Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article İnce, Erol and Kırbaşlar, Ş. İsmail(2004) 'Liquid-Liquid Equilibria of Water + Ethanol + Dibasic Esters Mixture (Dimethyl Adipate + Dimethyl Glutarate + Dimethyl Succinate) Ternary System', Separation Science and Technology, 39: 13, 3151 — 3162

To link to this Article: DOI: 10.1081/SS-200028823

URL: http://dx.doi.org/10.1081/SS-200028823

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 13, pp. 3151–3162, 2004

Liquid–Liquid Equilibria of Water + Ethanol + Dibasic Esters Mixture (Dimethyl Adipate + Dimethyl Glutarate + Dimethyl Succinate) Ternary System

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ABSTRACT

Liquid–liquid equilibrium data for the ternary system water + ethanol + mixture of dibasic esters (dimethyl adipate + dimethyl glutarate + dimethyl succinate) have been determined experimentally at 298.15, 308.15 and 318.15 K. Complete phase diagrams were obtained by determining solubility and tie-line data. Distribution coefficients and separation factors were evaluated for the immiscibility region.

Key Words: Ethanol; Dimethyl adipate; Dimethyl glutarate; Dimethyl succinate; Liquid–liquid equilibria.

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DOI: 10.1081/SS-200028823
0149-6395 (Print); 1520-5754 (Online)

INTRODUCTION

In the search of more benign solvents as potential replacements for chlorocarbons or aromatic hydrocarbons and as new solvents for separations, we have studied on the dibasic esters, which have excellent properties for industrial applications. Dupont dibasic esters are environmentally friendly high-boiling and oxygenated solvents. Dibasic esters are refined dimethyl esters of adipic, glutaric, and succinic acids. These esters are manufactured globally from a mixed acid coproduct stream obtained from Dupont's adipic plants.[1] They have low toxicity, thermally stability, rather high boiling points, and viscosity and density that are close to those of water. Despite extensive literature reports on liquid–liquid equilibria and phase diagrams, no liquid–liquid equilibrium data have been published for the dibasic ester systems of interest. On the other hand, the liquid–liquid equilibria (LLE) of the some dibasic esters were studied by Uusi-Penttilä.[2]

The separation of ethanol from dilute solutions resulting from fermentation processes is industrially important. Because of the lower energy cost of the process, (liquid + liquid) extraction is an alternative method to distillation. At the same time, (liquid + liquid) extraction is a technique known to separate the ethanol from water mixtures, and many solvents have been tried for this purpose.[3–10]

This study is part of a research program on the recovery of ethanol from dilute aqueous solutions using environmentally friendly solvents with high boiling point. Recently, İnce and Kırbaşlar studied water + ethanol + dimethyl succinate, water + ethanol + dimethyl adipate, and water + ethanol + dimethyl glutarate ternary systems.[11–13] In this paper, a dibasic esters mixture was studied as an agent for the extraction of ethanol from dilute aqueous solutions, and liquid–liquid equilibrium data were reported at each temperature for the ternary system.

EXPERIMENTAL SECTION

Chemicals

Ethanol (99.98 mass %) and dibasic esters mixture (98 mass %) (16 mass %, dimethyl adipate; 63 mass % dimethyl glutarate; 21% mass dimethyl succinate as indicated by the supplier) were purchased from Merck. Ethanol and dibasic esters mixture were used without further purification. Deionized water was further distilled before use.

Table 1. Experimental binodal curve data of water (1) + ethanol (2) + dibasic esters mixture (3) at temperatures, 298.15, 308.15, and 318.15 K.

