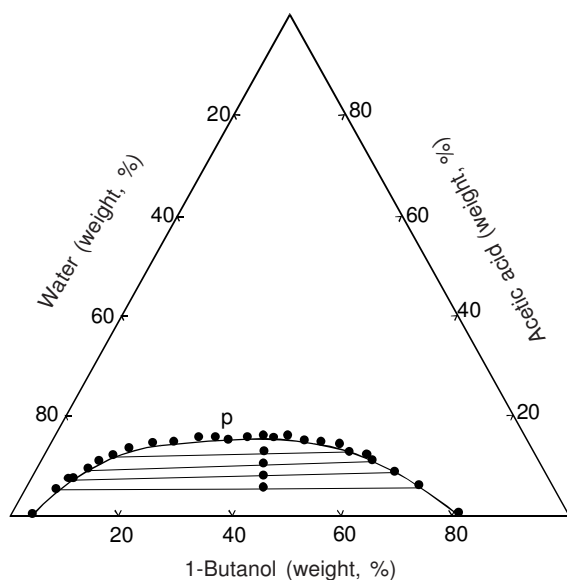


Fig. 1. Binodal curve for the water + acetic acid + 1-butanol system at 30 ± 0.1 °C.

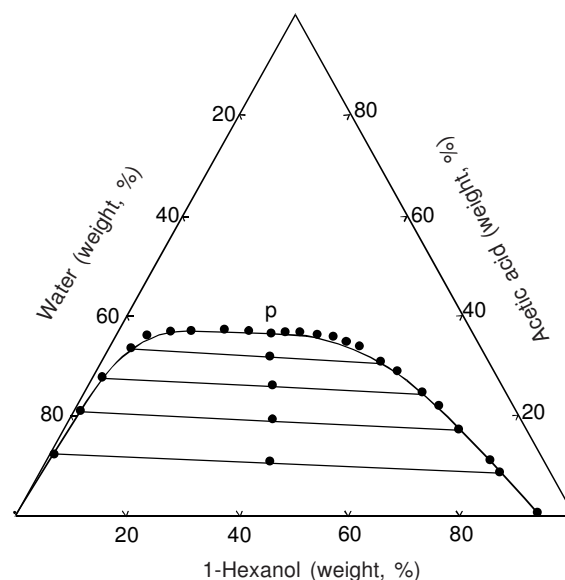


Fig. 3. Binodal curve for the water + acetic acid + 1-hexanol system at 30 ± 0.1 °C.

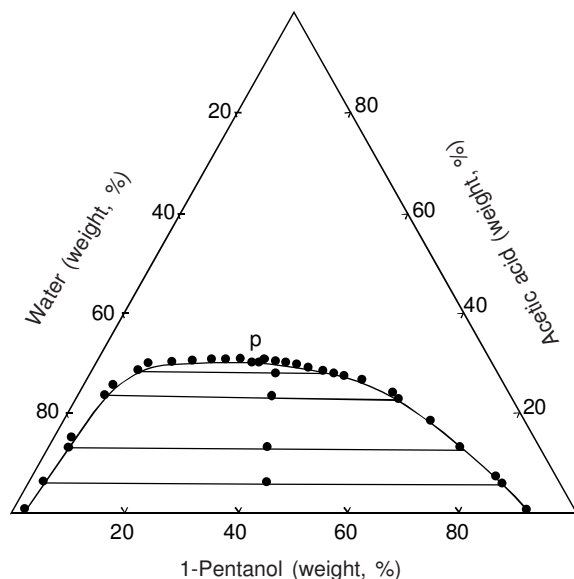


Fig. 2. Binodal curve for the water + acetic acid + 1-pentanol system at 30 ± 0.1 °C.

water + acetic acid + mesityl oxide system, distribution coefficient of almost the same magnitude was obtained by Hegazi and Salem (1983). The separation factors in the present studies were found to be of fairly high values, so that 1-butanol, 1-pentanol and 1-hexanol may be considered as good solvents.

