

# Liquid–Liquid Equilibria of Selected Dibasic Ester + Water + Solvent Ternary Systems

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Experimental liquid–liquid equilibria for various dibasic ester + solvent + water systems were obtained at 297 K. These systems are suggested as possible substitutes in applications where chlorocarbons and aromatic hydrocarbons are used. The dibasic esters can also be used as novel solvents in separation techniques.

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## Introduction

In the scope of investigating more benign solvents as potential replacements for chlorocarbons or aromatic hydrocarbons and as new solvents for separations, we have concentrated on the dibasic esters which have excellent properties for industrial applications. They are powerful solvents, and as such they are already widely used in the paint, coating, and polymer industry and as industrial cleaners. They have very low toxicity (diethyl succinate is FDA approved), great stability, rather high boiling points (190–300 °C), and viscosity and density that are close to those of water.

During this investigation we came across the unusual behavior of the dibasic esters in the presence of water and an alcohol. The dibasic esters are only slightly soluble in water but miscible with alcohols, with the exception of diethyl l-tartrate which is soluble in both water and alcohol. We observed that aqueous and organic phases produced a single phase upon addition of alcohol or some esters.

Despite extensive literature reports on liquid–liquid equilibria and phase diagrams (e.g., see Novák *et al.* (1987), Sørensen and Arlt (1980), and Scheibel (1978)), no liquid–liquid equilibrium data have been published for the dibasic ester systems of interest. Therefore, the binodal curves for seven different ternary systems involving dibasic esters are reported here. The following dibasic ester + solvent + water systems were studied: (1) dimethyl succinate (DMS) + methanol (MeOH) + water, (2) diethyl succinate (DES) + ethanol (EtOH) + water, (3) diisobutyl dibasic ester (DBE) + ethanol + water, (4) dimethyl succinate + monomethyl succinate (MMS) + water, (5) dimethyl adipate (DMA) + monomethyl adipate (MMA) + water, (6) diethyl succinate + ethyl l-lactate (EL) + water, and (7) diethyl succinate + diethyl l-tartrate (DET) + water.

## Experimental Section

**Chemicals.** Dimethyl succinate, dimethyl adipate, and diisobutyl dibasic ester (15 mass % diisobutyl adipate, 58 mass % diisobutyl glutarate, and 27 mass % diisobutyl succinate as indicated by the supplier) were graciously supplied by Du Pont. Methanol (absolute) was purchased from Mallinckrodt and ethanol (anhydrous) from Quantum Chemical Corp. Monomethyl succinate (>90%) and monomethyl adipate (>98%) were obtained from Fluka AG.

Diethyl succinate (99%), ethyl l-lactate (98%), and diethyl l-tartrate (99+%) were purchased from Aldrich. Distilled water was used in all the experiments. All chemicals were used without further purification.

**Binodal Curves.** The binodal curves of the liquid–liquid equilibria for the various systems were originally determined on a volumetric basis, except for the dimethyl succinate + monomethyl succinate + water system, which was determined on a mass basis due to the high melting point of monomethyl succinate. The total volume of liquid used to find a point on the binodal curve was about 1 cm<sup>3</sup>. All the binodal curves were determined at (297 ± 1) K which was measured by a calibrated thermometer accurate to 0.5 K.

