

LIQUID + LIQUID EQUILIBRIUM DATA FOR THE TERNARY MIXTURES OF 1-PROPANOL + WATER WITH 1-BUTANOL, 1-HEXANOL, 1-OCTANOL, OR 1-DECANOL AT 294.15 K

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Liquid-liquid equilibrium data are reported for the 1-propanol + water with 1-butanol, 1-hexanol, 1-octanol, or 1-decanol ternary systems at 294.15 K. Data for the bimodal curve have been determined by the cloud-point method. The tie lines were established by Newsham and Ng technique and were satisfactorily correlated by Othmer-Tobias and Hand equations on a mass-fraction basis. All ternary systems exhibit the type-1 behavior of LLE (after Treyball) the most frequent encountered situation of the measured ternary systems.

INTRODUCTION

Liquid-liquid equilibrium (LLE) data of ternary systems are very important for simulation, design and optimization of separation operations. Phase equilibrium data also provide valuable information about the molecular interactions and macroscopic behavior of fluid mixtures. In the recent years the phase equilibrium also useful for mixtures of three liquid components when the heterogeneous regions are necessary to be avoided.

The major factors, which influence the equilibrium characteristics of separation process, are the organic solvent type, the nature and concentration of solute, the three-phase appearance. Process consideration dealing with the experimental liquid-liquid equilibrium data in water + alcohol systems still remain a challenging problem since such systems show extreme 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 this study is to present liquid-liquid equilibrium data measured for ternary systems

1-propanol + water + 1-butanol, 1-hexanol, 1-octanol, or 1-decanol at 294.15 K temperature and atmospheric pressure. The data for 1-propanol + water + 1-butanol ternary system^{1,2} correspond satisfactorily with literature.³ According to our knowledge the ternary systems 1-propanol + water + 1-hexanol, 1-octanol, or 1-decanol have not been studied.

The liquid-liquid equilibria were studied by the cloud-point method⁴ and Newsham and Ng technique;³ the tie line compositions were correlated by the methods of Othmer-Tobias and Hand.⁵

EXPERIMENTAL

Materials

Pure grade chemicals from Merck Co. Inc. Germany were used without further purification. The purity of these materials was checked by gas chromatography, and the results has confirmed a purity higher than 0.995. Double distilled water was used throughout all experiments.

Apparatus and procedure

Liquid-liquid equilibria were investigated using two separate techniques. Data for the solubility of curves of the ternary systems were determined by the cloud-point method.

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The binary mixtures of known compositions were shaken in an equilibrium glass cell equipped with a magnetic stirrer and isothermal fluid jacket. The equipment, presented in a previous paper,^{1,2} is similar to that of Haddad and Edmister.⁶ The mixture temperature was regulated by a thermostated bath with an accuracy of ± 0.2 K. The inner temperature of the cell was measured within an accuracy of ± 0.1 K by a certified thermometer. The third component was added by means of a micro burette with an accuracy of ± 0.05 cm³. 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 ± 0.01 °C. The mixtures were prepared by weighting. An electronic balance accurate to ± 0.01 mg was used. The transition 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 procedure of Newsham and Ng.^{2,3} The tie lines were obtained by using the equilibrium apparatus as described above. A variety of mixtures about 40 cm³ within the heterogeneous gap were prepared for the four systems studies. 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 cm³ of each liquid layer was removed with a pipette for analysis.

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 solubility curve data and the experimental tie lines for 1-propanol (1) + water (2) + 1-butanol (3), 1-propanol (1) + water (2) + 1-hexanol (3), 1-propanol (1) + water (2) + 1-octanol (3) and 1-propanol (1) + water (2) + 1-decanol (3) ternary systems are presented in Tables 1, 2 and in Figs. 1-3 at 294.15 K. The W_i are the mass fraction of the components in the mixtures for the solubility curves data; the W_{i2} and W_{i3} are the mass fraction of the i^{th} component in aqueous phase and in n-alcohol phase (1-butanol, 1-octanol, 1-decanol), respectively, for the tie lines data.

The Figs. 1-3 present the binodal curves. After Treyball⁷ all ternary systems exhibit the type-1 behavior of LLE, the most frequent encountered situation of the measured ternary systems.

