Secondary Butyl Alcohol–Toluene–Water Ternary System at 25.0° C. and the Composition of the Ternary Azeotropes at Various Pressures

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The phase diagram at 25.0° C. has been determined for the system sec-butyl alcohol–toluene–water. Binodal solutions were determined by titration to turbidity with water or toluene of a binary of the other two components. Composition of the ternary was determined by weight. Refractive indices were used for determination of the tie lines. The composition and boiling point of the ternary and the composition of each of the two phases into which the ternary separated were determined at five pressures between 200 and 662 mm. of Hg.

THE systems *sec*-butyl alcohol–benzene–water (*4*) and *n*-butyl alcohol–toluene–water (*5*, *8*) have been reported. This report adds results of an investigation of the *sec*-butyl alcohol–toluene–water system.

MATERIALS AND APPARATUS

A comparison of our values with accepted values for the three starting materials is shown in Table I. The methods used to purify the materials are described.

Secondary butyl alcohol (Eastman Kodak Co.) was treated with magnesium sulfate, then metallic sodium, and fractionally distilled. Deionized water was treated with Deeminac demineralizer (Crystal Research Laboratories, Hartford, Conn.) and then distilled from alkaline permanganate solution. The toluene (J. T. Baker Chemical Co.) was fractionally distilled after being boiled over sodium.

A Bausch and Lomb 3L refractometer, maintained at 20.0° ± 0.02° C. was used to determine refractive indices. It was calibrated with the standard test piece supplied with the instrument. Densities were obtained using a Westphal balance, calibrated against liquids whose densities were determined using a density balance, weights were obtained on a Mettler balance, and the thermometers used were calibrated against the melting points of several authentic samples melting in the range of 0° to 90° C.

The solubilities and tie lines were measured in 50-ml., glass-stoppered, volumetric flasks which were placed in a motor-driven shaker and immersed in a constant temperature bath. The bath was maintained at 25° ± 0.05° C. throughout the study.

Experimental precautions were taken in all operations to ensure that the visual recognition of the end point in the solubility titrations, which was observed through a magnifying glass, would be the limiting factor in the accuracy of the measurements.

Table I. Physical Constants of Starting Materials

	Refractive Index at 20° C.		Density at 20° C.	
Compound	Observed	Reported (*12*)	Observed	Reported (*12*)
Water	1.3324	1.3330	0.9983	0.9982
sec-Butyl alcohol	1.3973	1.3978	0.8059	0.8063
Toluene	1.4963	1.4961	0.8667	0.8669

A fractionating column with a total reflux, partial drawoff type head was used during the study. The column was 4 feet high with an inside diameter of 25 mm. It had an evacuated jacket which was wrapped with aluminum foil to aid in the prevention of heat loss. The packing consisted of 1/8-inch glass helices. This packing and length produced about 12 theoretical plates within the column. While the ternary azeotrope was being obtained, a vacuum pump and a manometer were attached.

PROCEDURE AND RESULTS

The experimental procedure used in this study was essentially the same as that used in the study of *sec*-butyl alcohol, benzene, and water (*4*), and similar to techniques used in studies of other butyl alcohols with benzene and water (*1*, *9*, *11*), and in the azeotropic study of the system containing ethyl alcohol, benzene, and water (*2*).

Ternary System. The solubilities were determined by titrating weighed solutions of toluene and *sec*-butyl alcohol to the permanent appearance of a second phase. They were considered to have reached equilibrium when the second phase persisted after 1 hour of shaking in the constant temperature bath. The third component was added through a hypodermic syringe which could deliver drops of about 4 mg.

The evaporation loss from the flasks was about 20 mg. during the titrations. This amounted to 0.1 to 0.2% of the total solution.

The solubility of toluene in the water-rich solutions was too small to be measured accurately. In the determination of the refractive indices of solutions containing more than 84.6% water, the smallest drop of toluene that could be handled was added. Washburn and Spencer (*10*) stated in their study of the methanol-cyclohexane-water system that a small excess of the immiscible liquid did not appreciably affect the refractive index of the solution. Toluene was used to titrate the water-alcohol mixtures, and water was the titrant for the other solutions.

A preliminary study with materials of the same purity was conducted but not with the same accuracy. This study made the final titrations much easier and faster, because the necessary concentrations could be closely approximated at the start of the titrations, and any prolonged dropwise additions could thereby be avoided. The end points were

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viewed by diffused light through a magnifying glass and consisted of either toluene or water suspended as a fine mist in the solution.

