butyl peroxides have also been prepared having *t*-butyl alcohol of crystallization.

3. The pyrolysis of *t*-butyl hydroperoxide has been studied at 95–100° and at 250°. At 95–100° *t*-butyl alcohol and oxygen are the only products formed, while at 250° the products formed are acetone, methyl alcohol, *t*-butyl alcohol, formaldehyde and water.

4. The pyrolysis of di-*t*-butyl peroxide has been studied at 200, 250 and 300°. Acetone and ethane are the only products formed.

5. A free radical mechanism has been proposed to explain the pyrolysis of both *t*-butyl hydroperoxide and di-*t*-butyl peroxide.

CAMBRIDGE 39, MASSACHUSETTS

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[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY, PEORIA, ILLINOIS[1]]

Physical Chemical Properties of the 2,3-Butanediols

BY JOHN W. KNOWLTON,[2] N. CYRIL SCHIELTZ AND DUNCAN MACMILLAN

During the course of this Laboratory's work on the production of the 2,3-butanediols, it has been necessary to investigate a number of physical properties of these compounds. These investigations were made concurrently with the experiments on production, and consequently some of the earlier measurements were made on materials which were mixtures of stereo isomers. The most abundant material as it came from the pilot plant had a composition of about 97.5% *levo*- and 2.5% *meso*-2,3-butanediol. Another culture used for the fermentation produced a mixture composed of the *meso* isomer with small amounts of the dextro rotatory form. At an early stage of the work it was found that pure *meso*-2,3-butanediol could be obtained by fractional crystallization from isopropyl ether. Since the naturally occurring mixtures contained only one optically active form in addition to the *meso* isomer, separation by fractional distillation was possible. All three isomers were eventually obtained in pure condition by this method.

In this paper, values for the *meso* and *dextro* isomers are for the pure compounds. Many of the values for the *levo* form are also for the pure substance, and, in any case, the *levo*-2,3-butanediol was at least 97.5% pure, the contaminant being the *meso* isomer.

The data in Table I were obtained on pure stereo isomers.

TABLE I

MISCELLANEOUS PHYSICAL CONSTANTS OF 2,3-BUTANEDIOLS

	dextro	*levo*	*meso*
Density at 25°, g./ml.	0.9872	0.9869	0.9939
Index of refraction, n_D	1.4306 (25°)	1.4308 (25°)	1.4324 (35°)
Surface tension, 25°, dynes/cm.	30.67	30.61	
Viscosity, Hoeppler, centipoises		41.1 (25°) 21.8 (35°)	65.6 (35°)
Rotatory dispersion: λ, Å.			
4358	+25.24°/dcm.	−25.23°	
5481	+15.28	−15.32	
5791	+13.05	−12.95	
5896	+13.19	−13.19	
6234	+11.41	−11.38	
6908	+10.03	−10.03	

The conductivities of the 2,3-butanediols in 0.5 *N* boric acid solution have been reported recently by Lees, Fulmer and Underkofler.[3]

At this Laboratory a similar set of experiments in which 2 *N* boric acid was used gave results in substantial agreement with those of Lees, Fulmer and Underkofler. It was found that in the case of *levo*-2,3-butanediol the conductivity increased markedly with increase in concentration, but that the conductivity of the *meso* form decreased slightly with increased concentration. These results are presented in Table II.

TABLE II

SPECIFIC CONDUCTANCES OF SOLUTIONS OF *levo*- AND *meso*-2,3-BUTANEDIOLS IN 2 *N* BORIC ACID AT 20.0°

levo (Optical rotation = −12.9°/dcm., λ5896)		*meso* (Optical rotation = 0.00°/dcm., λ5896)	
Molar concn.	$\gamma \times 10^6$	Molar concn.	$\gamma \times 10^5$
0.000 (2N H_3BO_3)	7.13		
.506	10.79	0.452	6.50
.253	8.96	.226	6.76
.127	8.10	.113	6.91
.063	7.60		

Several aspects of solutions of 2,3-butanediols in water have been investigated. The freezing point diagrams of solutions of *levo*- and of *meso*-2,3-butanediols are shown in Fig. 1. The optical rotation (λ5896) for the *meso* form was 0.00° per decimeter; that of the *levo* form was −13.0°. It will be noticed that a compound is formed consisting by weight of about 45% *meso*-2,3-butanediol and 55% water. The *levo* isomer does not form a compound with water.