Table 1

The solubility curve data for the 1-propanol (1) + water (2) + n-alcohol (3) ternary system at 294.15 K

Exp. No.	W_1	W_2	W_3	W_1	W_2	W_3
	1-propanol + water + 1-butanol system			1-propanol + water + 1-hexanol system		
1.	0.0000	92.2960	7.7040	14.8433	84.5290	0.6278
2.	10.5247	83.4852	5.9901	19.2191	79.5986	1.1823
3.	18.1494	71.5790	10.2716	20.9371	77.3398	1.7231
4.	22.3463	63.8993	13.7544	23.4033	74.3869	2.2097
5.	24.5514	58.6236	16.8250	24.5007	72.7962	2.7031
6.	26.7592	53.9030	19.3378	25.1619	71.6456	3.1925
7.	28.5109	49.9748	21.5142	26.5605	69.8104	3.6291
8.	29.4866	46.9385	23.5749	27.5283	68.4075	4.0642
9.	0.0000	20.2872	79.7128	28.8073	66.7324	4.4603
10.	7.8701	27.1626	64.9673	29.6900	65.4494	4.8606
11.	18.8742	31.2680	49.8578	31.4457	63.2033	5.3509
12.	24.4400	34.4096	41.1504	34.4977	58.9369	6.5654
13.	27.4528	37.0760	35.4713	37.4540	54.4574	8.0886
14.	28.9147	39.5519	31.5334	40.2140	50.4241	9.3619
15.	29.2397	42.0349	28.7254	42.1963	47.2718	10.5319
16.	28.9757	44.4471	26.5771	43.7623	44.6357	11.6021
17.				44.8214	42.5412	12.6373
18.				45.7856	40.6346	13.5798
19.				46.5149	39.0024	14.4826
20.				22.7359	12.3591	64.9050
21.				37.5975	17.2107	45.1919
22.				43.3863	20.5828	36.0309
23.				45.8019	23.4329	30.7652
24.				47.2917	25.7073	27.0010
25.				47.9079	27.7785	24.3136
26.				48.4126	29.4746	22.1128
27.				48.3751	31.1660	20.4589
28.				47.9087	32.8961	19.1953

Table 1 (continued)

Exp. No.	1-propanol + water + 1-octanol system			1-propanol + water + 1-decanol system		
1.	20.3383	79.1048	0.5569	22.8249	76.6306	0.5445
2.	23.0806	75.8513	1.0680	25.3244	73.6292	1.0463
3.	24.7440	73.6994	1.5566	26.8151	71.6574	1.5275
4.	26.2795	71.7014	2.0192	28.1591	69.8555	1.9854
5.	27.6648	69.8755	2.4597	29.7663	67.8241	2.4096
6.	30.9988	65.3222	3.6791	31.0639	66.1173	2.8188
7.	33.5626	61.6621	4.7753	32.4785	63.8898	3.6318
8.	35.7518	58.4838	5.7644	34.1647	61.4677	4.3676
9.	37.7026	55.6383	6.6591	35.3591	59.5622	5.0786
10.	39.4285	53.0954	7.4761	36.8082	57.4744	5.7174
11.	41.7171	49.5600	8.7229	37.9219	55.7410	6.3371
12.	43.8091	46.3924	9.7985	39.9594	52.5699	7.4707
13.	45.3074	43.8801	10.8125	42.0061	49.2460	8.7480
14.	46.5452	41.7091	11.7457	43.8808	46.2584	9.8607
15.	47.5094	39.8619	12.6287	45.0466	44.0088	10.9447
16.	48.2296	38.2913	13.4791	46.1818	41.9072	11.9109
17.	49.4755	35.5202	15.0043	47.0972	40.0855	12.8173
18.	50.2263	33.3421	16.4316	48.0187	38.3548	13.6265
19.	50.7528	31.5036	17.7435	48.3281	37.1525	14.5194
20.	50.9237	30.0413	19.0349	48.7584	35.9255	15.3162
21.	14.6923	4.3123	80.9954	49.1490	34.7852	16.0658
22.	23.8031	7.3328	68.8641	49.4334	33.7699	16.7967
23.	30.3018	9.5992	60.0990	50.1184	32.5404	17.3412
24.	34.5353	11.4938	53.9709	21.6049	4.0066	74.3886
25.	38.1152	13.0106	48.8742	31.3446	6.6764	61.9791
26.	41.1899	14.2383	44.5718	33.5566	9.2425	57.2009
27.	43.1012	15.4481	41.4507	37.2341	11.1254	51.6405
28.	44.1129	16.6936	39.1935	39.7270	12.7877	47.4852
29.	45.0202	17.8104	37.1694	42.1060	14.1396	43.7544
30.	46.6275	19.3318	34.0407	43.3414	15.5128	41.1459
31.	48.0086	20.6077	31.3837	44.7169	16.6473	38.6358
32.	48.6559	21.9268	29.4172	45.8772	17.6700	36.4527
33.	49.5461	22.9452	27.5086	46.7808	18.6298	34.5894
34.	49.2470	23.0812	27.6717	47.8253	20.1335	32.0412
35.	50.1354	25.0758	24.7888	48.9685	21.3297	29.7018
36.	50.2499	27.0233	22.7268	49.3483	22.6348	28.0169
37.	50.2723	28.7147	21.0130	49.5327	23.8728	26.5944
38.				49.9373	24.8730	25.1897
39.				50.0770	25.8892	24.0339
40.				50.4156	27.6126	21.9718
41.				50.3231	29.2863	20.3906
42.				50.1334	30.8030	19.0637
43.				49.9280	32.1593	17.9128
44.				49.6476	33.4264	16.9260