A comparison of the results on the use of 1-butanol, 1-pentanol and 1-hexanol, as the solvents, showed that the heterogeneous region in the triangular diagram increased in the order of 1-butanol < 1-pentanol < 1-hexanol. Munson and King (1984) interpreted the solvent capacity and selectivity

in terms of electron donor-acceptor concepts, or on the basis of Lewis acidity and Lewis basicity. They argued that ethanol and water have both electron donating and electron accepting capabilities, but ethanol has a slightly larger electron donor number and lower electron acceptor number than water. Katayama *et al.* (1998) for their systems, however, interpreted their results in terms of polarities and dielectric constants of the solvents. In the present study, as the carbon chain in the alcohols increased the presence of more methylene groups ($=CH_2$ groups), the alcohol molecules become increasingly more electron donors and less electron acceptors. The heterogeneous region (binodal region) in the triangular diagram, the distribution coefficient, and the separation factor were, therefore, relatively large showing the order of 1-butanol < 1-pentanol < 1-hexanol. Similar results were obtained by Maeda *et al.* (1997) for water + fatty acids + acetone (or ethanol) systems, showing that as the carbon number of fatty acids increased the binodal region of the two liquid phases became larger.

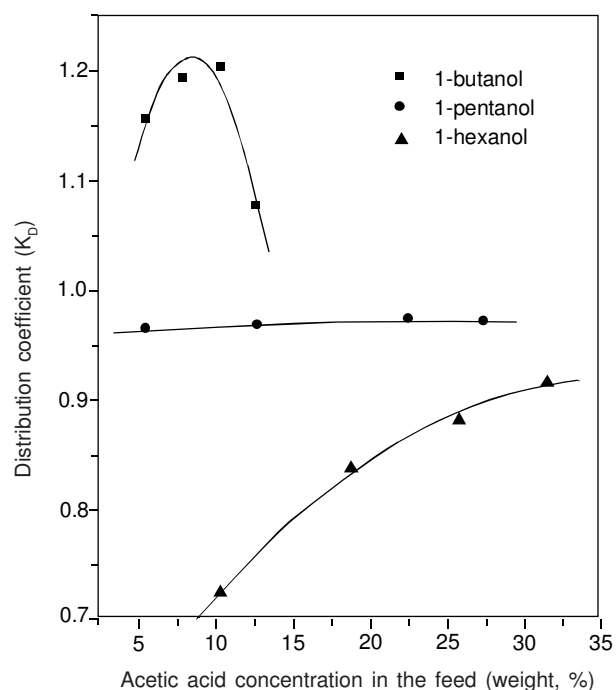
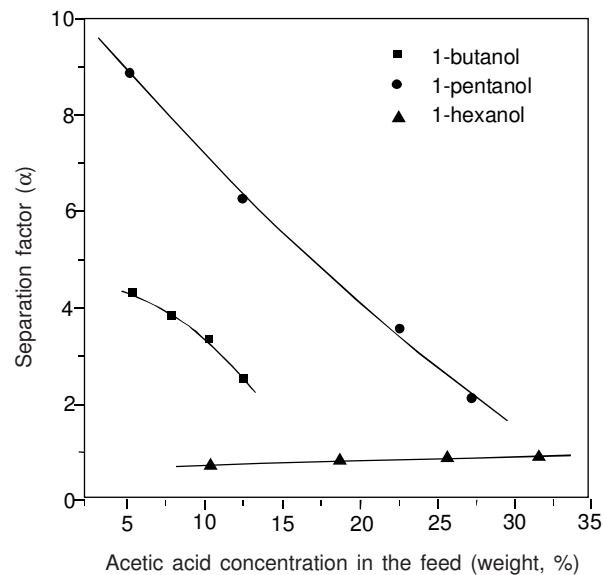
Direct separation of the observed tie lines is difficult to make from a triangular diagram (Feki *et al.*, 1994; Hand, 1930). Therefore, Hand's plots for each system, based on 1-butanol, 1-pentanol, or 1-hexanol were, respectively, drawn in Fig. 5, 6, and 7, so that interpolation could be done and the plait point compositions for these systems could be obtained graphically from these plots in accordance with the procedure of Perry *et al.* (1984). The plait point compositions for different systems were computed as (Tables 1-3): water + acetic acid + 1-butanol (54.2, 15.1, 30.7 by %, wt); water + acetic acid + 1-pentanol (41.4, 29.6, 29 by %, wt); and water + acetic acid + 1-hexanol (36.7, 36.3, 27.0, by %, wt).

