Part I

PHASE EQUILIBRIA

MOLECULAR TRANSPORT

THERMODYNAMICS

Secondary Butyl Alcohol–Benzene–Water Ternary System at 30° C. and Composition of the Ternary Azeotrope at Various Pressures

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MOST OF THE ternary systems containing benzene, water, and the lower alcohols have been investigated (*1, 6*). This report adds to these studies the results of an investigation of the system containing *sec*-butyl alcohol, benzene, and water.

MATERIALS AND APPARATUS

Secondary butyl alcohol, obtained from Matheson Co., Inc., was dried over metallic sodium for approximately 24 hours and then slowly fractionally distilled. The fraction used in this study had a refractive index at 20° C. of 1.3974 and a density at 20° C. of 0.8050.

Deionized water was distilled from an alkaline permanganate solution. The sample used had a refractive index at 20° C. of 1.3343 and a density at 20° C. of 0.9979.

The benzene used was treated in the same fashion as the *sec*-butyl alcohol and had a refractive index at 20° C. of 1.5001 and a density at 20° C. of 0.8785.

All of these values agree reasonably well with those reported in the literature.

The solubilities and tie lines were measured in 25-ml, glass-stoppered, volumetric flasks which were mounted in an air-driven shaker and immersed in a constant temperature bath. During the solubility measurements and the azeotropic study, the temperature of the bath did not vary from 30° C. by more than ±0.05° C. The temperature of the bath was controlled to ±0.02° C. throughout the study for the determination of the composition of the tie lines.

An Abbe 3L refractometer, which was kept at the desired temperature by the circulation of water from the constant temperature bath, was used to obtain the refractive indices.

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 ⅛-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.

Calibrated weights and thermometers were employed and

Table I. *Ternary Solubility Data at 30.0° C.*

sec-Butyl Alcohol, Wt. %	Benzene, Wt. %	Refractive Index	*sec*-Butyl Alcohol, Wt. %	Benzene, Wt. %	Refractive Index
3.11	96.78	1.4898	62.85	27.94	1.4130
5.80	94.03	1.4865	69.92	16.91	1.4014
9.91	89.66	1.4802	71.87	6.16	1.3900
19.61	79.35	1.4685	11.80	0.06	1.3438
29.64	69.12	1.4558	7.83	0.06	1.3396
38.87	58.41	1.4447	4.07	0.07	1.3360
47.60	47.52	1.4331	1.86	0.12	1.3336
56.65	36.02	1.4209			
Alcohol saturated with water			66.50% alcohol		1.3807
Water saturated with alcohol			84.77% water		1.3457
Benzene saturated with water			99.92% benzene(*4*)		1.4937[a]
Water saturated with benzene			99.85% water(*4*)		1.3318[a]

[a] Interpolated.

Table II. Conjugate Solutions at 30.0° C.

Water Layer			Benzene Layer		
Refractive index	*sec*-butyl alcohol, wt. %	Water, wt. %	Refractive index	*sec*-Butyl alcohol, wt. %	Benzene, wt. %
1.3339	2.18	97.74	1.4920	1.54	98.35
1.3372	5.30	94.62	1.4816	8.81	90.79
1.3388	6.90	93.04	1.4688	19.40	79.61
1.3397	7.81	92.13	1.4566	28.98	69.70
1.3404	8.49	91.47	1.4460	37.76	59.70
1.3417	9.78	90.17	1.4322	48.27	46.69
1.3419	9.99	89.96	1.4216	56.17	36.68
1.3422	10.28	89.68	1.4124	62.71	27.41
1.3435	11.54	88.41	1.4011	70.03	16.55
1.3455	13.47	86.50	1.3895	71.82	5.69

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

Pressure, Mm. Hg.	Ternary			Water Layer			Benzene Layer			Boiling Point, ° C.
	Water	Benzene	Alcohol	Water	Alcohol	Benzene	Water	Alcohol	Benzene	
200	7	88	5	96.2	3.7	0.1	0.2	5.1	94.7	38.2
300	7	87	6	95.9	4.0	0.1	0.2	5.8	94.1	47.0
400	7	87	6	95.8	4.2	0.1	0.2	6.1	93.7	53.8
500	7	87	6	95.8	4.2	0.1	0.2	6.7	93.1	59.0
665	8	86	6	95.4	4.6	0.1	0.2	6.7	93.1	65.5

experimental precautions were taken to ensure that the visual recognition of the end point in the solubility titrations would be the limiting factor in the accuracy of the measurements.

