C–H distance, 1.09Å.; C–C–H angle, 109°28′; and the Cl–C–C angle 110°. The symmetry number for the rigid molecule was taken as three.

The following natural constants, given by Birge,[11] were used in the calculations: 0°C. = 273.16°K., R = 1.9870 cal./deg./mole, r, the Boltzmann constant, = 1.3805×10^{-16} erg/deg., $N = 6.023 \times 10^{23}$ and $h = 6.624 \times 10^{-27}$ erg sec.

The difference between the calorimetric entropy value and the one calculated using molecular constants is 1.25 calories per mole, and this corresponds to a barrier of 2700 calories per mole. This value was calculated using the tables of Pitzer and Gwinn.[12] The reduced moment of inertia of the methyl group of the molecule was taken to be 5.26×10^{-40} c. g. s. units.

(11) R. T. Birge, *Rev. Modern Phys.*, **13**, 233 (1941).

(12) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

We wish to thank Professor Alexander Goetz for supplying us with liquid hydrogen.

Summary

The heat capacity of 1,1,1-trichloroethane has been measured from 14°K. to room temperature. There is a transition point in the solid at 224.20°K. The heat of transition is 1786 ± 2 cal./mole. An approximate value for the melting point is 240.2 ± 0.5°K., and a rough value for the heat of fusion is 450 ± 300 cal./mole. The heat of vaporization is 7962 ± 12 cal./mole at 286.53°K. The entropy of the ideal gas at 286.53°K. and 1 atm. is 76.22 ± 0.16 cal./deg./mole, and 76.97 ± 0.16 cal./deg./mole at 298.16°K. and 1 atm. The entropy of the liquid at 298.16°K. is 54.37 ± 0.11 cal./deg./mole. A comparison of the statistical and calorimetric values of the entropy indicates a barrier of 2700 ± 350 cal./mole.

ITHACA, N. Y. RECEIVED JULY 21, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Ternary System: Dioxane–Benzene–Water

BY ROBERT J. BERNDT AND CECIL C. LYNCH

Several ternary liquid systems have been examined by Hand[1] for dineric distribution between conjugate phases. Bancroft and Hubbard[2] have recently presented a new method of determining dineric distribution in such systems and have examined two ternary systems in some detail.

The object of this work has been to study the ternary liquid system dioxane–benzene–water, in which the dioxane is the consulate liquid, for dineric distribution between the conjugate phases at 25°. Because of the extensive region of immiscibility in the system, we have employed both the method of Bancroft and an analytical method for determining the composition of conjugate phases.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Co. was purified by the method described by Eigenberger.[3] The product was kept over metallic sodium, from which it was distilled when needed; density d^{25}_4 1.0276, n^{25}_D 1.4197.

Benzene.—Thiophene-free benzene was dried with calcium oxide, from which it was fractionally distilled. It was kept in bottles protected from moisture with suitable drying tubes.

Freshly boiled redistilled water was used also in all mixtures.

Experimental Method

Mixtures were prepared in glass-stoppered flasks by direct weighing and were allowed to reach equilibrium in a water thermostat (25 ± 0.05°). The conjugate phases were sampled with pipets; for the lower layer, the tips of the pipets used were drawn off and sealed. These tips were broken off under the lower layer for sampling to avoid any contamination with the upper layer. Densities of all solutions were determined with 25-cc. or 10-cc. pycnometers to a precision of ± 0.0001 unit. All refractive indicex measurements were made with an Abbe refractometer to a precision ± 0.0002 unit.

The Binodal Curve.—The binodal curve for the 25° isotherm was determined by titration of binary mixtures of benzene and dioxane with water and of mixtures of dioxane and water with benzene to the first indication of immiscibility. In the overlapping portions from the two sets of titrations, these data were found to agree within ±0.2%. The data for the binodal curve are given in Table I, and the plot in Fig. 1.

TABLE I

DATA FOR THE BINODAL CURVE OF THE SYSTEM: DIOXANE–BENZENE–WATER AT 25°

% Dioxane	% Water	% Benzene	% Dioxane	% Water	% Benzene
10.24	89.66	0.10	9.97	0.14	89.89
20.38	79.49	.13	19.89	.26	79.85
30.10	69.73	.17	30.53	.58	68.89
39.76	59.98	.26	40.80	.84	58.36
50.21	49.10	.69	50.11	1.34	48.55
58.39	39.90	1.71	58.81	2.09	39.10
64.53	32.08	3.39	63.43	2.70	33.87
67.58	27.69	4.73	67.79	3.73	28.48
70.21	23.05	6.74	69.69	4.34	25.97
72.50	18.24	9.26	71.66	5.09	23.25
71.51	20.33	8.16	73.23	6.06	20.71
73.60	15.44	10.96	74.21	7.43	18.36
74.45	13.31	12.24	74.59	12.43	12.98
74.86	8.33	16.81	73.37	15.78	10.85
72.92	5.71	21.37			
75.01	10.24	14.75			

(1) Hand, *J. Phys. Chem.*, **34**, 1961 (1930).

(2) Bancroft and Hubbard, THIS JOURNAL, **64**, 347 (1942).