Literature values were employed for the solubilities of toluene in water (*7*), water in toluene (*3*), *sec*-butyl alcohol in water, and water in *sec*-butyl alcohol (*6*). The solubility data are recorded in Table II and plotted in Figure 1.

To determine the tie lines, solutions with known over-all compositions of the three components were prepared and shaken in a constant-temperature bath for 6 hours. The solutions were made up to have two layers of approximately equal volume. The refractive indices were taken and the compositions of the two layers were then determined from the plot of composition *vs.* refractive index. These curves were plotted on 10 × 10 to the one-half inch graph paper, where each line on the ordinate represented 0.1% by weight, and each line of the abscissa represented 0.0001 unit of refractive index. The sum of the three percentages for any one liquid was 100.0 ± 0.1. Concentrations of the conjugate solutions are plotted in Figure 1 and recorded in Table III.

The Azeotropic System. Since a preliminary study had shown that the composition of the ternary was about 15% water, 60% toluene, and 25% *sec*-butyl alcohol, a mixture of this composition was charged to the fractionating column. After heat had been applied and the manometer correctly adjusted to a predetermined pressure, the mixture was allowed to reflux for 1 hour, and then successive cuts were taken until a constant composition was obtained. A 25-ml. sample was then collected and used in the determination of the composition. This sample was transferred directly into a weighted 50-ml. flask and shaken for 6 hours in the constant temperature bath.

After the solutions reached equilibrium, the total weight was determined and the two layers were separated using a pipet with a capillary tip. The water-rich layer was drawn off, and then the hydrocarbon-rich layer was weighed, and the weight of the water layer calculated by difference. The refractive indices of the two layers were determined, and using data previously obtained, the total composition of each layer of the azeotrope was determined. The data so obtained are recorded in Table IV.

Table II. Ternary Solubility Data at 25.0° C. for sec-Butyl Alcohol–Toluene–Water System

sec-Butyl Alcohol, Wt. %	Toluene, Wt. %	Refractive Index
5.07	94.69	1.4864
10.75	88.58	1.4799
17.14	81.89	1.4720
30.32	67.34	1.4565
35.29	61.53	1.4500
39.85	56.16	1.4456
47.42	47.09	1.4356
55.88	36.14	1.4238
57.05	34.39	1.4224
62.60	26.50	1.4141
66.18	20.44	1.4076
67.84	17.40	1.4045
70.68	9.40	1.3950
71.04	6.67	1.3918
70.97	6.11	1.3908
70.61	4.34	1.3883
67.10	0.90	1.3820
15.41	0.0	1.3465
10.44	0.0	1.3416
6.96	0.0	1.3379
2.51	0.0	1.3332

Alcohol saturated with water	35.5% water	(*6*)[a]
Water saturated with alcohol	18.6% alcohol	(*6*)[a]
Toluene saturated with water	0.053% water	(*3*)[a]
Water saturated with toluene	0.054% toluene	(*7*)

[a] Interpolated.

Table III. Conjugate Solutions at 25.0° C. for sec-Butyl Alcohol–Toluene–Water System

Water Layer			Toluene Layer		
Refractive index	*sec*-Butyl alcohol, wt. %	Water, wt. %	Refractive index	*sec*-Butyl alcohol, wt. %	Toluene, wt. %
1.3374	6.50	93.50	1.4842	7.00	92.70
1.3408	9.70	90.32	1.4565	30.35	67.29
1.3426	11.41	88.58	1.4242	55.70	36.45
1.3435	12.35	87.65	1.4126	63.36	25.20
1.3457	14.57	85.44	1.3935	70.95	8.15

