

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

Some Properties of the Dioxane-Ethanol System

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In recent years considerable attention has been given to the solvent dioxane, and the dioxane-water system.^{1,2} It was believed that a study of the dioxane-ethanol system also should prove interesting. Accordingly some of the properties—densities, refractive indices, viscosities, and boiling points—of the dioxane-ethanol system have been determined.

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.

Ethanol.—Commercial absolute ethanol was refluxed for twenty-four hours over lime and barium oxide, and distilled from the mixture. The product was treated with metallic sodium to remove remaining water and the re-distilled product was used. This alcohol had a density at 25° of 0.7852.

Density Measurements.—All solutions were prepared by direct weighing in glass-stoppered flasks, and measurements were made on the freshly prepared mixtures. Two pycnometers of approximately 50 cc. each were employed. The pycnometers with solutions were allowed to reach equilibrium (requiring twenty to thirty minutes) at 25.00 ± 0.05° in a water thermostat. Each value is the result of four independent measurements; the precision ± 0.02%. Data are given in Table I.

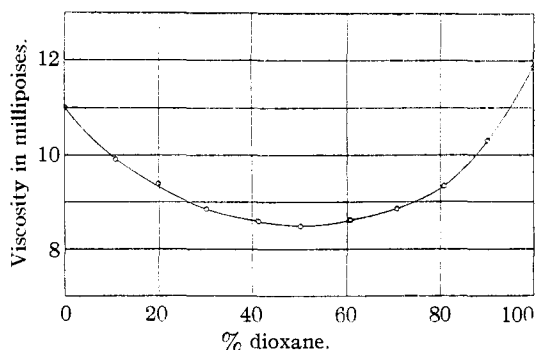


Fig. 1.—Viscosities for the dioxane-ethanol system at 25°.

Refractive Indices.—Solutions used were those prepared for the density measurements. An Abbe refractometer accurate to ± 0.0002 unit of refractive index was employed using sodium light as a source of illumination. Each value is the mean of four measurements. Data are included in Table I.

Viscosity Measurements.—The solutions used were those prepared under density measurements. The Ostwald modification of the Poiseuille viscosimeter was used, care being taken to introduce the same volume (7 cc.) of liquid for each measurement. Timing was accurate to ± 0.2 second. Each value given is the mean of at least five measurements. Data are given in Table I and in Fig. 1.

TABLE I
DENSITIES, REFRACTIVE INDICES, AND VISCOSITIES FOR THE DIOXANE-ETHANOL SYSTEM AT 25.00 ± 0.05°

% dioxane	Mole fraction dioxane	Refractive index, n_D	Density, d_4^{25}	Viscosity, millipoises
0.00	0.0000	1.3597	0.7852	11.00
5.54	.0298	1.3619	.7960	
10.84	.0584	1.3648	.8067	9.92
15.78	.0893	1.3671	.8166	
20.00	.1156	1.3694	.8252	9.38
25.27	.1503	1.3718	.8361	
30.05	.1834	1.3745	.8463	8.84
35.68	.2250	1.3774	.8584	
41.13	.2678	1.3810	.8706	8.60
45.66	.3052	1.3830	.8808	
50.04	.3438	1.3859	.8912	8.49
54.02	.3809	1.3884	.9008	
60.74	.4473	1.3926	.9172	8.63
70.77	.5589	1.3991	.9429	8.85
80.82	.6890	1.4058	.9700	9.33
90.11	.8264	1.4125	.9966	10.29
95.02	.9088	1.4159	1.0116	
100.00	1.0000	1.4201	1.0276	11.84

A minimum viscosity was observed in the neighborhood of 50% dioxane.

Boiling Points.—Measurements were made using the Othmer apparatus.⁴ Mixtures of approximate composi-

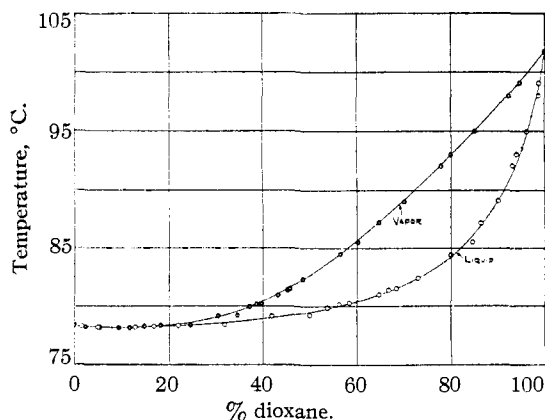


Fig. 2.—Boiling point-composition diagram for the dioxane-ethanol system at 760 mm. pressure.

