Properties of the Water-Benzene–Triethylene Glycol Dimethyl Ether System at 25° C.

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THE DIMETHYL ethers of ethylene glycols, and of the di-, tri-, and tetraethylene glycol form a group of compounds of interesting properties. They are water soluble ethers which can dissolve some inorganic salts, so an investigator has available a series of solvents in which to study reactions with water-sensitive materials. This series of compounds with gradually changing properties may serve as solutes for study of the effect of molecular size and of varying physical properties on transport and transfer phenomena.

Separation of heat sensitive compounds from solutions in the polyglycol ethers by vacuum distillation is difficult. However, because mixtures of these ethers with water and benzene show a region of immiscibility, extraction methods of separation may be developed. The first step in the development of such a procedure is the determination of the three-component phase diagrams for the systems.

In this study, the phase diagram for the system water-benzene–dimethyl ether of triethylene glycol (E-161) was determined. To determine the compositions for the system, the refractive indices of the saturated phases, the tie line data, and the distribution coefficients were determined.

Table I. Refractive Indices of Solutions of Triethylene Glycol Dimethyl Ether in Water and Benzene at 25° C.

Composition of Solution: Polyether in Water (No Benzene) Wt. %			Refractive Index
	0.00		1.33251
	4.23		1.33781
	10.00		1.34316
	20.00		1.35471
	40.00		1.37766
	59.97		1.39792
	80.00		1.41257
	89.93		1.41774
	100.00		1.42181
Polyether in Benzene (Anhydrous)			
	0.00		1.49788
	10.06		1.49081
	20.74		1.48327
	39.99		1.46905
	60.10		1.45391
	80.00		1.43829
	89.98		1.42966
	95.29		1.42496
	100.00		1.42181
Benzene	Polyether (Benzene Phase)	Water	
14.8	69.2	17.0	1.4113
17.5	69.0	13.5	1.4317
38.0	57.0	5.0	1.4517
59.0	39.0	2.0	1.4689
79.75	19.75	0.5	1.4834
89.88	9.87	0.25	1.4910
100.00	0.00		
	(Water Phase)		
0.1	0.0	99.9	1.3328
0.2	9.9	89.9	1.3443
0.4	19.8	79.8	1.3554
1.7	39.3	69.0	1.3796
6.0	56.0	38.0	1.4001

MATERIAL AND EQUIPMENT

Triethylene glycol dimethyl ether (E-161), from Ansul Chemical Co., was purified by vacuum distillation after treatment with sodium hydride to destroy the peroxides which form very readily. The intermediate fraction from the distillation was used.

Benzene from the General Chemical Co. was refractionated. Single distilled water was used.

The refractive indices of the solutions were measured with a Bausch and Lomb Dipping Refractometer equipped with three prisms calibrated against fluorite chips, one prism calibrated against distilled water, and one prism calibrated with a sodium chloride solution. The temperatures for the system were controlled by a constant temperature bath regulated to ±0.05° C. The analytical balance had an accuracy ±0.0001 gram.

REFRACTIVE INDICES

The refractive indices were determined on solutions of E-161 and water and of E-161 and benzene. These solutions were prepared gravimetrically in glass-stoppered bottles and, after standing at 25° C., were transferred to the closed cup of the dipping refractometer. The cup was immersed in the water bath, at 25° C. The refractive index was read periodically until it had reached a steady value, indicating no further change in temperature.

The refractive indices of solutions of E-161 in benzene saturated with water, and of E-161 in water saturated with benzene were also determined. To be sure the solutions were saturated, benzene (or water) was added to a solution of E-161 in water (or in benzene) until the solution became cloudy. The cloudy solutions became clear on standing in the bath at 25° C., and the refractive index could be determined.

In Table I and Figure 1 are assembled the data for the refractive index-composition relations. These data were thus

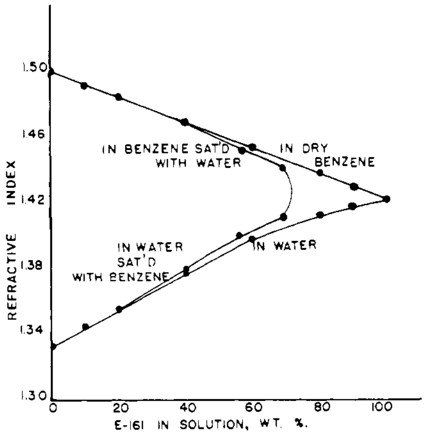

Figure 1. Refractive indices of solutions of triethylene glycol dimethyl ether–benzene-water at 25° C.

available for use in determining the composition of the saturated phase of the three-component system.