T = 298.15 K, mass %			T = 308.15 K, mass %			T = 318.15 K, mass %		
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
94.78	0	5.22	95.85	0	4.15	95.08	0	4.92
91.52	3.59	4.89	91.60	3.94	4.46	90.91	3.96	5.13
86.99	7.55	5.46	86.76	7.25	5.99	85.09	7.85	7.06
82.78	11.21	6.01	81.81	10.80	7.39	80.45	10.99	8.56
76.61	14.99	8.40	74.85	14.45	10.70	74.36	14.00	11.64
72.04	17.91	10.05	68.71	16.83	14.46	67.33	16.39	16.28
61.21	20.59	18.20	56.61	18.88	24.51	55.32	17.74	26.94
23.17	16.55	60.28	27.75	16.30	55.95	26.97	15.80	57.23
17.01	14.11	68.88	19.65	13.99	66.36	20.16	13.17	66.67
13.69	11.36	74.95	16.05	11.82	72.13	17.3	11.57	71.13
11.51	9.89	78.60	13.99	10.53	75.48	14.76	10.12	75.12
9.62	8.09	82.29	12.17	9.19	78.64	12.49	8.61	78.90
8.78	7.2	84.02	10.51	7.63	81.86	10.48	7.08	82.44
6.84	5.05	88.11	7.86	5.87	86.27	9.02	5.63	85.35
5.31	3.61	91.08	7.58	5.55	86.87	8.86	3.96	87.18
3.67	1.63	94.70	4.44	1.93	93.63	5.57	2.25	92.18
3.20	0	96.80	4.08	0	95.92	5.10	0	94.90

Apparatus and Procedure

The binodal curve for the water + ethanol + dibasic esters mixture ternary system was determined by cloud-point method. The known composition of binary mixture was shaken in a glass-stoppered cell equipped with a magnetic stirrer and jacketed for circulating water from a constant temperature bath at 298.15 ± 0.02, 308.15 ± 0.02, and 318.15 ± 0.02 K. The third component was progressively added until the transition point was reached. The end point was determined by observing the transition from homogenous to heterogeneous.

Tie-line data were obtained by preparing ternary mixtures (water + ethanol + dibasic esters mixture) of known overall compositions lying within the heterogeneous region and after being stirred vigorously and allowed to reach equilibrium in the isothermal conditions. Samples were carefully taken from each phase and analyzed to obtain the tie-lines. An electronic balance, which is accurate to $\pm 1.10^{-4}$ g, was used during the experiments. The solvent was added by a microburet (Metrohm) with an accuracy of

Table 2. Experimental tie-line data of water (1) + ethanol (2) + dibasic esters mixture (3) at temperatures, 298.15, 308.15, and 318.15 K.

	Water-rich phase, mass %			Solvent-rich phase, mass %		
T/K	w_1	w_2	w_3	w_1	w_2	w_3
298.15	85.45	6.92	7.63	5.78	2.58	91.64
	80.57	10.50	8.93	7.12	4.31	88.57
	76.95	12.67	10.38	8.07	5.55	86.38
	73.30	14.91	11.79	10.04	7.44	82.52
	69.92	17.03	13.05	11.95	9.51	78.54
	66.69	18.51	14.80	13.92	10.93	75.15
308.15	85.51	5.98	8.51	4.13	1.68	94.19
	81.67	9.08	9.25	6.68	3.52	89.80
	76.95	12.67	10.38	9.23	6.48	84.29
	73.60	14.57	11.83	11.13	8.06	80.81
	71.61	15.58	12.81	13.17	9.59	77.24
	68.27	17.77	13.96	15.41	11.69	72.90
318.15	85.55	6.55	7.90	6.08	2.64	91.28
	83.12	8.28	8.60	6.39	3.33	90.28
	78.14	11.53	10.33	8.28	5.25	86.47
	72.70	14.22	13.08	10.50	8.06	81.44
	69.60	16.24	14.16	12.88	9.96	77.16
	67.13	17.48	15.39	14.25	11.13	74.62

$\pm 3.10^{-3}\,cm^3$. Temperature was controlled using a PID (Proportional-Integral-Derivative) controlled thermostat with an accuracy of ±0.02 K.