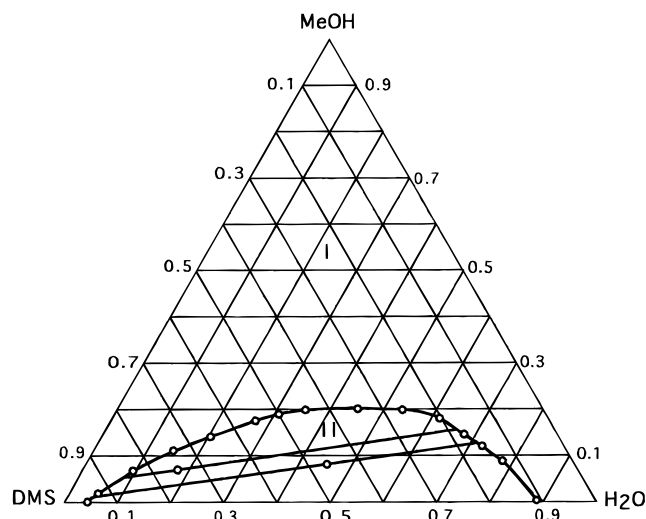
The volumetric determinations were begun within the two-phase region. Fixed amounts of dibasic ester and water were mixed in a vial, and the solvent was added 10 μL at a time. After each solvent addition the vial was shaken vigorously on a vortex touch mixer (Fisher Scientific) for a few seconds. These additions were continued until the two phases could no longer be visually observed, and the solution formed only one phase. This marked a point on the binodal curve, and the procedure was repeated for several different compositions in order to determine the entire two-phase region. To increase the accuracy in determining the binodal curves visually, additional determinations were done using trace amounts of Nile Red (<10<sup>-6</sup> M) as an indicator. Nile Red is preferentially dissolved in the dibasic ester phase and causes the ester phase to have a pink color and the water phase to remain colorless. This helps the visual detection of the boundary between the two-phase region and the single-phase region. To verify the accuracy of the previous method, the binodal curves for the diethyl succinate + ethanol + water and dimethyl succinate + methanol + water diagrams were determined using a Coulter counter (model N4MD) sub-micrometer particle size analyzer. The Coulter counter was used in determining whether the mixture was a solution or a microemulsion. Size distributions detectable by the instrument range from 3 nm to 3 μm. It was concluded that the accuracy obtained by the visual observation of the mixture (±1 mass %) was acceptable for industrial applications. After the volumetric binodal curve was established, it was mathematically converted to a mass-based curve assuming zero volume change on mixing.

The mass fraction diagram for the dimethyl succinate + monomethyl succinate + water system was determined essentially in the same manner by adding small increments

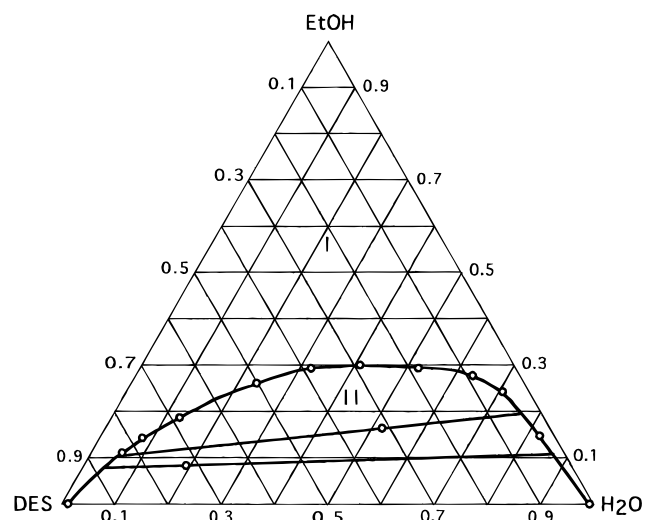
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**Figure 1.** Experimental ternary diagram for the system dimethyl succinate (DMS) + methanol (MeOH) + water (H<sub>2</sub>O) at 297 K. Compositions are expressed in mass fractions.



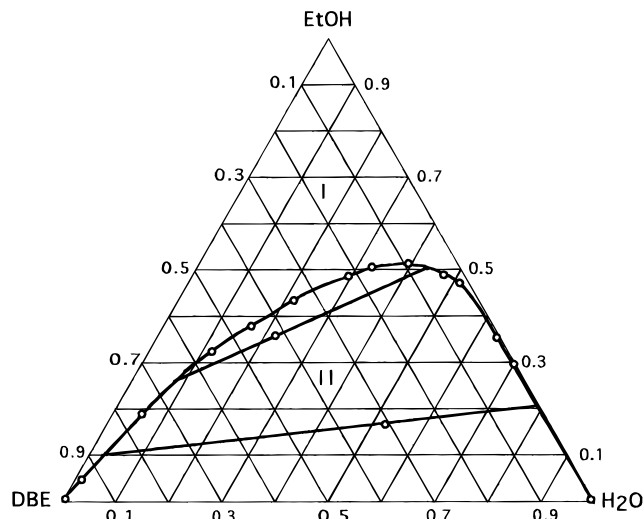
**Figure 2.** Experimental ternary diagram for the system diethyl succinate (DES) + ethanol (EtOH) + water (H<sub>2</sub>O) at 297 K. Compositions are expressed in mass fractions.