Table 2. Solubility data of the water + acetic acid + 1-pentanol system at 30 ± 0.1 °C

	Weight (%)		
	water	1-pentanol	acetic acid
Water-rich phase	97.6	2.4	0
	82.7	3.4	13.9
	70.7	5.7	24.3
	61.2	9.9	28.9
	56.9	13.8	29.3
	53.2	17.2	29.6
	49.9	20.2	29.9
	47.0	23.0	30.0
	44.8	25.4	29.8
	42.7	27.5	29.8
	40.7	29.6	29.7
	39.0	31.5	29.5
	1-Pentanol-rich phase	8.0	92.0
10.3		83.2	6.5
16.3		65.8	17.9
20.8		56.0	23.2
24.5		49.7	25.8
27.9		45.2	26.9
30.7		41.4	27.9
33.2		38.4	28.4
35.4		35.8	28.8
37.1		33.4	29.5
Plait point		41.4	29.0

Table 3. Solubility data of the water + acetic acid + 1-hexanol system at 30 ± 0.1 °C

	Weight (%)		
	water	1-hexanol	acetic acid
Water-rich phase	100	0	0
	70.9	1.7	27.4
	64.1	3.1	32.8
	59.3	5.3	35.4
	54.1	9.2	36.7
	50.6	12.3	37.0
	44.8	18.2	37.0
	40.3	23.1	36.6
	36.7	27.0	36.3
	1-Hexanol-rich phase	5.8	94.2
9.5		79.9	10.6
13.5		64.8	21.7
17.8		53.4	28.8
22.0		44.7	33.3
24.0		42.0	34.0
26.0		39.0	35.0
28.3		36.0	35.7
31.7		32.0	36.3
34.0		29.7	36.3
Plait point	36.7	27.0	36.3

**Fig. 4.** Distribution coefficients for the extraction of acetic acid from water by different solvents (1-butanol, 1-pentanol, 1-hexanol) at 30 ± 0.1 °C.**Fig. 5.** Separation factors for the extraction of acetic acid from water by different solvents (1-butanol, 1-pentanol, 1-hexanol) at 30 ± 0.1 °C.

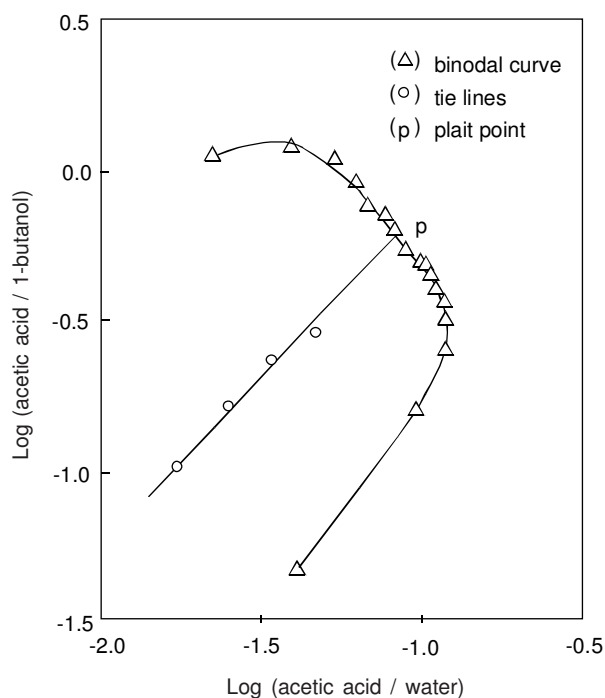
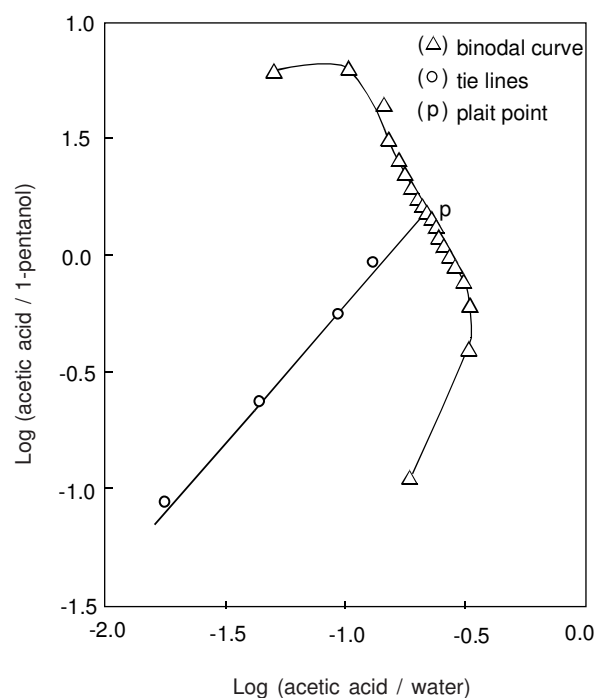
Conclusion

The liquid-liquid phase equilibria of water + acetic acid + 1-butanol, or 1-pentanol, or 1-hexanol systems were measured at a temperature of 30 ± 0.1 °C. The binodal curves, tie lines, distribution coefficients and separation factors were deter-