Analysis

The liquid samples were analyzed by Gas Chromatograph (Hewlett Packard GC, Model 6890 Series), equipped with a Thermal Conductivity Detector (TCD) for the quantitative determination of water, ethanol, and dibasic esters mixture. A 15-m long HP-Plot Q column (320 μm diameter with a 20 μm film thickness) was used with a temperature-programmed analysis. The oven temperature was fixed at 523.15 K. The detector temperature was kept 523.15 K, while injection-port temperature was held at 473.15 K. The flow rate of carrier gas, nitrogen, was kept $6\,cm^3/min$. Samples with known

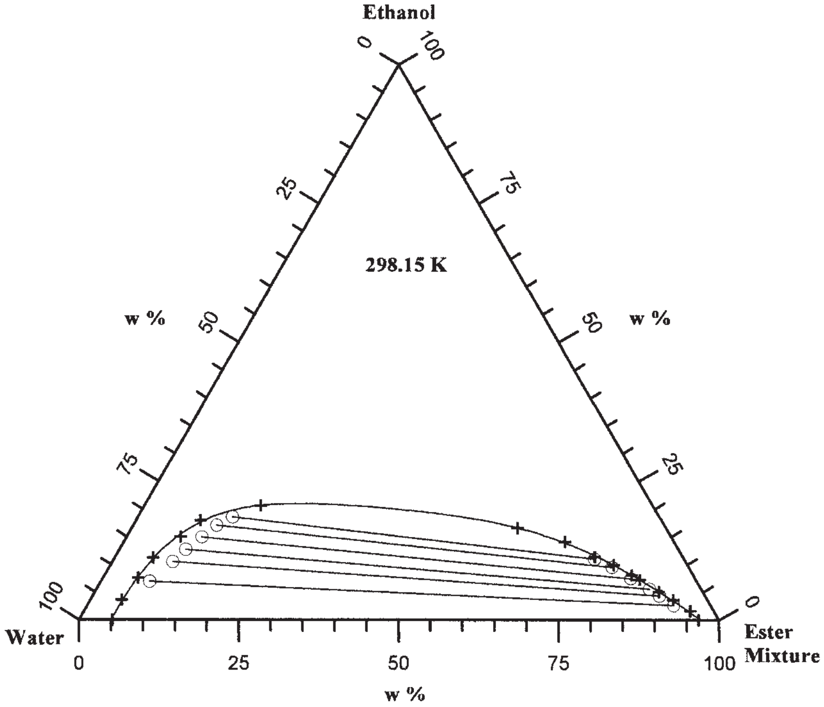

Figure 1. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dibasic esters mixture (3) at 298.15 K, - + -, binodal curve data; -O-, tie-line data.

compositions were used to calibrate the instrument in the composition range of interest.

RESULTS AND DISCUSSION

The experimental binodal curve and tie-line data of water + ethanol + dibasic esters mixture ternaries are given in Tables 1 and 2, respectively. It was found that dibasic esters mixture was only slightly soluble in water but miscible in ethanol. The experimental binodal curves and tie-lines for the system at each temperature were plotted and shown in Figs. 1–3. The area of the heterogeneous region was not changed when the temperature increased from 298.15 to 318.15 K.