(1) Åkerlöf and Short, *THIS JOURNAL*, **58**, 1241 (1936).

(2) Hovorka, Schaefer and Dreisbach, *ibid.*, **58**, 2263 (1936).

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

(4) Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928).

tion were introduced into the apparatus and runs were made until equilibrium had been established between liquid and vapor phases. This required three to four hours for each run. Temperatures were measured with a thermometer (0–110°) with 0.1° divisions, which was checked frequently for accuracy, the precision $\pm 0.03^\circ$. Pressure correction to one atmosphere and stem corrections were made for all readings. The equilibrium residue and distillate were analyzed through refractive index. Data are given in Table II, and Fig. 2 shows the boiling point–composition diagram for the system.

TABLE II

BOILING POINT–COMPOSITION DATA FOR THE DIOXANE–ETHANOL SYSTEM AT ONE ATMOSPHERE

B. p., °C.	% dioxane	
	Liquid	Vapor
78.32		Ethanol
78.22	1.5	2.2
78.19	5.0	5.3
78.13 (min.)	9.3	9.3
78.17	13.0	11.7
78.23	16.8	14.8
78.35	22.0	18.3
78.36	32.0	24.7
79.10	42.0	30.5
79.87	54.0	37.3
80.15	56.5	38.7
80.18	58.5	39.7
80.93	64.7	43.3

81.32	66.7	45.1
81.40	68.5	45.5
82.33	73.0	48.4
84.42	79.9	56.5
85.43	84.8	60.3
87.17	86.4	64.9
89.08	90.2	70.5
92.02	93.3	78.0
93.00	94.0	80.0
94.89	96.3	85.0
97.99	98.7	92.5
99.05	98.8	94.8
101.07		Dioxane

A minimum boiling point of 78.13° was observed for the composition 9.3% dioxane.

Summary

1. Density, refractive index and viscosity data for the dioxane–ethanol system have been presented. The viscosity curve apparently passes through a minimum in the vicinity of 50% dioxane.

2. Boiling points and the boiling point–composition diagram for the dioxane–ethanol system have been determined. A minimum boiling temperature of 78.13° was observed at 9.3% dioxane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of 1,4-Dimethyl-6,7-dihydroxyphenanthrene from *para*-Xylylacetic Acid and 6-Nitroveratraldehyde by the Pschorr Reaction

BY JACK TARKINGTON CASSADAY¹ AND MARSTON TAYLOR BOGERT

Eddy² has reported that phenanthrene derivatives carrying a hydroxyl group on carbon no. 3 (no. 6 in our formula) are likely to possess analgesic properties in higher degree than when this group is in other positions on the phenanthrene nucleus.

Small, Eddy, Mosettig and Himmelsbach³ state that: "No generalizations can be made as to the influence on pharmacological action of the entrance of another substituent in a given monosubstituted phenanthrene. The changes in pharmacological action are very likely dependent to some extent upon changes in chemical or physical properties, among others, differences in acidity or basicity, and in solubility. There was a de-

cidated increase in effectiveness from 3-hydroxyphenanthrene to 3,4-dihydroxyphenanthrene, but at the same time also, from 3-hydroxyphenanthrene to 3-hydroxy-4-aminophenanthrene."

So far as our examination of the literature has gone, the hydroxyphenanthrenes reported to date are all insoluble in water, and but few of them are appreciably soluble in cold olive oil.

We have therefore synthesized the 1,4-dimethyl-6,7-dihydroxyphenanthrene (V), in order that its physical, chemical, and pharmacological properties can be studied. It is a white crystalline solid, m. p. 164–164.5° (corr.), appreciably soluble in water, and dissolving in cold olive oil.

In a previous communication⁴ from these Laboratories, we reported some unsuccessful attempts to obtain this compound by the hydrolysis of the 1,4-dimethyl-6,7-methylenedioxyphenan-

(1) Ferguson Fellow, Columbia University, 1938–1939.

(2) Eddy, *J. Pharmacol.*, **48**, 183 (1933); **51**, 75 (1934).(3) Small, Eddy, Mosettig and Himmelsbach, "Studies on Drug Addiction," *U. S. Pub. Health Repts., Suppl.* No. **138**, 143 pp., 1938, p. 71.(4) Akin and Bogert, *THIS JOURNAL*, **59**, 1564 (1937).