Table 2

The tie-line compositions for the 1-propanol + water + n-alcohols systems at 294.15K

Exp. No.	Water-rich phase			n-Alcohol-rich phase		
	W ₁₂	W ₂₂	W ₃₂	W ₁₃	W ₂₃	W ₃₃
1-propanol + water + 1-butanol system						
1.	0.0670	0.8579	0.0751	0.0982	0.2682	0.6336
2.	0.1273	0.7812	0.0915	0.1929	0.3135	0.4935
3.	0.1976	0.6842	0.1182	0.2935	0.4440	0.2625

Table 2 (continued)

1-propanol + water + 1-octanol system						
1.	0.0692	0.9255	0.0053	0.0989	0.0321	0.8690
2.	0.1229	0.8686	0.0085	0.2843	0.0868	0.6289
3.	0.1443	0.8454	0.0103	0.3920	0.1316	0.4764
1-propanol + water + 1-decanol system						
1.	0.0949	0.9000	0.0051	0.1852	0.0313	0.7835
2.	0.1229	0.8686	0.0085	0.3221	0.0803	0.5976
3.	0.1525	0.8394	0.0081	0.4326	0.1463	0.4211

Fig. 4 presents comparatively the experimental solubility curves for 1-propanol (1) + water (1) + 1-butanol (3), 1-hexanol, 1-octanol or 1-decanol ternary systems. The miscibility in homologous series water + n-alcohols decreases with the increase of the carbon number of alcohols.⁸ This fact can be explained by the formation of hydrophobic effect in the alcohols which affects the solubility of water in alcohol negatively. For ternary system the area of the two-phase heterogeneous region decreases in the order 1-butanol < 1-hexanol < 1-octanol < 1-decanol, with the biggest difference between 1-butanol and 1-hexanol.

The reliability of experimentally measured tie line data is ascertained by applying Othmer-Tobias (Eq. 1) and Hand (Eq. 2) equations.⁵

$$\ln\left(\frac{1-W_{33}}{W_{33}}\right) = a_1 + b_1 \ln\left(\frac{1-W_{11}}{W_{11}}\right) \quad (1)$$

$$\ln\left(\frac{W_{13}}{W_{33}}\right) = a_2 + b_2 \ln\left(\frac{W_{12}}{W_{22}}\right) \quad (2)$$

The correlation coefficients (a, b) and correlation factors (r^2) were determined by the least-squares method and are given in Table 3. The correlations are shown in Figs. 5 and 6. The Othmer-Tobias and Hand equations show a good correlations and straight lines for each ternary system. The linearity of the plot indicates the good degree of consistency of related data.