MUTUAL SOLUBILITIES

Mutual solubilities at 25° C. for the three component system were determined by the cloud point titration. Water, or benzene, was added from a weighing buret into a 125-ml. flask, fitted with a foil-covered stopper and containing 20 ml. of a weighed solution of known composition of the other two components (E-161 and water or E-161 and benzene). At the first appearance of a persistent clouding of the solution, the composition was calculated from the weigh added and the known starting composition. The solubility data is given in Table II.

Table II. Mutual Solubilities in the System Triethylene Glycol Dimethyl Ether–Water-Benzene at 25° C.

(Cloud Point Compositions)

Water, Wt. %	Benzene, Wt. %	Polyether, Wt. %
79.5	0.844	19.85
59.3	2.458	38.3
37.83	6.20	56.3
17.14	14.9	68.3
14.14	17.36	68.9
4.86	37.95	57.2
1.655	58.9	39.2
0.742	79.7	19.85
0.655	89.6	9.96

TIE LINE DETERMINATION

For the system E-161-benzene-water, the tie line compositions were determined by accurately weighing six mixtures of benzene and water (about 1:1) and adding an accurately weighed amount of E-161 so that the composition of the polyether would vary in about 10% increments over the total system. This gravimetric synthesis of the system gave a composition which could be plotted as a point on the three-component diagram (A on Figure 2). Then the index of refraction of each layer was measured after the system had reached equilibrium at 25° C. From these refractive indices, the compositions could be determined by referring to an enlarged plot of Figure 1. The compositions of the two layers should fall on a straight line through A, as at B and C on Figure 2. Table III shows the composition of the of the solutions and the refractive indices of the layers.

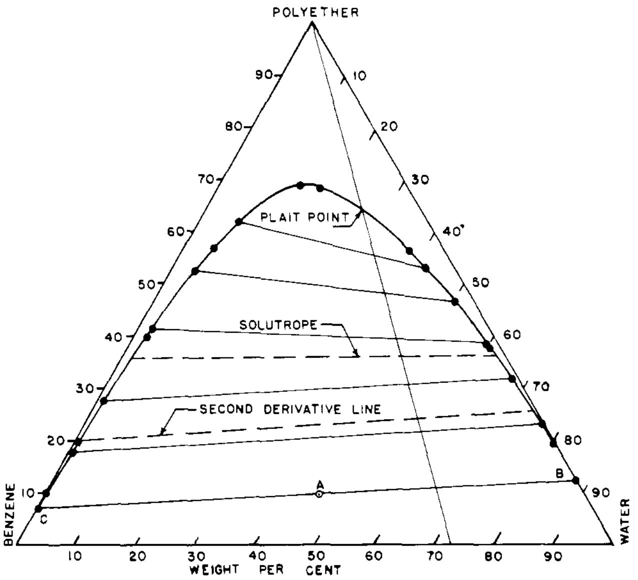

Figure 2. Solubility curve and tie lines for system triethylene glycol dimethyl ether–benzene-water at 25° C.

CORRELATION OF SYSTEM

Solubilities and Selectivities. The data for mutual solubilities and for the tie lines were correlated using the method of Treybal, Weber and Daley (*9*). The data for determining new tie lines are listed in Table IV and as Figure 3. The plait point composition is at a system composition of 65.8% E-161, 8.9% benzene and 25.3% water. The tie line data does not plot as a straight line on this figure. The equation for such a straight line would be:

$$x_{32}/x_{22} = r(x_{31}/x_{11})^n \qquad (1)$$

where the concentrations are as follows:

x_{32} = of E-161 in the water phase
x_{31} = of E-161 in the benzene phase
x_{11} = of benzene in the benzene phase
x_{12} = of benzene in the water phase
x_{22} = of water in the water phase
x_{21} = of water in the benzene phase

Here "*n*" is reported (*7*) to account for the effect of mutual solubility of the solvents at the concentration of the solute other than zero. Figure 4 is a plot showing the effect of concentration of E-161 on the solubility of benzene in the water layer and of water in the benzene layer. When plotted on log-log paper, Figure 5, the solubility curve for benzene in the water layer is almost a straight line function of the content of E-161; but in the water phase, the logarithmic

Table III. Experimental Tie Line Data for Tri-ethylene Glycol Dimethyl Ether–Benzene–Water System at 25° C.

