

## EQUILIBRIUM EXPERIMENTAL DATA IN TERNARY SYSTEM CONTAINING WATER + 1-PROPANOL+ 1-BUTANOL, 1-PENTANOL or 1-HEXANOL

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Experimental data of liquid-liquid equilibrium in (water + 1-propanol + 1-butanol, 1-pentanol, or 1-hexanol) systems are presented. The aim of this work is to verify the experimental installation and the techniques for determination of the binodal curves and the tie lines for futures liquid-liquid experimental studies and to obtain new data. The cloud-point method to obtain the solubility curve and technique of Newsham and Ng for determination of the tie lines were utilized.

### INTRODUCTION

Liquid-liquid equilibria (LLE) of ternary systems have been the subject of interest of many researchers from various aspects. Liquid-liquid equilibrium data are required for extraction processes and are also useful for mixtures of three liquid components when the immiscibility region is necessary to be avoided.

The efficient separation of organic compounds from aqueous solutions is an important application in the chemical, pharmaceutical, food industries where many solvents are utilized in this purpose. The major factors which influence the equilibrium characteristics of separation process are: the type of organic solvents, the nature and concentration of solute, the third-phase formation. Process consideration dealing with the experimental liquid-liquid equilibrium data in water + alcohols systems still remain a challenging problem since such systems show extremely non-ideal behavior.

The study of liquid-liquid equilibria in systems containing substances below the boiling point under normal conditions is not very difficult. The major problems are the analysis of the equilibrium phases, especially at low solubility.

The aim of the present investigation is to determine the phase-equilibrium data for the ternary systems (water + 1-propanol + 1-butanol, 1-pentanol or 1-hexanol) at different temperatures and atmospheric pressure. The purpose is to verify the experimental installation and the technique for determination of the binodal curves and the tie lines for futures liquid-liquid experimental studies. Newsham and Ng method is utilized for determining composition of the conjugate phases, without analysis. The solubility curves were determined by the cloud-point method.

### EXPERIMENTAL

#### Materials

Pure grade compounds 1-propanol, and 1-butanol and 1-hexanol were supplied by Merck Co. Inc., Germany. Double distilled water was used throughout all experiments. However, the purity of each component was checked by gas chromatography, and the results confirmed the mass fraction purity was higher than 0.99.

#### Apparatus and procedure

The solubility curve was determined by the cloud-point method. Binary mixtures of known compositions were shaken in an equilibrium glass cell equipped with a magnetic stirrer

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and isothermal fluid jacket presented in Fig. 2. The equipment is similar to that of Haddad and Edmister.<sup>1</sup> The mixture temperature was regulated by a thermostated bath with an accuracy of  $\pm 0.2$  K. The inner temperature of the cell was measured within an accuracy of  $\pm 0.1$  K by a certified thermometer. The third component was added by means of a microburet with an accuracy of  $\pm 0.05$  cm<sup>3</sup>. The third component was added until the turbidity had disappeared in the sample. During titration, the samples were maintained at the desired temperature remained steady to within  $\pm 0.01$  °C. The mixtures were prepared by weighting. An electronic balance accurate to  $\pm 0.01$  mg was used. The transitions point between the homogeneous and heterogeneous was determined visually. All visual experiments were repeated to acquire high accuracy.

The technique for the determination of the tie lines is the graphical procedure of Newsham and Ng.<sup>2,3</sup> The tie lines were obtained by using the equilibrium apparatus as described above. Various ternary mixtures about 40 cm<sup>3</sup> with composition within the heterogeneous domain were prepared for each temperature. Each of these mixtures was filled into the cell and vigorously stirred, to bring the layers to equilibrium (usually about 1 hour), under isothermal conditions. The mixture was allowed to separate until each layer appeared perfectly clear (approx. 1.5 hour), and then portion of 4 cm<sup>3</sup> of each liquid layer was removed with a pipette for analysis. The graphical technique followed to determine composition of the samples is illustrated in Fig. 1.