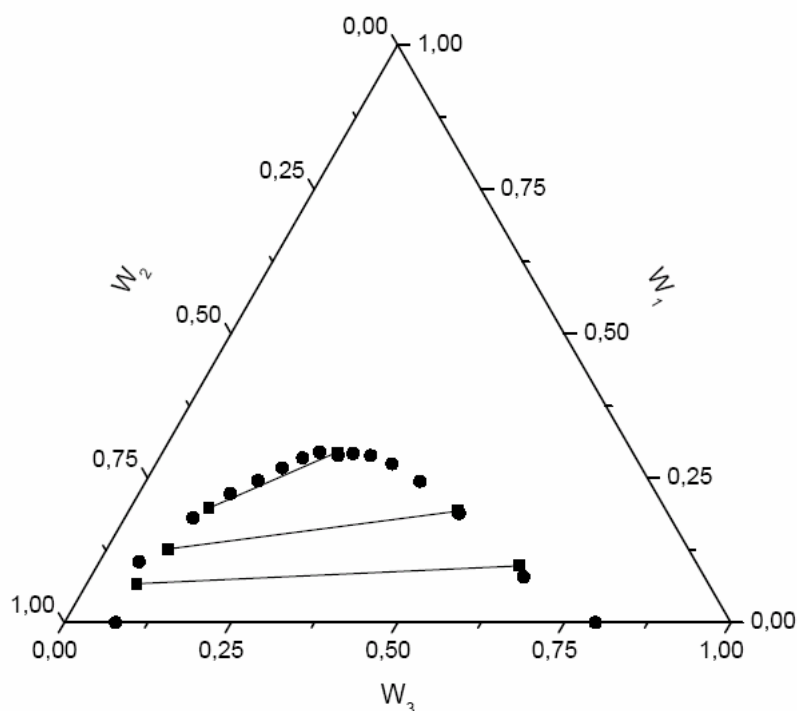


Fig. 1 – Ternary liquid-liquid equilibrium data (mass fraction) at 294.15 K for 1-propanol (1) + water (2) + 1-butanol (3) system at 294.15 K; (●) solubility curve data; (■) experimental tie lines data.

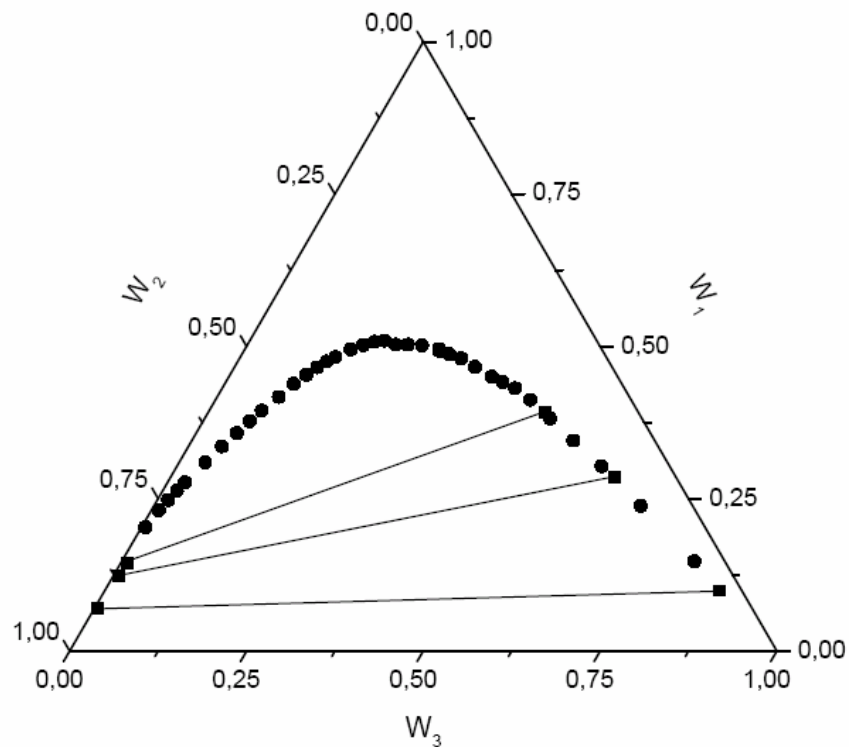


Fig. 2 – Ternary liquid-liquid equilibrium data (mass fraction) at 294.15 K for 1-propanol (1) + water (2) + 1-octanol (3) system at 294.15 K; (●) solubility curve data; (■) experimental tie lines data.