Refractive indices of solutions of *levo*-butanediol (97.8% pure) in water have been determined and are shown in Table III.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

[2] Present address: Bureau of Mines, U. S. Department of Interior, Bartlesville, Oklahoma.

[3] Lees, Fulmer and Underkofler, *Iowa State Coll. J. Sci.*, **18**, 359 1944).

TABLE III

REFRACTIVE INDICES OF SOLUTIONS OF *levo*-2,3-BUTANEDIOL AND WATER

Weight % diol	n^{25}_D	Weight % diol	n^{25}_D
100	1.4309	32.9	1.3727
90.7	1.4257	21.9	1.3521
83.0	1.4206	11.6	1.3462
71.0	1.4121	8.9	1.3430
58.3	1.4010	0.0	1.3324
45.0	1.3865		

The vapor pressures of *meso*- and *levo*-2,3-butanediols were determined at several temperatures, using a Swietoslawski ebulliometer,[4] in which the boiling temperature of the material under investigation was directly compared with the boiling temperature of water in a closed system filled with nitrogen gas, and whose pressure could be set arbitrarily.

The boiling temperatures and the corresponding vapor pressures were calculated from the experimental data. These values were then correlated by the functions

For *levo*-2,3-butanediol, $\log_{10} p = 8.95845 - (2748.1/T)$
For *meso*-2,3-butanediol, $\log_{10} p = 9.14412 - (2852.58/T)$

For the *levo* isomer the maximum deviation from the calculated pressure was 0.62%, and the average deviation was 0.27%. For the *meso* isomer the maximum deviation was 0.68%, and the average deviation was 0.40%.

The boiling temperatures of solutions of *levo*-2,3-butanediol in water were determined in a simple Swietoslawski ebulliometer, and directly compared with the temperature of water boiling under the same pressure. The butanediol used in this investigation had a rotation of −12.9° per decimeter for the sodium D lines, and was 97.8% pure. These data are presented in Table IV.

TABLE IV

BOILING POINT–COMPOSITION DATA FOR *levo*-2,3-BUTANEDIOL–WATER

Weight % diol	Boiling point, °C., at mm. 200	400	600	800
0.0	66.44	82.96	93.51	101.44
2.87	66.65	83.07	93.61	101.53
10.40	66.89	83.38	93.97	101.95
21.59	67.42	83.96	94.52	102.54
39.26	68.42	84.98	95.60	103.55
60.21	70.55	87.02	97.68	105.78
80.44	75.88	92.99	104.30	112.59
90.18	87.72	104.99	116.32	124.88
96.32	106.51	125.51	137.70	147.02
100.00	140.07	159.09	171.37	180.70

Equilibrium liquid–vapor composition measurements were made in a special apparatus, constructed from two simple ebulliometers. With this apparatus it is possible to measure simultaneously the boiling temperature of a solution and that of the vapor in equilibrium with it. The butanediol solutions were made at random, since on reaching equilibrium in the still a given concentration is changed. From the observed equilibrium temperature data, the compositions were deduced from the boiling point–composition data, and the equilibrium vapor curve was plotted. From this, the liquid–vapor concentrations were read off, and are presented in Table V. The butanediol was 97.8% *levo*.