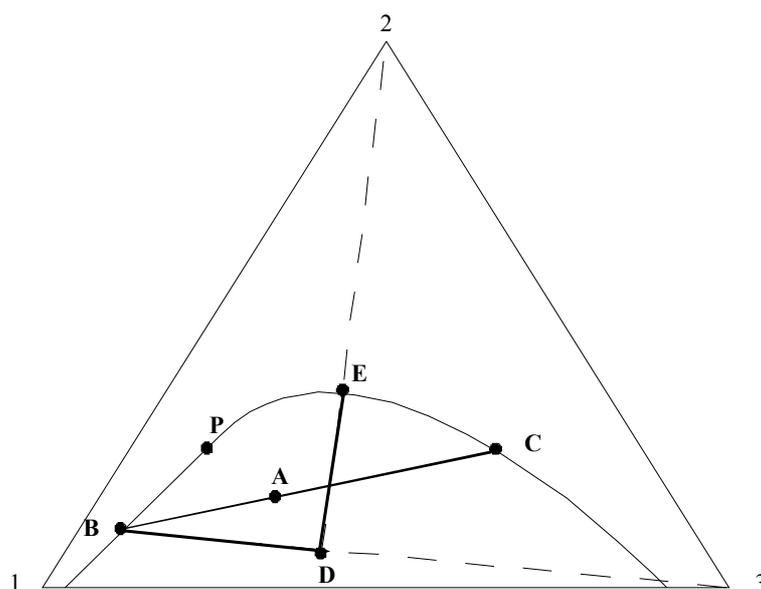


Fig. 1 – Graphical procedure for determining compositions of the coexisting phases by the method of Newsham and Ng<sup>3</sup>.

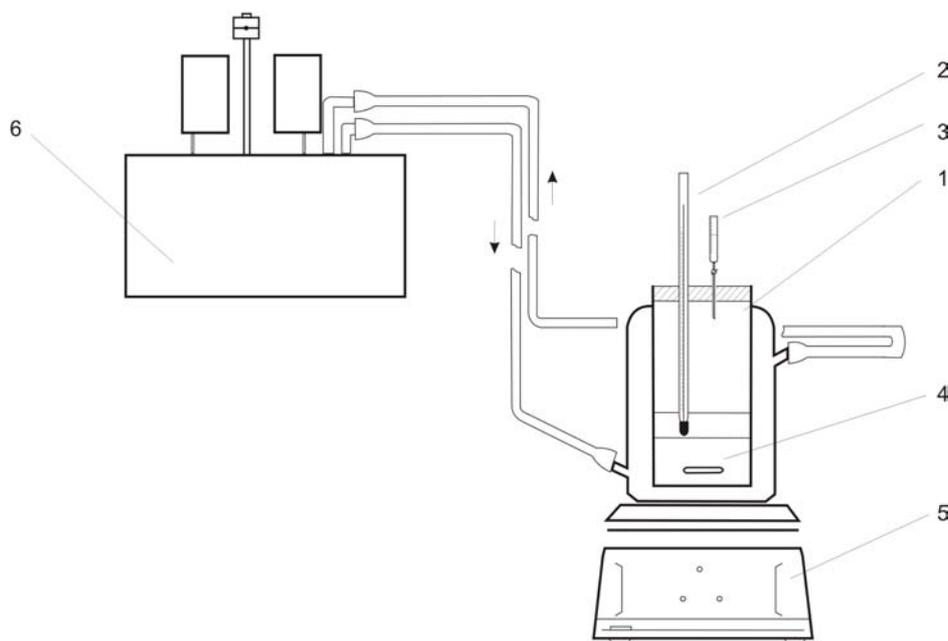


Fig. 2 – Installations for measuring liquid-liquid equilibria by cloud-point method  
1- glass cell; 2-thermometer; 3-microburette 4-stir bar; 5-stirrer; 6-thermostatic bath.

The initial ternary mixture A, with known overall composition is left to separate into two layers B and C. A weighed amount of one phase (e.g. layer B) is taken and a known amount of pure 3 is added, yielding heterogeneous mixture D. The mixture is titrated with pure substance 2, until the turbidity disappears, and the end point E is reached. The required composition, B, cannot be obtained directly from the

$$\overline{BD}/\overline{D3} = m_3/m_B \text{ or } \overline{BD}/\overline{B3} = m_3/(m_3 + m_B) \quad (1)$$

and

$$\overline{DE}/\overline{E2} = m_2/(m_B + m_3) \text{ or } \overline{D2}/\overline{E2} = (m_B + m_3 + m_2)/(m_B + m_3) \quad (2)$$

where,  $m_3$  is the mass of pure component 3 added to the sample of composition B,  $m_2$  is the mass of pure component 2 introduced by titration, and  $m_B$  known mass of sample B.

The graphical procedure of Newsham and Ng to obtain the point B which satisfies these equations was applicable.<sup>4</sup> A similar experimental and graphical procedure for determining the composition of layer C was utilized. Finally, to verify the results we checked that the points A, B, and C let it be on a straight line. The precision of the measurements of composition of mixtures of the tie lines of the binodal curves is  $\pm (1-2)$  wt%.