(0.5 mg) of the solid substance, monomethyl succinate, into the liquid mixture until a single-phase composition was achieved.

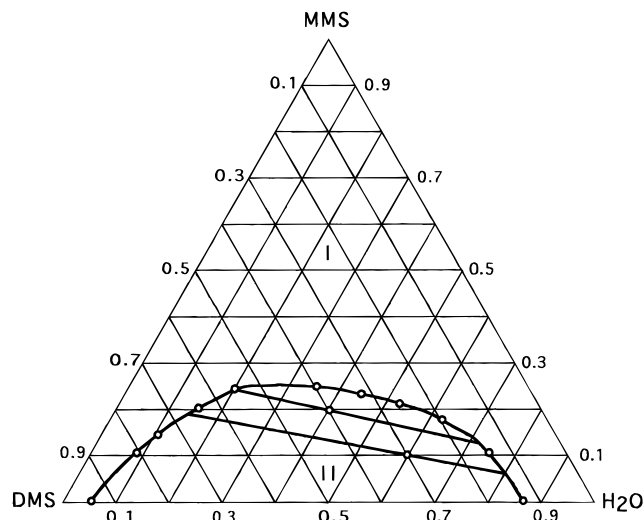
**Tie Lines.** The tie lines were constructed using the lever rule by Othmer (1942). Thus, the tie lines are only estimates, and more precise methods should be applied before the tie lines are used for quantitative work. For each diagram, two arbitrary points were chosen within the two-phase region to yield two tie lines (three points and three tie lines for the adipate system, respectively). A total volume of 20 mL of the solution was prepared with a trace amount of Nile Red. The solutions were mixed vigorously and allowed to reach equilibrium (1–14 days). After equilibrium was reached the two phases were separated using a separatory funnel. The phases were weighed, and the two tie lines were constructed using the lever rule.

## Results

The experimental binodal curves for the seven dibasic ester + solvent + water systems are plotted in Figures 1–7, and the numerical data are presented in Tables 1 and 2. The binodal curves are hand-drawn, and no curve fitting was done. The single-phase region is denoted by I and the two-phase region by II. All data are reported in mass



**Figure 3.** Experimental ternary diagram for the system dibutyl dibasic ester (DBE) + ethanol (EtOH) + water (H<sub>2</sub>O) at 297 K. Compositions are expressed in mass fractions.



**Figure 4.** Experimental ternary diagram for the system dimethyl succinate (DMS) + monomethyl succinate (MMS) + water (H<sub>2</sub>O) at 297 K. Compositions are expressed in mass fractions.

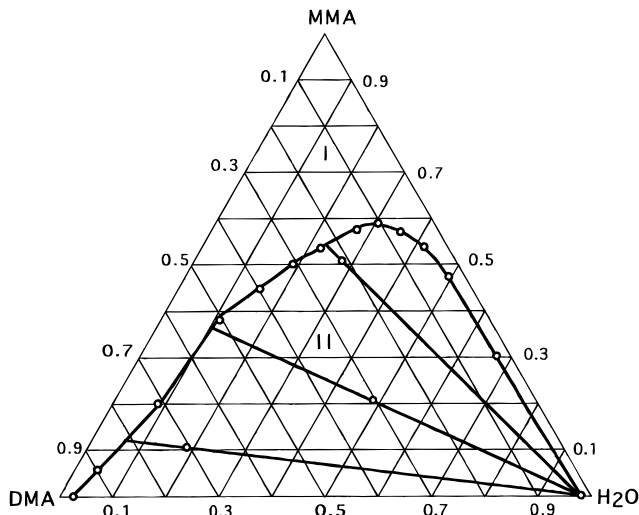
fractions. The temperature dependence of the phase diagrams was not studied. The accuracy of the binodal curves is  $\pm 1$  mass %. Positions of the tie lines have been roughly estimated.