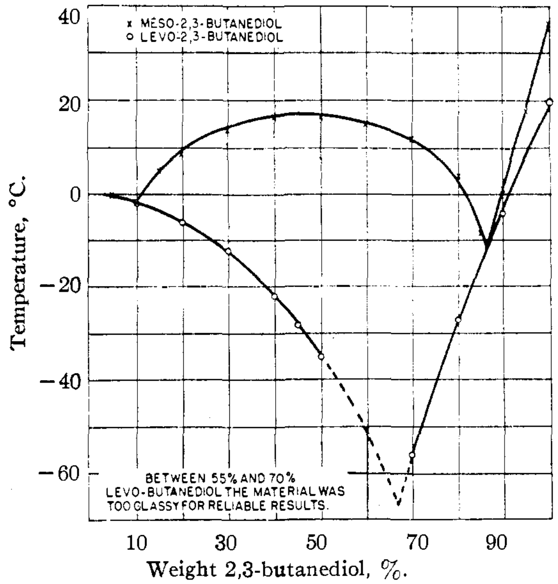

Fig. 1.—Freezing point diagram of aqueous solutions of *levo*- and *meso*-2,3-butanediol.

TABLE V

EQUILIBRIUM LIQUID–VAPOR COMPOSITIONS OF THE SYSTEM *levo*-2,3-BUTANEDIOL–WATER

Weight % diol in liquid	Weight % diol in vapor at mm. 200	400	600	800
99.0	89.6	89.8	89.4	90.9
98.0	80.2	77.2	77.6	77.2
96.0	63.5	58.2	55.3	56.6
94.0	51.2	43.9	42.0	44.0
92.0	37.6	32.7	33.3	34.1
90.0	23.6	23.9	26.4	26.5
85.0	9.1	12.0	14.2	14.6
80.0	5.7	6.9	8.3	8.5
70.0	4.4	4.8	5.8	5.8
60.0	4.2	4.4	5.4	5.6
50.0	3.8	4.4	5.0	5.5
40.0	3.2	4.0	4.6	5.0
30.0	2.5	3.2	3.9	4.4
20.0	1.8	2.4	3.0	3.4
10.0	0.9	1.2	1.8	2.1
5.0	0.4	0.8	0.9	1.1

Summary

1. The diastereoisomeric 2,3-butanediols have been obtained in what is believed to be a high degree of purity.

2. Densities, refractive indices, surface tensions, viscosities, and rotatory dispersions have been obtained for these pure materials.

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[4] W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corporation, New York, N. Y., 1945, p. 6.

3. Conductivities of boric acid solutions of *meso* and *levo* isomers have been measured, and the freezing points, boiling points, and liquid-vapor equilibrium data of aqueous solutions have been obtained.

PEORIA, ILL. RECEIVED OCTOBER 22, 1945

[CONTRIBUTION FROM SUN OIL COMPANY, EXPERIMENTAL DIVISION, NORWOOD, PA.]

Freezing Points and Polymorphism of the Eight C_9H_{12} Alkylbenzenes[1]

BY ALFRED E. HIRSCHLER AND W. B. M. FAULCONER

All of the eight isomeric C_9H_{12} alkylbenzenes have been prepared in this Laboratory; freezing points, purities, densities and refractive indices were determined in each case. Two freezing points were observed for four hydrocarbons, namely, pseudocumene, 1,2- and 1,3-methylethyl benzenes, and *n*-propylbenzene; while mesitylene was found to exhibit three, two of which were previously reported.[2]

In each case, the freezing point of the pure hydrocarbon was calculated. The values obtained agree well with those in a recent compilation by F. D. Rossini and associates at the National Bureau of Standards.[3]

Two additional freezing points have been calculated for hemimellitene, although they have not as yet been observed.

Experimental

Apparatus and Procedure.—The apparatus and procedure were in general similar to those described by Mair, Glasgow and Rossini.[4] For most of this work, the freezing cell was of such size that 27 ml. of hydrocarbon filled it to a depth of about 11 cm. In every case, that amount of hydrocarbon which would occupy 27 ml. at the freezing point was weighed into the cell. The temperature coefficients of density given by Lipkin and Kurtz[5] were used in calculating the desired weight of hydrocarbon. The stirrer consisted of a coil of nichrome wire.