(3) Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

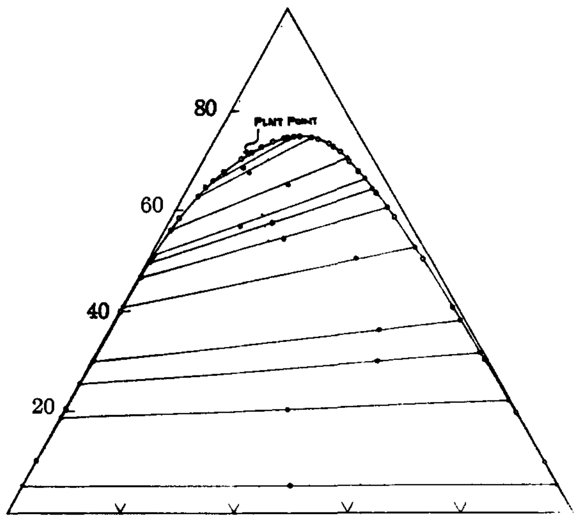

Fig. 1.—25° isotherm for the system: dioxane-benzene-water.

Analysis Data for the System.—Refractive indices and density data have been used for analytical purposes in the system. It was first necessary to consider refractive indices and densities for the binary systems. Hovorka, Shaefer and Dreisbach[4] have determined these data for the dioxane-water system, and Lynch[5] has extended the data on refractive index to lower concentrations for this system. Recently Teague and Felsing[6] have presented refractive index and density data for the dioxane-benzene system for a limited number of points. Accordingly, we have measured the refractive index and density of a number of benzene-dioxane mixtures. These data are included in Table II. All solutions were prepared by direct weighing in glass-stoppered flasks, and all measurements were made at 25°.

TABLE II

DENSITIES AND REFRACTIVE INDICES FOR THE BINARY SYSTEM DIOXANE-BENZENE AT 25°

% Dioxane	Density d^{25}_4	Refractive index, n^{25}_D
0.00	0.8730	1.4978
10.83	.8877	1.4900
19.81	.9004	1.4837
29.83	.9147	1.4762
39.49	.9290	1.4685
50.19	.9452	1.4602
60.44	.9612	1.4530
69.19	.9752	1.4456
79.90	.9930	1.4370
84.20	1.0003	1.4324
90.92	1.0120	1.4270
100.00	1.0278	1.4197

(4) Hovorka, Schaefer and Dreisbach, THIS JOURNAL, **58**, 2264 (1936).

(5) Lynch, *J. Phys. Chem.*, **46**, 366 (1942).

(6) Teague and Felsing, THIS JOURNAL, **65**, 485 (1943).

For the ternary system all mixtures were prepared by direct weighing in glass-stoppered flasks, care being taken to keep in the miscible region, yet to cover the whole miscible area. The refractive index and density data at 25° for the ternary mixtures are given in Table III. From these

TABLE III

ANALYSIS DATA FOR THE SYSTEM DIOXANE-BENZENE-WATER AT 25°

% Dioxane	% Benzene	% Water	Density d^{25}_4	Refract. index n^{25}_D
29.73	69.92	0.35	0.9151	1.4760
39.21	60.07	.73	.9297	1.4690
49.81	49.92	.77	.9458	1.4597
59.79	39.12	1.09	.9621	1.4511
68.37	30.45	1.18	.9761	1.4440
81.91	15.37	2.72	1.0019	1.4308
79.49	14.92	5.59	1.0041	1.4282
86.96	8.68	4.36	1.0145	1.4241
83.40	8.32	8.28	1.0168	1.4214
79.77	7.96	12.27	1.0189	1.4175
76.64	7.65	15.71	1.0204	1.4146
63.94	1.89	34.17	1.0332	1.3952
74.03	2.24	23.73	1.0320	1.4049
72.40	4.39	23.21	1.0277	1.4067
77.36	19.46	3.18	0.9953	1.4338
75.36	18.96	5.68	0.9972	1.4310
83.08	2.79	14.13	1.0289	1.4124
80.83	5.43	13.74	1.0239	1.4149
77.89	8.87	13.24	1.0174	1.4171
89.10	4.82	6.08	1.0220	1.4200
84.87	9.34	5.79	1.0138	1.4237
80.89	13.59	5.52	1.0064	1.4273
77.10	17.64	5.26	0.9993	1.4314
73.67	21.31	5.02	0.9928	1.4343

data the compositions of common refractive index and of common density were determined, and Fig. 2 shows the analysis diagram constructed therefrom.

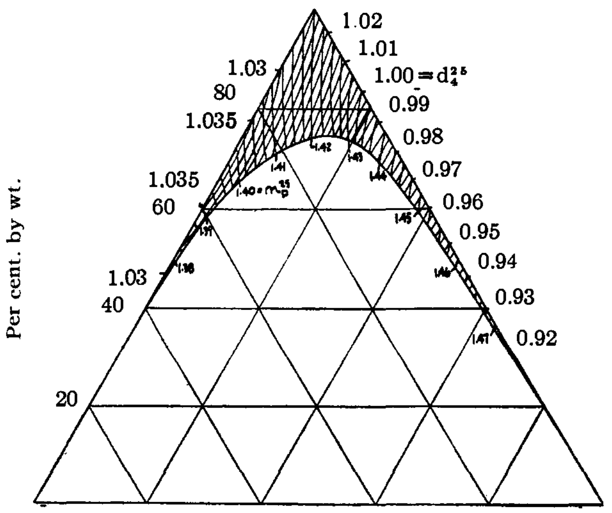

Fig. 2.—Analysis diagram for the system: dioxane-benzene-water at 25°.