The results for the equilibria between water and dimethyl succinate, diethyl succinate, and dimethyl adipate were compared with the results published by Stephenson and Stuart (1986) and Stephenson (1992), and they were found to be in good agreement.

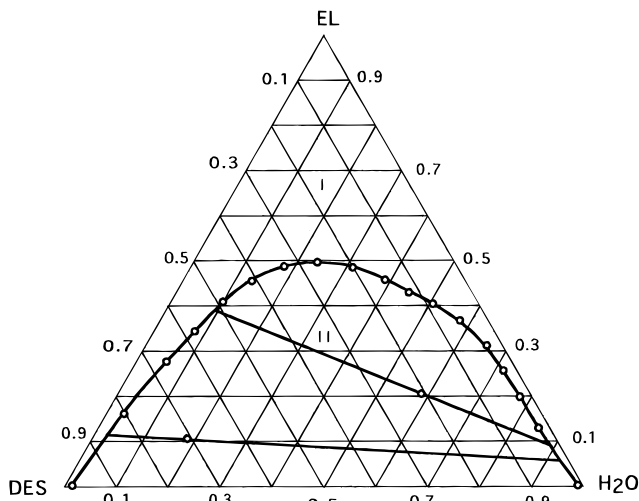
## Conclusions

Experimental liquid–liquid equilibrium phase diagrams were determined for seven dibasic ester + solvent + water systems at 297 K. The dibasic esters were chosen on the basis of their suitability for industrial applications. Two different types of solvents were chosen as phase breakers, i.e., esters and alcohols. The solvents were chosen on the basis of their solubilities in water and dibasic esters.

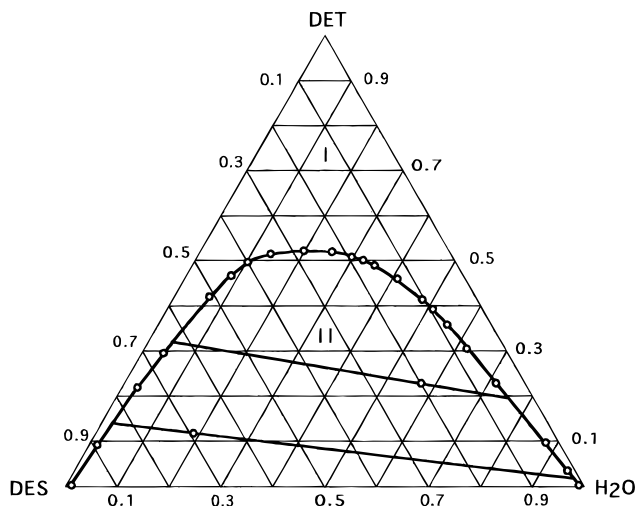
Since the solubilities are temperature dependent, the binodal curves and tie lines are only accurate at the temperature that they were obtained. Experimental errors occurred in the form of loss of the sample especially when small volumes had to be transferred from one vessel to



**Figure 5.** Experimental ternary diagram for the system dimethyl adipate (DMA) + monomethyl adipate (MMA) + water ( $H_2O$ ) at 297 K. Compositions are expressed in mass fractions.



**Figure 6.** Experimental ternary diagram for the system diethyl succinate (DES) + ethyl l-lactate (EL) + water ( $H_2O$ ) at 297 K. Compositions are expressed in mass fractions.