In several cases (1,2- and 1,3-methylethylbenzenes) a larger freezing cell, containing 53 ml. at the freezing point, was also used. The freezing tube was a duplicate of that described by Glasgow, Streiff and Rossini.[6] The stirrer was the same as that described[6] except that the four $^1/_8''$ holes in each of the circular fins of the stirrer were absent.

Temperatures were measured by means of a 5-junction copper-constantan thermocouple which had been calibrated by the National Bureau of Standards to ±0.05°. The calibration was checked at the freezing point of mercury, and the sublimation temperature of carbon dioxide, and also by the determination of the freezing points of lots of *n*-heptane and 2,2,4-trimethylpentane whose freezing points were certified by the Bureau of Standards. A Leeds and Northrup Type K-2 Potentiometer was employed to measure the thermocouple e. m. f. The sensitivity was such that a 1-mm. scale deflection of the galvanometer corresponded to 0.003 to 0.006° over the range -40 to $-100°$. The cold junction was immersed in a stirred ice-bath; the ice used was prepared from distilled water.

The hydrocarbons were prepared in this Laboratory.[7] Densities were obtained by the use of Sun Oil Company Precision pycnometers,[8] and refractive indices by means of a Valentine Abbe refractometer.

Except in the case of mesitylene, the time-temperature freezing curves proved to be unsatisfactory for the determination of the freezing point and purity. Time-temperature melting curves were therefore employed. The procedure was as follows: The hydrocarbon was cooled by a bath of liquid nitrogen until enough of the sample was frozen so that the stirrer showed signs of laboring; whereupon the nitrogen was replaced with a constant-temperature warming bath such that the warming head of temperature was 25–50°. Crushed ice, a mush of carbon tetrachloride, or chloroform, or a mush of solid carbon dioxide in 50–50 carbon tetrachloride-chloroform provide suitable temperatures for this purpose. Frequent readings of time and temperature were taken until a temperature of about 10° above the freezing point was reached.

Due to the changing temperature head, the warming curve of the liquid is not a straight line. To find the slope of the warming curve at the melting point, the slope was measured at three or more points beginning somewhat above the point at which the last trace of solid disappears (indicated by an inflection in the warming curve). These time-temperature slopes were plotted against temperature and extrapolated to the melting point.

A complete time-temperature freezing curve was then obtained. The total time of freezing was calculated, correcting for change in temperature head and energy of stirring as described by Mair, Glasgow and Rossini.[4] The slope of the time-temperature cooling curve of the liquid at the freezing point was measured. The complete time of melting was calculated by multiplying the corrected time of freezing by the ratio of the slopes (absolute value) of the time-temperature cooling and the time-temperature melting curves. This value was used to estimate the fraction of solid phase at any point of the melting curve in a manner similar to that described by Mair, *et al.*,[4] for time-temperature freezing curves.

Test for Thermodynamic Equilibrium.—For the purpose of measurement of freezing points or purities, it is most important to know what portion of the time-temperature freezing or melting curve represents thermodynamic equilibrium between solid and liquid phases. Taylor and Rossini[9] have proposed a graphical method which indicates what portion of a given freezing or melting curve has the hyperbolic form which it should have if the liquid and solid phases are in thermodynamic equilibrium, and the rate of crystallization or melting is constant. According to

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[1] Paper presented before Philadelphia Section "Meeting in Miniature," June 13, 1945, and before the American Chemical Society Petroleum Division "Meeting in Print," Sept., 1945.

[2] Mair and Schicktanz, *J. Research Natl. Bur. Standards*, **11**, 665 (1933).

[3] Private communication with F. D. Rossini.

[4] Mair, Glasgow and Rossini, *ibid.*, **26**, 591 (1941).

[5] Lipkin and Kurtz, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 291 (1941).

[6] Glasgow, Streiff and Rossini, *J. Research Natl. Bur. Standards*, **35**, in press (1945).

[7] Unpublished work of H. L. Johnson and R. A. Clark.

[8] Lipkin, Davison, Harvey and Kurtz, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 55 (1944).

[9] Taylor and Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944).