Weight, Gross				Composition, Gross			C_6H_6 Layer		H_2O Layer		Dist. Coeff. wt. % in C_6H_6
E-161, g.	C_6H_6, g.	H_2O, g.	Total, g.	E-161, wt. %	C_6H_6, wt. %	H_2O, wt. %	Refr. index	E-161, wt. %	Refr. index	E-161, wt. %	wt. % in H_2O
5.7053	25.0536	25.0936	55.7664	10.25	44.92	44.83	1.49230	7.6	1.34669	11.6	0.655
12.6944	25.2543	25.0103	62.9590	20.2	40.1	39.7	1.48524	17.5	1.35902	22.5	0.777
21.4663	25.0810	25.0627	71.5740	30.0	35.0	35.0	1.477492	27.5	1.36962	31.5	0.875
33.7185	25.2722	25.0224	84.0131	40.2	30.1	29.7	1.46704	41.0	1.37855	38.5	1.065
49.9990	25.0253	25.0712	100.0935	50.0	25.0	25.0	1.45643	52.2	1.38693	45.9	1.135
75.2781	25.1022	25.1272	125.3075	60.0	20.05	19.95	1.44455	61.7	1.39597	52.5	1.175

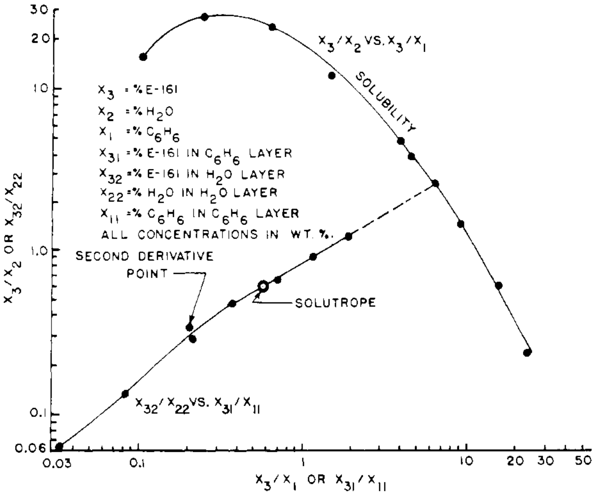

Figure 3. Estimation of plait point for system E-161-benzene-water

relation is not a straight line. These curves indicate that the relation is not a simple exponential one as stated in Equation 1. Possibly this is another anomolous effect of the non-ideality of water solutions.

The constants of the Equation 1 were found to be

$$n = 0.6177 \qquad r = 0.8180$$

for the tie lines in the upper portion of the two-phase region.

Table IV. Data for Estimation of Plait Point for System E-161 Water-Benzene at 25° C.

Solubilty Data

E-161 x_3 wt. %	C_6H_6 x_1 wt. %	H_2O x_2 wt. %	x_3/x_2	x_3/x_1
		Benzene Layer		
68.9	17.36	14.14	4.87	3.97
57.2	37.95	4.86	11.75	1.51
39.2	58.9	1.65	23.7	0.6665
19.85	79.7	0.74	26.8	0.249
9.96	89.6	0.65	15.2	0.111
		Water Layer		
19.85	0.844	79.5	0.249	23.5
39.3	2.45	59.3	0.664	16.0
56.3	6.20	37.83	1.49	9.10
68.3	14.9	17.14	3.99	4.58
		Plait Point		
65.8	8.9	25.3	2.6	7.4

Tie Line Data

Water Layer			C_6H_6 Layer				
C_6H_6 x_{12} wt. %	Water x_{22} wt. %	E-161 x_{32} wt. %	C_6H_6 x_{11} wt. %	Water x_{21} wt. %	E-161 x_{31} wt. %	x_{32}/x_{22}	x_{31}/x_{11}
0.5	87.9	11.6	91.9	0.5	7.6	0.132	0.083
1.0	76.5	22.5	81.9	0.6	17.5	0.294	0.214
1.7	66.8	31.5	71.7	0.8	27.5	0.471	0.384
2.3	59.2	38.5	57.2	1.8	41.0	0.650	0.717
3.5	50.6	45.9	44.3	3.5	52.2	0.908	1.176
5.0	42.5	52.5	31.6	6.7	61.7	1.235	1.950

The selectivity of water for E-161 has been determined. This has been defined by Treybal (*8*) as:

$$\beta_{32} = x_{32}x_{11}/x_{31}x_{12} \tag{2}$$

and the selectivity of benzene for E-161 as:

$$\beta_{31} = x_{31}x_{22}/x_{32}x_{21} \tag{3}$$

These selectivities have been calculated and plotted against the composition of E-161 in the benzene-rich phase, as shown in Figure 6. Since β_{31} represents the ratio of x_{31}/x_{21} (ratio of the concentration of E-161 to that of water in the benzene phase) to x_{32}/x_{22} (ratio of the concentration of E-161 to that of water in the water phase), the higher the value of β_{31}, the greater the enrichment of E-161 by benzene extraction. Figure 6 indicates that the enrichment of E-161 will be 100 times when benzene is used to extract it from water solutions of less than 20%.