## RESULTS AND DISCUSSION

The results of determinations for solubility curves at 294.15 K and 302.15 K for water (1) + 1-propanol (2) + 1-butanol (3) system are presented in Tab. 1. In Fig. 3 the binodal curves at 294.15 K

known weights of the materials used in the titration since, initially, only the composition at A is known. To obtain the composition point B the procedure of Newsham and Ng is utilized.<sup>2</sup>

The application of mass balance (the lever rule) permits determination of the original phase by trial and error, by since the following relationship must be accomplished:

and 302.15K are presented. For comparison in the same figure, the results of Newsham and Ng at the temperature 304.15 K are given.<sup>2</sup> The agreement with the data in literature is good. The mutual solubilities for water and 1-butanol were taken from ICT.<sup>5</sup>

The result of determinations for the tie lines, the compositions of liquid phases at equilibrium: butanol-rich phases and water rich phase, are presented in Tab. 2, and in Fig. 3 at 302.15K. The  $w_1$  and  $w_2$  are the compositions (mass %) in the butanol-rich phase and water rich phase. In Fig. 3, A and A', represent the original first and second mixtures, B and C, B' and C' are compositions of equilibrium phases, for the first and second mixtures, respectively.

Table 1

Limit of solubility for system water + 1-propanol + 1-butanol at 294.15 K and 302.15K - data for binodal curves

Nr. exp.	294.15 K		302.15 K	
	$w_1$	$w_2$	$w_1$	$w_2$
1.	92.30	0	92.19	0
2.	76.94	16.14	77.02	14.09
3.	65.33	21.52	76.35	14.84
4.	43.32	28.59	65.46	19.44
5.	38.82	29.69	64.96	20.04
6.	34.02	29.21	57.27	22.91
7.	28.52	25.25	50.62	26.04
8.	20.45	13.18	46.31	26.99
9.	20.29	0	43.09	27.10
10.			40.31	27.17
11.			38.17	26.61
12.			40.20	27.35
13.			35.77	25.76
14.			29.99	21.60
15.			22.19	6.20
16.			22.39	5.38
17.			20.53	0

Table 2

Composition of liquid phases at equilibrium for system water + 1-propanol + 1-butanol at 303.15K (lit.) and 302.15K (exp.)

Nr. exp.	Butanol – rich phase				Water – rich phase			
	w <sub>1</sub> (%)		w <sub>2</sub> (%)		w <sub>1</sub> (%)		w <sub>2</sub> (%)	
	Exp	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
1.	26.3	28.1	15.4	19.3	83.5	86.6	9.1	6.5
2.	25.9	28.1	15.1	19.3	83.9	86.6	9.3	6.5
3.	34.8	38.8	25.5	26.4	81.5	82.1	11.0	10.3