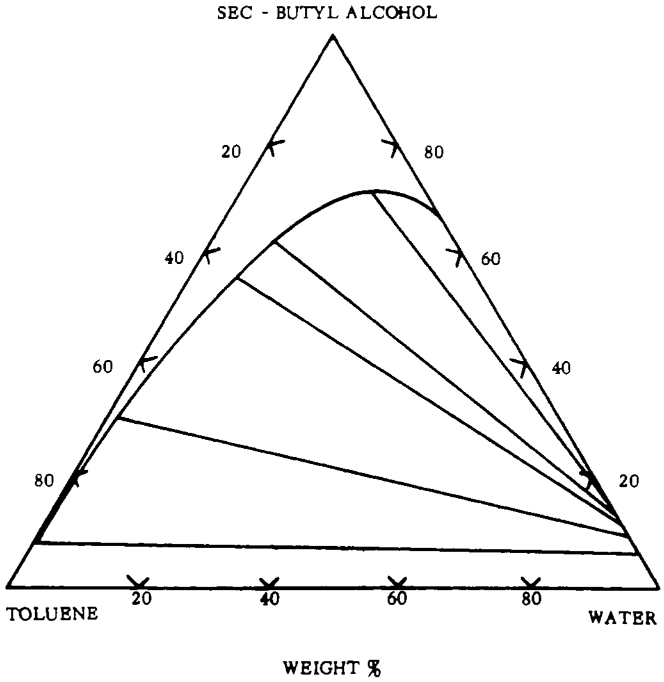

Figure 1. System sec-butyl alcohol–toluene–water at 25° C.

Table IV. Composition Weight Per Cent and Boiling Point of Azeotrope at Various Pressures

Pressure, Mm. Hg	Ternary			Water Layer			Toluene Layer			Boiling Point, ° C.
	Water	Toluene	Alcohol	Water	Toluene	Alcohol	Water	Toluene	Alcohol	
200	14.4	63.8	21.8	91.5	0.0	8.6	1.6	74.4	24.0	50.0
300	14.9	61.5	23.6	91.2	0.0	8.8	1.8	72.1	26.1	58.9
400	15.4	59.7	24.8	91.2	0.0	8.8	1.9	70.3	27.7	65.5
500	16.0	58.2	25.8	91.1	0.0	9.0	2.1	68.9	28.9	70.9
662	16.5	56.4	27.1	91.0	0.0	9.0	2.4	67.1	30.5	78.0

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Pressure-Volume-Temperature Behavior of Difluoromethane

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The pressure-volume-temperature properties of difluoromethane are correlated using the Martin-Hou equation of state to within ±0.94% standard deviation over the experimental ranges: 25° to 200° C., 8 to 200 atm., and 47 to 1.8 cc. per gram. Vapor pressures have been determined from −83° to +78.4° C., the measured critical temperature. Using liquid densities measured between −25° and +78° C. and densities of saturated vapor computed from the Martin-Hou equation of this work, a rectilinear diameter line has been developed. The critical pressure is 57.54 atm., and the critical density is 0.430 grams per cc.

IN A cooperative program between the Bellevue Laboratory for High Pressure and the Industrial Chemicals Research Laboratory, Morristown, the physical properties of difluoromethane have been studied. These include the equation of state, vapor pressure, liquid density, and critical constants.

This compound has uses as a refrigerant (Refrigerant 32) and also as a component in refrigerant mixtures such as Refrigerant 504, which is an azeotrope of difluoromethane and pentafluorochloroethane. No experimental data on either vapor pressures, or *PVT* properties are available in the literature except the boiling point (*1*).

MATERIAL PURITY

The samples of CH_2F_2 (Genetron 32), were obtained from the Industrial Chemicals Division of Allied Chemical Corp. For the earlier samples, purification was made by a preparative scale gas chromatograph. The more recent samples were purified by distillation through a 50 x 1/2 inch vacuum jacketed column packed with nickel Helipaks. The entire sample was degassed several times by freezing the sample with liquid nitrogen and pumping off noncondensables (*4*). The purity was determined by gas chromatography to be 99.95 mole % or better for all samples used.

VAPOR PRESSURE MEASUREMENTS

Experimental Methods. Below room temperature where sample condensation was not a problem, and at pressures near or below atmospheric, the usual static manometric techniques served to measure the vapor pressure of the liquid. Here a manometer connects directly to an equilibrium cell located in a cryostat. The cryostat used at Bellevue consisted of a thermostatically controlled copper block. Its temperature was controlled to ±0.005° C. for periods up to 10 minutes by circulating chilled methanol through the block. A platinum resistance thermometer, calibrated by the U.S. National Bureau of Standards (degrees Centigrade. Int. 1948) (*6*) and monitored by a Type M-3 Mueller Bridge determined the temperature. For pressure observations, a cathetometer determined the mercury column height in the manometer to ±0.2 mm. At higher temperatures, the Bellevue *PVT* equipment, method I of