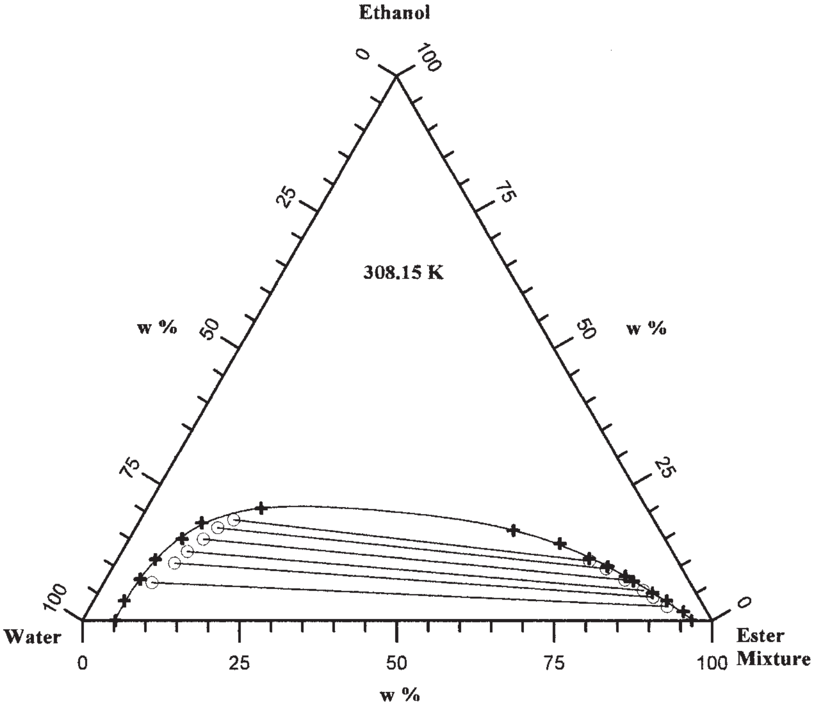

Figure 2. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dibasic esters mixture (3) at 308.15 K, - + -, binodal curve data; -O-, tie-line data.

Distribution coefficients, (d_i), for water ($i = 1$), ethanol ($i = 2$), and separation factors were calculated as follows:

$$d_i = \frac{w_{i3}}{w_{i1}} \tag{1}$$

$$s = \frac{\text{(distribution coefficient of ethanol)}}{\text{(distribution coefficient of water)}} = \frac{(w_{23}/w_{13})\ \text{solvent-rich phase}}{(w_{21}/w_{11})\ \text{water-rich phase}} \tag{2}$$

where w_{23}: mass fraction of ethanol in the solvent-rich phase; w_{13}: mass fraction of water in the solvent-rich phase; w_{21}: mass fraction of ethanol in the water-rich phase; w_{11}: mass fraction of water in the water-rich phase.

The effectiveness of extraction of ethanol by dibasic esters mixture is given by its separation factor, which is an indication of the ability of

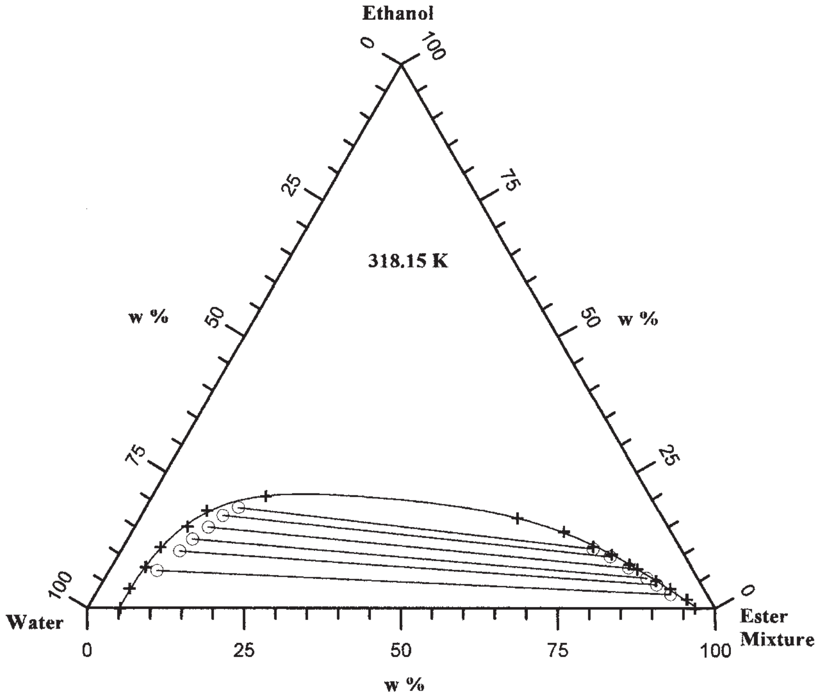

Figure 3. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dibasic esters mixture (3) at 318.15 K, - + -, binodal curve data; -O-, tie-line data.

dibasic esters mixture to separate the ethanol from water.[14] This quantity is found to be greater than 1 (separating factors varying between 2.83 and 5.85) for the system reported here, which means that extraction of ethanol by dibasic esters mixture is possible.

The distribution coefficients and separation factors for each temperature are given in Table 3. The extraction power of the solvent at each temperature, plots of (d_2) vs. (w_{21}) and (s) vs. (w_{21}) are given in Figs. 4 and 5, respectively.