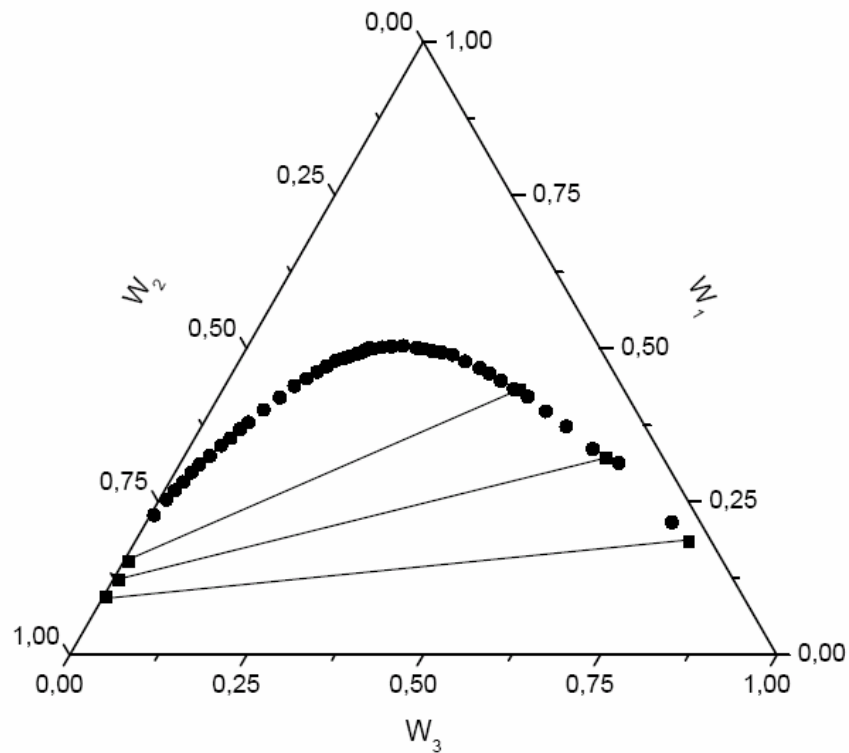


Fig. 3 – Ternary liquid-liquid equilibrium data (mass fraction) at 294.15 K for 1-propanol (1) + water (2) + 1-decanol (3) system at 294.15 K; (●) solubility (binodal curve) data; (■) experimental tie lines data.

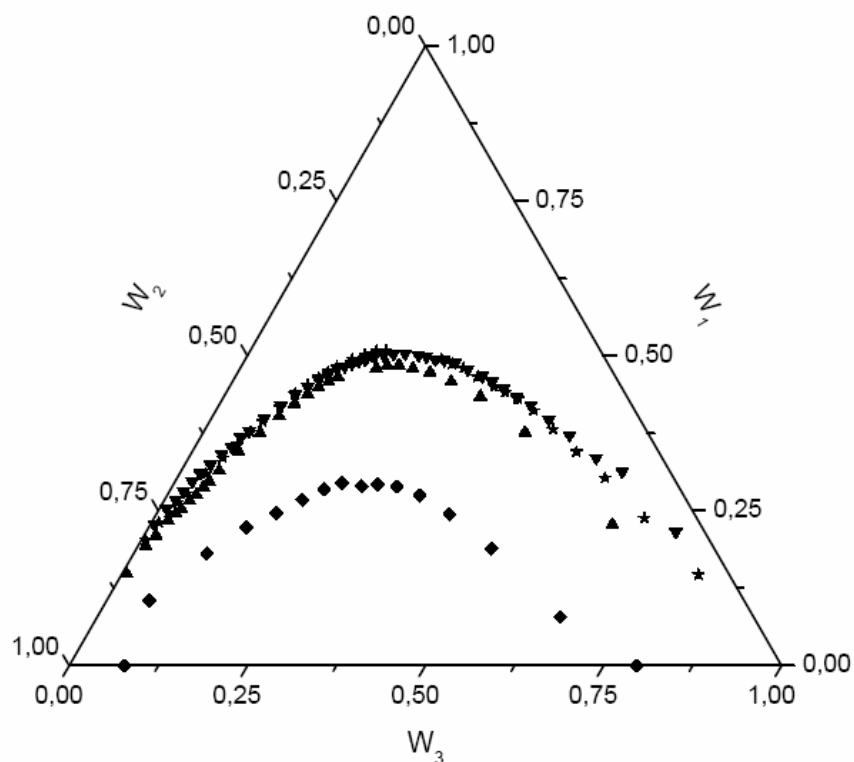


Fig. 4 – Ternary liquid-liquid equilibria (mass fraction) at 294.15 K for (♦) 1-propanol (1) + water (2) + butanol (3); (▲) 1-propanol (1) + water (2) + 1-hexanol (3); (★) 1-propanol (1) + water (2) + 1-octanol (3) and (▼) 1-propanol (1) + water (2) + 1-decanol (3) systems.