PROCEDURE AND RESULTS

The experimental procedure used in this study was essentially the same as that employed in the studies of the other butyl alcohols (*1, 5, 6*), and in the azeotropic study of the system containing ethyl alcohol, benzene, and water (*2*).

Ternary System. The solubilities were determined by titration of weighed solutions to the appearance of a permanent second phase. The third component was added by hypodermic syringe. The magnitude of the drops that could be administered in this manner ranged from 2 to 3 mg., depending upon the titrant. A study of the evaporation losses from the titration flasks was conducted, and when the loss was more than 17 mg. (at most 0.20%), the titration was repeated. Benzene was the titrant for the ternary solutions containing less than 1% benzene, and water was the titrant in all other ternary 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 viewed by diffused light through a magnifying glass and consisted of either benzene or water suspended as a fine mist in the solution.

Refractive indices were measured immediately following the final weighing of the solutions.

The solubilities of benzene in water and of water in benzene as recorded in the literature (*4*) were employed. New determinations were made, however, of the solubilities of water in *sec*-butyl alcohol and of *sec*-butyl alcohol in water. The method used was the same as that for the determinations of the ternary solutions. These solubilities were reproducible. They are recorded in Table I and plotted in Figure 1.

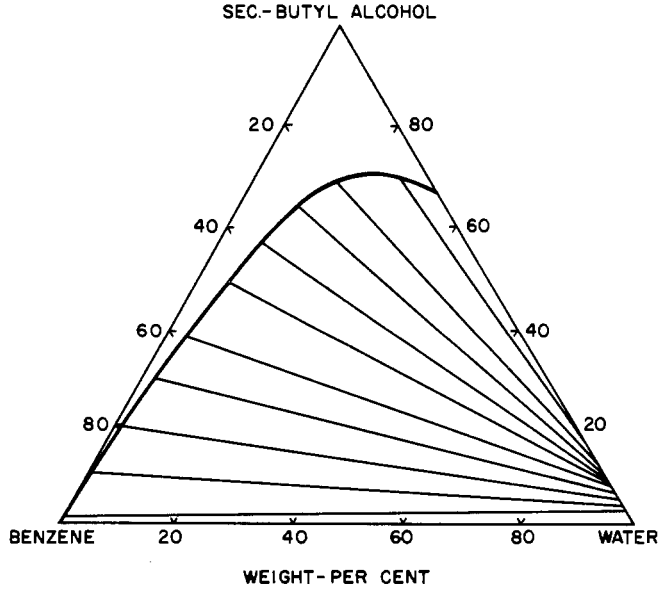

Figure 1. The system sec-butyl alcohol–benzene–water at 30° C.

The tie lines were determined by adding alcohol in varying amounts to mixtures of benzene and water. The refractive indices of the conjugate layers were determined after equilibrium at the desired temperature was reached. The concentration of each of the three components in each of the two layers was then read from curves plotted from data obtained in the solubility study. These curves were plotted on 10 by 10 to the half-inch graph paper where each line on the ordinate represented 0.1% by weight and each line on the abscissa represented 0.0001 unit in 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 II.

The Azeotropic System. The pot of the column was charged with a mixture containing 8.63% water, 5.82% *sec*-butyl alcohol, and 85.55% benzene. This is the reported composition of the ternary azeotrope at 760 mm. of mercury from unpublished Dow Chemical Co. data (*3*). After heat had been applied and the manometer correctly adjusted to the predetermined pressure, the mixture was allowed to reflux until successive cuts were found to have the same composition. A cut of 25 ml. was then collected to be used in the determination of the composition. This cut was transferred directly into a weighed 50-ml. flask.

The ternary azeotropic mixtures were placed in the water bath and shaken at 30.0° C. for 4 hours to allow equilibrium to be reached. Then, they were reweighed to determine possible losses due to evaporation. The two layers were then separated by a separatory funnel whose outlet had been pulled to a very fine capillary tube. The water-rich layer, approximately 7% of the total in each case, was drawn off and weighed, thereby yielding the weights of the individual layers. The refractive indices of the two layers were taken, and from the graph obtained in the solubility studies, the composition of the individual layers was obtained. The respective weights and compositions of the upper and lower phases of the distillate (Table III) yielded the over-all compositions of the heterogeneous solutions.

Since small droplets of the water phase stuck to the sides of the separatory funnel and could not be drawn out to be weighed, the values obtained range in accuracy from 0.06 to 0.1%. More accurate measurements, in all cases, would increase the relative amount of the water-rich phase.

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