The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer-Tobias correlation with Eq. (3) at each temperature.[15]

$$\ln\left(\frac{(1 - w_{33})}{w_{33}}\right) = a + b \times \ln\left(\frac{(1 - w_{11})}{w_{11}}\right) \tag{3}$$

where w_{33}: mass fraction of dibasic esters mixture in the solvent-rich phase, a and b are constant and slope of Eq. (3), respectively. The linearity of the plot

Table 3. Distribution coefficients d_i of water (1) – ethanol (2) and separation factors at 298.15, 308.15, and 318.15 K.

T/K	d_1	d_2	s
298.15	0.068	0.373	5.49
	0.088	0.411	4.67
	0.105	0.438	4.17
	0.137	0.499	3.64
	0.171	0.558	3.26
	0.209	0.591	2.83
303.18	0.048	0.281	5.85
	0.082	0.388	4.73
	0.120	0.511	4.26
	0.151	0.553	3.66
	0.184	0.616	3.35
	0.226	0.658	2.91
318.15	0.071	0.403	5.68
	0.077	0.402	5.22
	0.106	0.455	4.29
	0.144	0.567	3.94
	0.185	0.613	3.31
	0.212	0.637	3.00

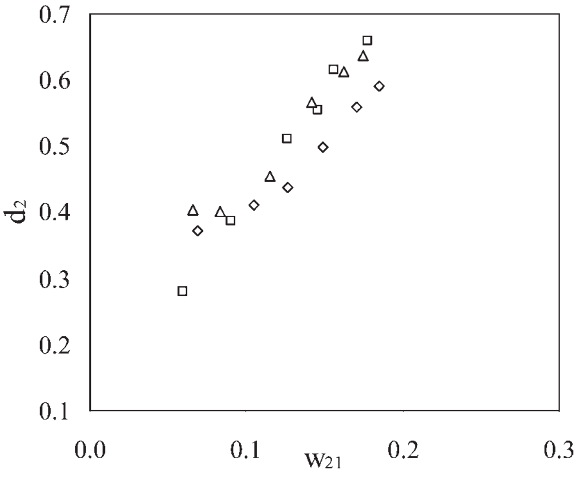

Figure 4. Distribution coefficient (d_2) of ethanol as a function of the mass fraction (w_{21}) of ethanol in aqueous phase of the ternary system at each temperature (◇ 298.15, □ 308.15 and △ 318.15 K).

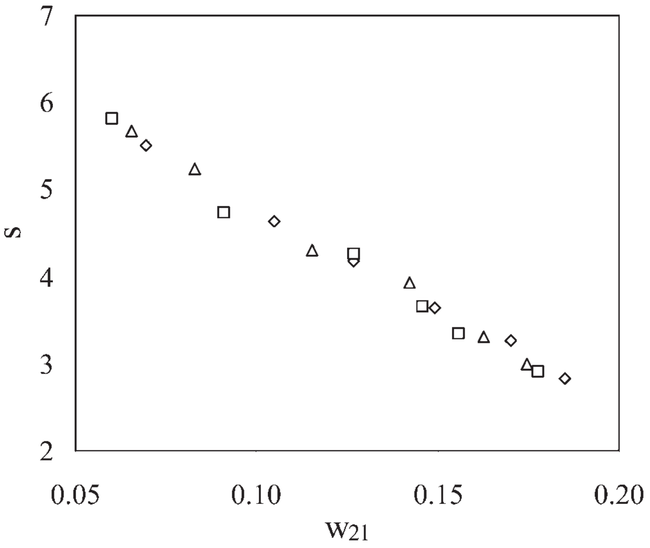

Figure 5. Separation factors as a function of the mass fraction (w_{21}) of ethanol in the aqueous phase of the ternary system at each temperature (◇ 298.15, □ 308.15 and △ 318.15 K).