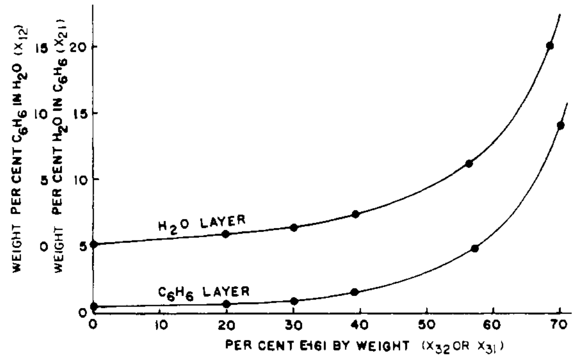

Figure 4. Effect of E-161 on solubility of benzene in water and of water in benzene

Solutrope and "Second Derivative" Line. The system E-161 benzene-water belongs to a group whose correlation characteristics are unusual. Treybal (*6*) has pointed out that 2-propanol-benzene–water shows a reversal in the distribution ratio. Mote (*1*) has shown that acetone-toluene-water also shows this behavior. Recent, as yet unpublished, results of a study of the systems polyethers-toluene-water have also shown reversals in the distribution ratios (*5*).

The reversal in the distribution ratio occurs in systems with solutropes—i.e., systems having a horizontal tie line connecting two phases with equal concentrations of solute.

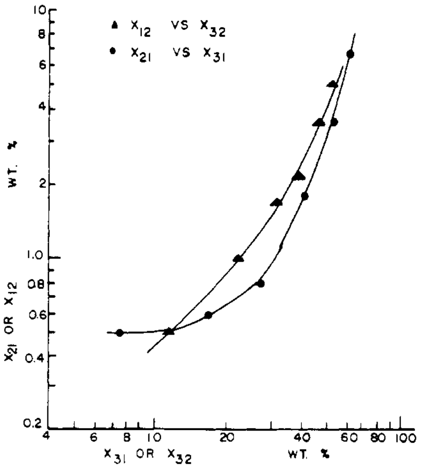

Figure 5. Logarithmic plot of effect of E-161 on solubility of benzene on water and of water in benzene

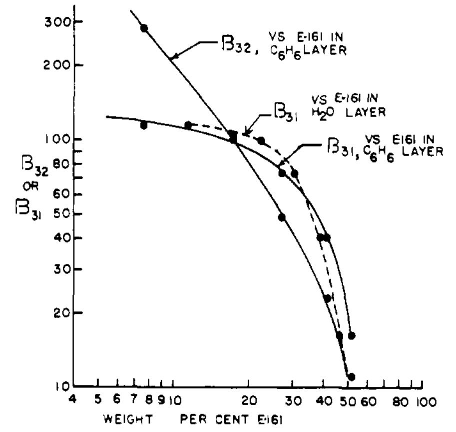

Figure 6. Selectivity of benzene and of water for E-161 at 25° C.

The composition of the solutrope may be determined by plotting the compositions in each phase and showing where the distribution line crossed the line of equal concentration. In most systems, the tie lines change slope gradually from the base line to the plait point. However when a solutrope occurs in the system, the slope of the tie lines reverses. On a rectangular phase diagram, the slope of the tie line is $\Delta x_3/\Delta x_2$, where x_3 is the system concentration of the solute and x_2 is the system concentration of one of the other components, in this case, water. Assuming $\Delta x_3/\Delta x_2$ is negative, but tending to become positive as the solute concentration decreases. It may continue this trend while passing through the solutrope. Then, because the slope of the tie line approaches zero at zero solute concentration, the trend must reverse. We have chosen to call this tie line of reversal of trend, the "second derivative line" since for this line, the change in slope is zero. This corresponds to the point in the Hand plot, where the tie line curve shows a change in slope.

This second derivative line may occur in systems with no solutrope; as in the systems: acetic-water-2,6-dimethyl-4-heptanone (di-isobutyl ketone) (*3*), acetic acid-water-fenchone (*3*), acetic acid-water-monochlorobenzene (*4*), and acetic acid-water-heptadecanol (*10*).