**Figure 7.** Experimental ternary diagram for the system diethyl succinate (DES) + diethyl l-tartrate (DET) + water ( $H_2O$ ) at 297 K. Compositions are expressed in mass fractions.

another, i.e., while phases were separated for tie line determination.

**Table 1. Binodal Points for the Systems Studied at 297 K<sup>a</sup>**

	100w <sub>1</sub>	100w <sub>2</sub>	100w <sub>3</sub>	100w <sub>1</sub>	100w <sub>2</sub>	100w <sub>3</sub>
Dimethyl Succinate (1) + Methanol (2) + Water (3)						
91	2	6	49	19	32	
78	9	13	33	20	47	
64	14	22	17	14	69	
Diethyl Succinate (1) + Ethanol (2) + Water (3)						
92	5	3	34	31	35	
79	14	7	17	31	52	
65	21	14	3	21	76	
49	26	24				
Diisobutyl Dibasic Ester (1) + Ethanol (2) + Water (3)						
98	0	2	12	37	51	
55	33	12	3	49	48	
45	38	17	1	29	70	
22	43	35				
Dimethyl Succinate (1) + Monomethyl Succinate (2) + Water (3)						
81	11	8	40	25	35	
67	19	15	26	21	54	
55	24	21	15	11	74	
Dimethyl Adipate (1) + Monomethyl Adipate (2) + Water (3)						
90	6	4	31	50	19	
71	20	9	16	57	27	
44	42	14	5	53	42	
Diethyl Succinate (1) + Ethyl Lactate (2) + Water (3)						
72	23	5	13	43	44	
39	46	14	6	35	59	
23	48	29	2	19	79	
Diethyl Succinate (1) + Diethyl Tartrate (2) + Water (3)						
73	26	2	8	36	56	
36	51	13	5	23	72	
21	52	27	3	8	89	
13	45	41				

<sup>a</sup> w is mass fraction.

**Table 2. Tie Line Data for the Systems Studied at 297 K<sup>a</sup>**

	ester rich phase			water rich phase		
	100w <sub>1</sub>	100w <sub>2</sub>	100w <sub>3</sub>	100w <sub>1</sub>	100w <sub>2</sub>	100w <sub>3</sub>
Dimethyl Succinate (1) + Methanol (2) + Water (3)						
86	6	8	18	17	65	
94	2	4	16	13	71	
Diethyl Succinate (1) + Ethanol (2) + Water (3)						
85	10	5	4	19	77	
88	8	4	2	11	87	
Diisobutyl Dibasic Ester (1) + Ethanol (2) + Water (3)						
66	26	8	7	50	43	
87	10	3	1	21	78	
Dimethyl Succinate (1) + Monomethyl Succinate (2) + Water (3)						
56	24	20	15	13	72	
67	19	14	14	6	80	
Dimethyl Adipate (1) + Monomethyl Adipate (2) + Water (3)						
22	55	23	2	0	98	
53	36	11	2	0	98	
81	12	7	2	0	98	
Diethyl Succinate (1) + Ethyl Lactate (2) + Water (3)						
52	39	9	2	9	89	
86	11	3	2	6	92	
Diethyl Succinate (1) + Diethyl Tartrate (2) + Water (3)						
53	32	5	5	20	75	
84	14	2	1	2	97	

<sup>a</sup> w is mass fraction.

The tie lines in Figures 1–3 show, as was expected, that in the alcohol systems the alcohol is more readily soluble in the water phase than in the ester phase. Similarly, in Figures 4–7, where esters were used as phase breakers, the tie lines slope oppositely. Therefore, the esters are more readily soluble in the ester phase.

**Registry Numbers Supplied by the Author.** Diethyl succinate, 123-25-1; diethyl l-tartrate, 87-91-2; diisobutyl adipate, 141-04-8; diisobutyl glutarate, 71195-64-7; diisobutyl succinate, 925-06-4; dimethyl adipate, 627-93-0; dimethyl succinate, 106-65-0; ethyl l-lactate, 687-47-8; monomethyl adipate, 627-91-8; monomethyl succinate, 6878-55-5.

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