Table 4. Comparison of coexisting phase in acetic acid + water + 1-butanol, or 1-pentanol, or 1-hexanol systems at 30 ± 0.1 °C

Compositions of initials mixtures (weight, %)			Compositions of organic pahse (weight, %)			Compositions of aqueous phase (weight, %)			Distribution coefficients (K_D^a)	Separation factor (α^b)
water	1-butanol	acetic acid	water	1-butanol	acetic acid	water	1-butanol	acetic acid		
52.2	42.3	5.5	24.0	70.1	5.9	89.0	5.9	5.1	1.157	4.28
50.8	41.2	8.0	27.0	64.4	8.6	85.6	7.2	7.2	1.194	3.79
49.5	40.1	10.4	29.8	59.0	11.2	81.5	9.2	9.3	1.204	3.29
48.2	39.1	12.7	33.3	54.0	12.7	76.0	12.2	11.8	1.076	2.46
water	1-pentanol	acetic acid	water	1-pentanol	acetic acid	water	1-pentanol	acetic acid		
52.2	42.3	5.5	10.0	84.7	5.3	91.5	3.0	5.5	0.964	8.84
48.2	39.1	12.7	13.0	74.9	12.1	84.0	3.5	12.5	0.968	6.24
42.8	34.7	22.5	20.0	57.9	22.1	72.3	5.0	22.7	0.974	3.52
40.1	32.5	27.4	29.4	43.4	27.2	63.6	8.4	28.0	0.971	2.10
water	1-hexanol	acetic acid	water	1-hexanol	acetic acid	water	1-hexanol	acetic acid		
49.5	40.2	10.3	8.8	82.5	8.7	84.3	7.0	12.0	0.725	7.18
44.8	36.5	18.7	11.8	71.0	17.2	78.5	1.0	20.5	0.839	5.59
41.0	33.3	25.7	14.8	61.0	24.2	70.7	1.9	27.4	0.883	4.22
37.8	30.7	31.5	19.5	50.0	30.5	63.0	3.7	33.3	0.916	2.95

K_D^a = expressed as weight per cent acetic acid in organic phase/weight per cent acetic acid in aqueous phase, at equilibrium

**Fig. 6.** Hand-type ternary diagram for the water + acetic acid + 1-butanol system.**Fig. 7.** Hand-type ternary diagram for the water + acetic acid + 1-pentanol system.

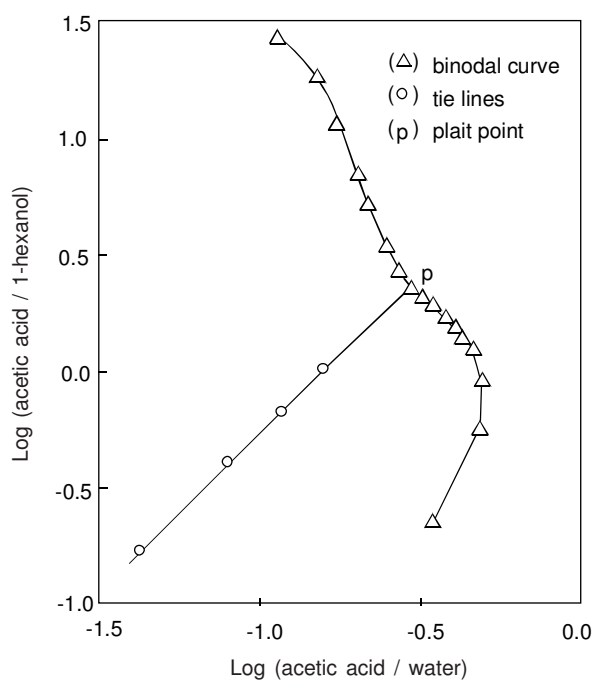


Fig. 8. Hand-type ternary diagram for the water + acetic acid + 1-hexanol system.

mined. Hand's method was used to correlate the tie lines and to calculate coordinates of plait points. The heterogeneous region of 1-hexanol appeared to be broader than those of 1-pentanol and 1-butanol systems. The solubility of these systems increased with the increase in the carbon chain length of the alcohol used as the solvent, giving high values of the distribution coefficient and the separation factor. For water + acetic acid + 1-butanol, water + acetic acid + 1-pentanol, and water + acetic acid + 1-hexanol systems, the distribution coefficients were found to be in the range of 1.767-2.488, 1.543-2.989, and 1.801-2.544, respectively, while the separation factors were found to be in the range of 2.456-4.296, 2.103-8.454, and 2.961-7.200, respectively.

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