It is interesting that if the composition of this system is expressed in mole per cent instead of in weight per cent, the solutrope disappears, but one still obtains a break in the tie line curve on the Hand plot.

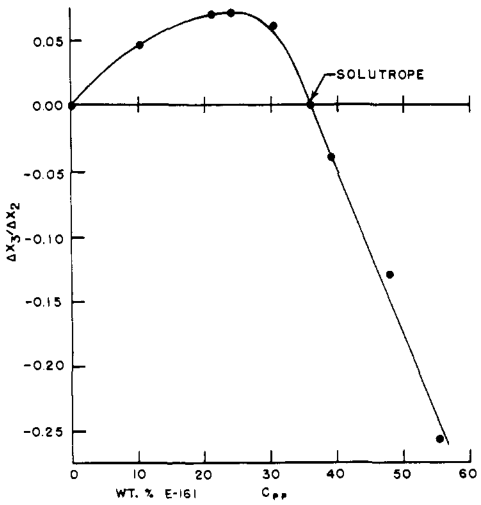

Figure 7. Change in slope of tie lines for system E-161-benzene-water

The second derivative line may be better illustrated by plotting the slope of the tie lines, "*m*", against the concentration of the solute at the plait point ratio of the other two components, "Cpp", for the system, on a rectangular phase diagram (*2*). These Cpp concentrations would fall along a line through the solute and the plait point, as shown in Figure 2. Table V illustrates the evaluation of these slopes from the data of Table III. The data in the column labeled Δx_3 represent the difference in concentration of the solute (E-161) at the ends of the tie lines. That data labeled Δx_2 represent the difference in the concentration of water at the ends of the same tie lines. The evaluated slopes, *m*, are plotted against Cpp in Figure 7. The maximum in the curve represents the second derivative concentration and the point where the curve crosses the line of zero slope represents the solutrope concentration. The value selected from this study for this second derivative line passes through the composition of about 24% E-161 (at the plait point ratio) and corresponds to a tie line $x_{31} = 20.7$; $x_{32} = 25.5$ weight %. This is shown on Figure 3.

Table V. Evaluation of Slopes of Tie Lines and Concentrations at Plait Point Ratios for Determinations of Second Derivative Line and Solutrope.

Δx_3 Wt. %	Δx_2 Wt. %	$m = \Delta x_3/\Delta x_2$	Cpp. Wt. %
0.0	...	0.000	0.0
4.0	86.9	0.046	10.4
5.0	75.5	0.066	21.1
3.5	66.7	0.052	30.0
0.0	61.0	0.000	35.9
−2.5	58.2	−0.043	41.2
−6.2	48.0	−0.129	52.6
−9.2	36.0	−0.255	63.4

Since very little is known regarding the molecular behavior in polycomponent solutions, it is impossible to conjecture on the cause of the change in the trend of the slope of the tie line. Possibly a change in molecular species present results in a change in the distribution of the solute between the two phases. The reason for the change in molecular specie and the magnitude of the change must still be determined.

LITERATURE CITED

(1) Mote, J. F., "Effect of Interfacial Tension on the Rate of Mass Transfer in Ternary Liquid-Liquid Extraction," p. 132, Ph. D. thesis, Virginia Polytechnic Institute, Blackburg, Va., 1957.
(2) Murphy, N. F., Lastovica, J. E., Fallis, J. G., *Ind. Eng. Chem.* **49**, 1035-42 (1957).
(3) Othmer, D. F., White, R. E., Trueger, E., *Ibid.*, **33**, 1240-8, 1513 (1941).
(4) Peake, J. S., Thompson, K. E., Jr., *Ibid.*, **44**, 2439-41, (1952).
(5) Pusey, R. H., "Over-all Mass-Transfer Coefficients for a Homologous Series of Polyglycol Ethers Between Toluene and Water," M. Sci. thesis, Virginia Polytechnic Institute, Blacksburg, Va., 1958.
(6) Treybal, R. E., "Liquid Extraction," pp. 29, 31, McGraw-Hill, New York, 1951.
(7) *Ibid.*, p.74.
(8) *Ibid.*, p. 89.
(9) Treybal, R. E., Weber, L. D., Daley, J. F., *Ind. Eng. Chem.* **38**, 817-21 (1946).
(10) Upchurch, J. C., VanWinkle, M., *Ibid.*, **44**, 618-21 (1952).

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