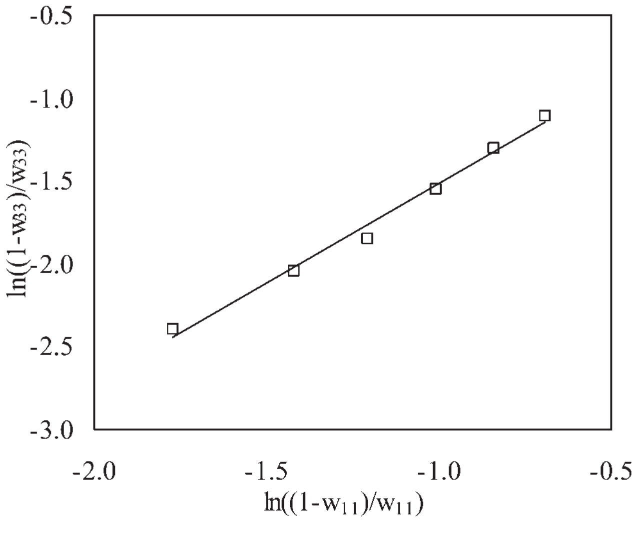

Figure 6. Othmer-Tobias plot of the water + ethanol + dibasic esters mixture system at T = 298.15 K.

Table 4. Constants of Othmer-Tobias equation for the water + ethanol + dibasic esters mixture ternary system (r^2: regression coefficient).

T/K	a	b	r^2
298.15	−0.3063	1.2105	0.989
308.15	0.3899	1.7562	0.995
318.15	−0.2371	1.2254	0.994

indicates the degree of consistency of the data. Othmer-Tobias plot is shown in Fig. 6 only at 298.15 K. The parameters of Othmer-Tobias correlation are given in Table 4. The approximation of the regression coefficient r^2 to 1 indicates the degree of consistency of related data.

Selectivity diagrams on a solvent-free basis are shown at each temperature in Fig. 7. The effect of temperature change on the selectivity values was found to be insignificant.

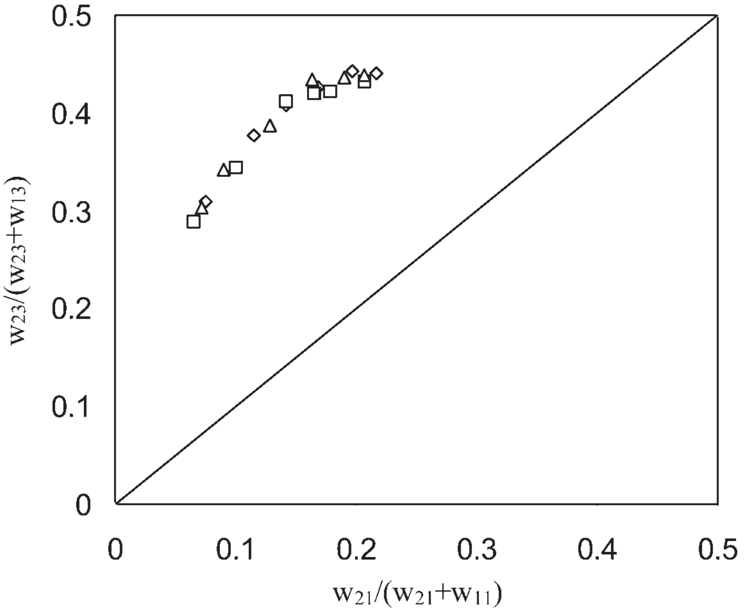

Figure 7. Selectivity diagram at each temperatures (◇ 298.15, □ 308.15 and △ 318.15 K, free-solvent basis).

CONCLUSION

The experimental binodal curves data have been plotted to show the miscibility and immiscibility regions for the ternary system of water (1) + ethanol (2) + dibasic esters mixture (3). The data were experimentally obtained at atmospheric pressure and 298.15, 308.15, and 318.15 K. The separation factors are greater than 1 for all temperatures and compositions reported here, indicating that extraction of ethanol using dibasic esters mixture is possible. Otherwise, it is not constant over the whole two-phase region. The dibasic esters mixture is a good solvent for extracting ethanol from aqueous solutions.

ACKNOWLEDGMENTS

The authors would like to thank to Emel Keskinocak for GC analysis.

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Received January 26, 2004
Accepted June 8, 2004