TABLE IV

DINERIC DISTRIBUTION IN THE DIOXANE-BENZENE-WATER SYSTEM AT 25°

Samples 7, 8, 9, 10 were analyzed by the titration method of Bancroft and Hubbard; all others were analyzed by means of the analysis diagram.

Sample number	Original mixture % Dioxane	% Benzene	% Water	Upper layer % Dioxane	% Benzene	% Water	Lower layer % Dioxane	% Benzene	% Water	Log K
1	5.13	47.69	47.18	5.2	94.7	0.1	5.1	0.1	94.8	0.415
2	20.47	39.52	40.01	22.5	77.3	0.2	18.9	.1	81.0	0.298
3	30.16	50.88	18.96	32.0	67.4	0.6	25.2	.1	74.7	0.299
4	36.16	47.93	15.91	38.5	60.8	0.7	29.8	.2	70.0	0.291
5	35.05	39.93	25.02	37.5	61.8	0.7	29.5	.2	70.3	0.281
6	50.53	37.06	12.41	53.0	45.5	1.5	40.8	.3	58.9	0.277
7	57.11	18.82	24.07	64.4	32.8	2.8	49.8	.7	49.5	0.290
8	55.23	14.39	30.37	66.5	30.1	3.4	50.8	.8	48.4	0.316
9	67.64	9.47	22.89	74.9	16.6	8.5	62.8	2.7	34.5	0.311
10	68.60	8.44	22.96	74.5	13.7	11.8	66.3	4.0	29.7	0.275
11	54.25	22.64	23.11	60.5	37.2	2.3	46.7	0.6	52.7	0.281
12	64.71	18.02	17.27	70.0	25.5	4.5	56.1	1.5	42.4	0.278

$\log K = \log (a_1/b_1) - 1.32 \log (a_2/w_2)$ Average value $\log K = 0.290$

Dineric Distribution for the System.—For determining the compositions of the conjugate phases, two methods were resorted to: (1) the titration method, which was given in detail by Bancroft and Hubbard[2] and (2) the use of the analysis diagram.

The distribution data for the system are given in Table IV, and the tie lines are plotted in Fig. 1.

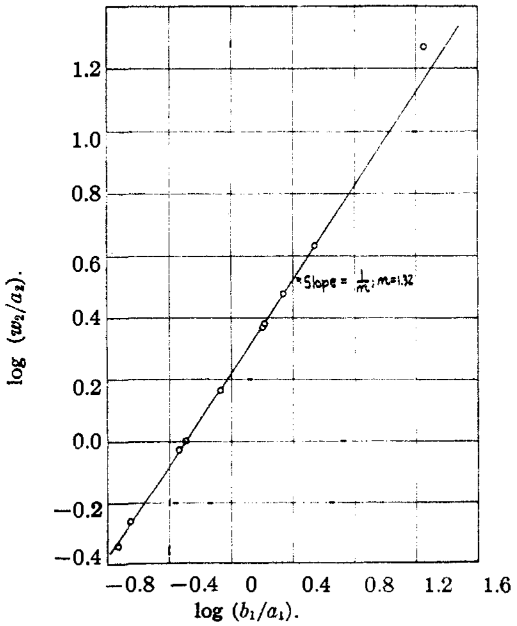

Fig. 3.—Logarithmic plot of the isotherm.

The equation ($\log a_1/b_1 - n \log a_2/w_2 = \log K$) has been shown by Bancroft[2] to satisfy the equilibrium distribution data for such a system. The value of n should be determined simply from the slope of the curve (straight line) in plotting ($\log b_1/a_1$) against ($\log w_2/a_2$), where a_1 and b_1 represent the percentage of dioxane and benzene, respectively, in the benzene-rich layer and a_2 and w_2, the percentage dioxane and water, respectively, in the water-rich layer. Such a plot of the above data is shown in Fig. 3, and the value of n obtained, 1.32. From the above relation employing this value of the slope, the distribution constants in Table IV were obtained. Except for the first value in the $\log K$ column, satisfactory distribution constants resulted. This first value is off, probably due to limitations in attaining equilibrium and in analysis. The plait point estimated from these data corresponds to 71% dioxane, 7.5% benzene, 21.7% water.

Summary

1. The 25° isotherm of the dioxane–benzene–water system has been presented.

2. Refractive index and density data at 25° for the dioxane–benzene and the ternary system dioxane–benzene–water has been given, as well as an analysis diagram for the miscible region of the ternary system.

3. Dineric distribution in the ternary system has been shown to satisfy the relation employed by Bancroft and Hubbard for several ternary liquid systems.

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