Table 3

The correlation coefficients and correlation factors for the Othmer-Tobias and Hand equations for the 1-propanol + water + n-alcohols systems at 294.15K

Systems	Othmer-Tobias coefficients			Hand coefficients		
	a_1	b_1	r^2	a_2	b_2	r^2
1-Propanol + Water + 1- Butanol	2.1417	1.5386	0.9709	1.9041	1.4992	0.9882
1-Propanol + Water + 1- Octanol	4.0214	2.3562	0.9922	3.8663	2.3368	0.9934
1-Propanol + Water + 1- Decanol	5.1875	2.9489	0.9998	4.6489	2.7036	0.9994

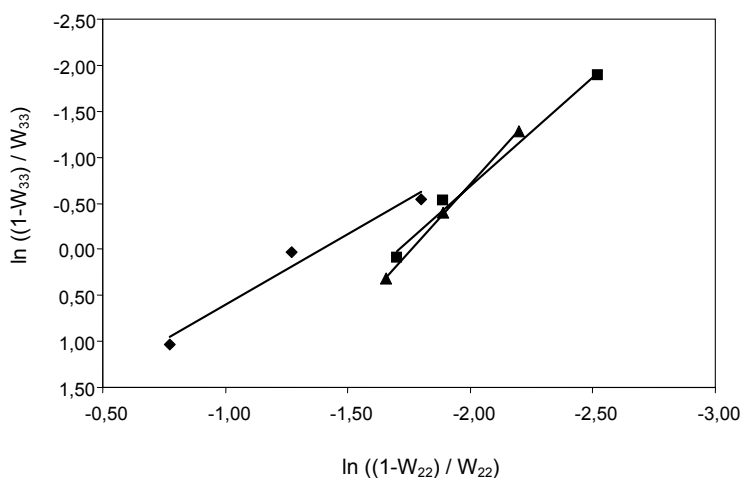


Fig. 5 – Othmer-Tobias Plot at 294.15 K for (♦) 1-propanol + water + 1-butanol; (■) 1-propanol + water + 1-octanol; (▲) 1-propanol + water + 1-decanol systems.

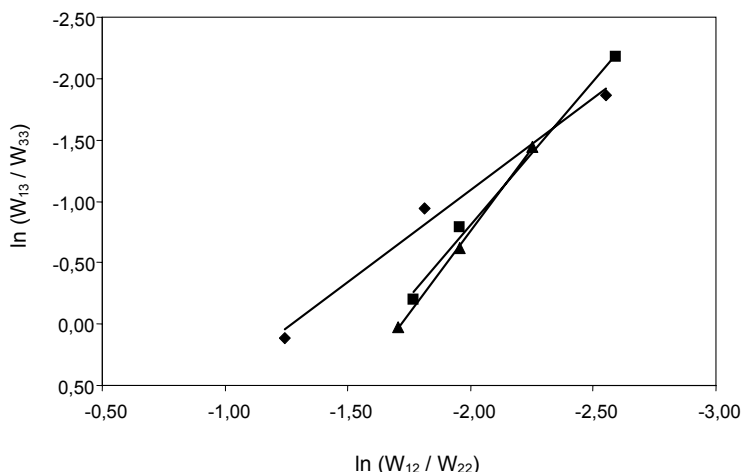


Fig. 6 – Hand Plot at 294.15 K for (◆) 1-propanol + water + 1-butanol; (■) 1-propanol + water + 1-octanol; (▲) 1-propanol + water + 1-decanol systems.

CONCLUSIONS

Liquid-liquid equilibria were measured at 294.15K at atmospheric pressure for {1-propanol (1) + water (2) + 1-butanol (3)}, {1-propanol (1) + water (2) + 1-hexanol (3)}, {1-propanol (1) + water (2) + 1-octanol (3)}, {1-propanol (1) + water (2) + 1-decanol (3)} ternary systems. The solubility curves and the tie lines were obtained. All these ternary systems exhibit the type-1 behavior of LLE, the most frequently encountered situation of the measured ternary systems. The heterogeneous area gap increase as carbon chain length of alcohols increase.

The Othmer-Tobias and Hand correlations indicate a good degree of consistency of the related data.

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