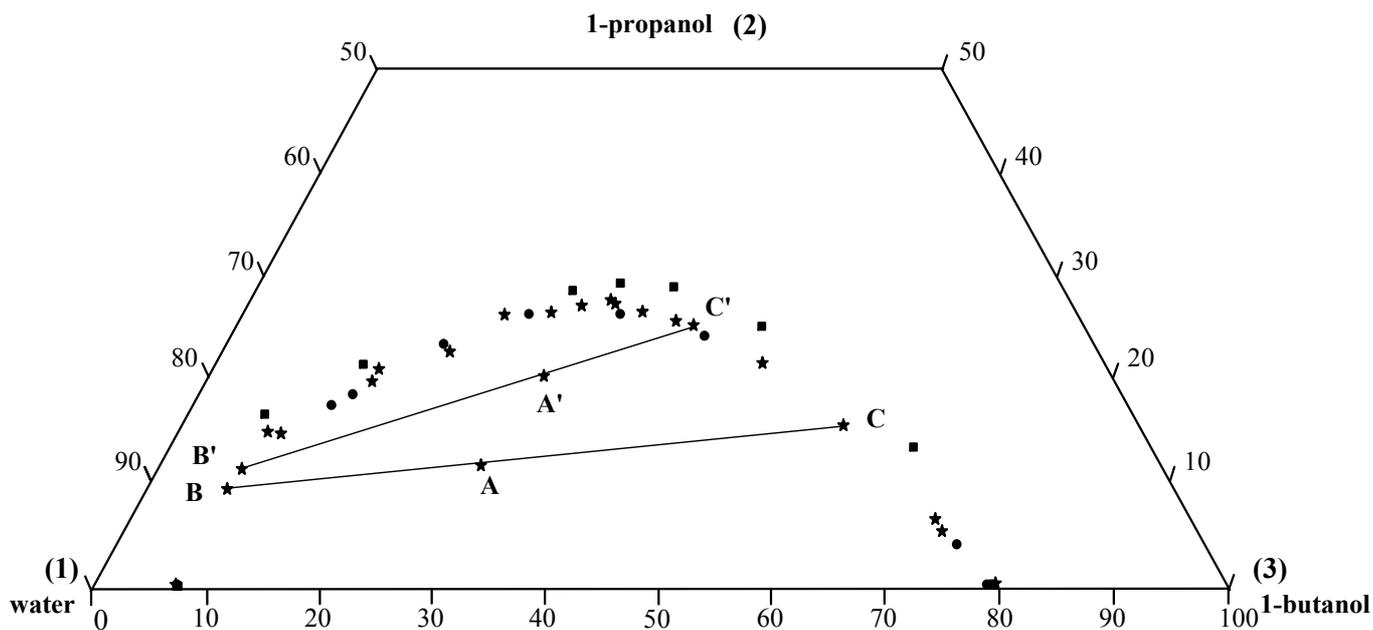


Fig. 3 – Ternary diagram of experimental LLE for water (1) + 1-propanol (2) + 1-butanol (3)  
 Experimental data (★) 302.15K, (■) 294.15K; literature data (●) 304.35K; tie line data — 302.15K;  
 A, A'- original mixtures for the primary and the secondary samples, B, C and B', C' - compositions of primary and secondary conjugated phases.

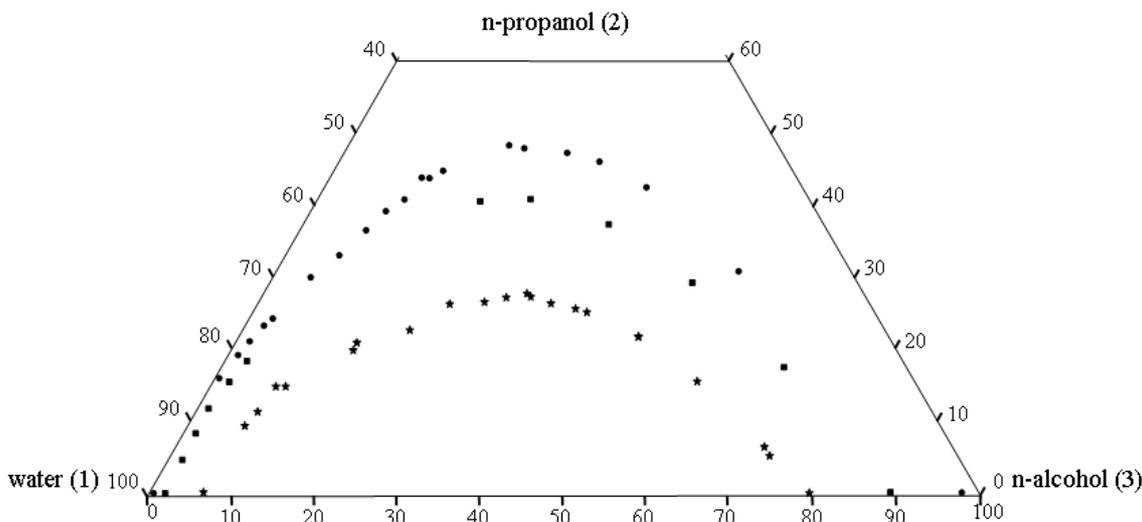


Fig. 4 – Ternary diagram for experimental LLE of (★) (water (1) + 1-propanol (2) + 1-butanol (3) system at 302.15 K, (●) water (1) + 1-propanol (2) + 1-hexanol (3) system at 298.15 K (our data) and (■) (water (1) + 1-propanol (2) + 1-pentanol (3) at 298.15 K.<sup>6</sup>

The Fig. 4 presents comparatively the experimental solubility curves for {(water (1) + 1-propanol (2) + 1-butanol (3)), 1-pentanol or 1-hexanol} ternary systems. The data for {(water (1) + 1-propanol (2) + 1-pentanol (3))} system are from literature.<sup>6</sup> The water + 1-butanol binary system presents the mutual solubility of the compounds greater than the water + 1-pentanol system and this, greater than water + 1-hexanol system. This is agreement with the fact that the miscibility in homologous series water + 1-alcohols decreases with the increase of the carbon number of alcohols.

Similarly, for ternary system the area of the two-phase heterogeneous region decreases in the order 1-butanol < 1-pentanol < 1-hexanol.

### CONCLUSIONS

The cloud-point methods and Newsham and Ng graphical technique were selected for study of liquid-liquid equilibria in mixtures of water, 1-propanol and 1-butanol system, to verify the

experimental installation and procedural techniques to obtain the solubility curve and tie line data. The experimental data for binodal curve and tie line correspond satisfactorily with literature.

The experimental solubility curves for {(water (1) + 1-propanol (2) + 1-butanol, 1-pentanol or 1-hexanol (3))} ternary systems was obtained and compared. The miscibility in the presented systems decreases with the increase of the carbon number of alcohols.

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