[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermodynamic Properties of 2-Methylpentanol-2

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I. Introduction.—This is the first part of an investigation dealing with the effect of various types of branching of a saturated hydrocarbon chain upon the physical properties of its monohydroxyl derivatives. The hexanols were selected because the preparation of any of them in a high degree of purity and in sufficient quantity for study is reasonably convenient and because they consist of seventeen structural isomers, a number sufficiently large to offer promise in searching for general relations between physical properties and chemical constitution.

II. Preparation of 2-Methylpentanol-2.—Normal propyl bromide was slowly added to a mixture of dry ether and magnesium turnings. From the resulting Grignard reagent the crude 2-methylpentanol-2 was obtained by the method of Deschamps.[1] This product was then fractionated and the fraction boiling between 119 and 124° was collected. This fraction was further purified by fractional distillation from aluminum amalgam as the drying agent. The column used was a bead-filled Pyrex tube, 2 cm. by 108 cm., equipped with a liquid divided still head. The temperature around the column was kept at 110° by means of an asbestos covered nichrome heating coil. Distillation of 300 cc. of crude 2-methylpentanol-2 yielded about 200 cc. of alcohol with a boiling range of one degree, 120.5–121.5°; and two fractionations of this product yielded about 125 cc. of alcohol boiling over a range of 0.03°. This latter fraction was used in the determination of the physical constants.

III. Apparatus and Procedure. Temperature Control.—In all the measurements with the exception of index of refraction, Dewar flasks were used as containers for the thermostatic baths. The temperature around 25° was controlled within 0.005°. At higher temperatures the control was not as low, but even at the highest temperature, 123°, the variation did not exceed 0.05°.

Vapor Pressure and Boiling Point.—The vapor pressure was determined by using Smith and Menzies'[2] "Static isoteniscope." The boiling point of the alcohol was obtained from the vapor pressure–temperature curve.

Surface Tension.—The capillary rise method was used and the apparatus employed was similar to that described by Richards and Coombs.[3] A cathetometer accurate to 0.001 cm. was used to measure the rise.

Viscosity.—A method described by Bingham[4] was followed. How-

(1) Deschamps, THIS JOURNAL, **42**, 2670 (1920).

(2) Smith and Menzies, *ibid.*, **32**, 1412 (1910).

(3) Richards and Coombs, *ibid.*, **37**, 1654 (1915).

(4) Bingham, *J. Ind. Eng. Chem.*, **6**, 233 (1914); Bingham and Jackson, *Bur. Standards Sci. Paper* No. 298.

ever, some changes were made to keep the driving pressure constant, so that checks within 0.01% were obtained.

The other physical properties were determined by the usual methods.

IV. Discussion of Results.—The vapor pressure and temperature were found to be related by the Rankine formula, $\log P = -(4607.5/T) - 14.6555 \log T + 52.61145$, where P is pressure in mm. of mercury and T the absolute temperature. The average deviation of the calculated vapor pressure from the observed is about 0.6% over most of the range.

The boiling point of the alcohol was found by interpolation to be 121.09 ± 0.03° at a pressure of 760 mm. This value is within the range of other reported values.

The heat of vaporization obtained from the slope of a curve by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature was about 9700 cal. at the boiling point. Calculation from the Clausius–Clapeyron equation yields a value of 9540 near the boiling point. The freezing point found was −103 ± 1.5°.

TABLE I

SURFACE TENSION, DENSITY, INDEX OF REFRACTION, VISCOSITY, VAPOR PRESSURE, SUGDEN'S PARACHOR AND EÖTVÖS CONSTANT OF 2-METHYLPENTANOL-2

Temp., °C.	Surface tension	Absolute density	Index of refraction	Absolute viscosity	Vapor pressure in mm.	Parachor observed	Eötvös constant
5.0	24.61	0.82602	1.4183			270.21	1.83
15.0	23.77	.81712	1.4138		3.1	275.80	1.74
25.0	22.90	.80970	1.4089	0.02194	8.6	276.05	1.86
35.0	22.05	.80112	1.4039	.01631	16.5	275.50	1.37
45.0	21.16	.79235	1.3993	.01245	28.2	277.97	1.76
55.0	20.46	.78304	1.3939	.00994	49.4	277.85	2.20
65.0	19.62	.77374	1.3890	.00784	83.2	277.85	2.25
75.0	18.62	.76434	1.3835	.00644	131.9	277.84	2.28
85.0	17.60	.75413	1.3781	.00537	204.2		
95.0				.00456	305.7		
105.0				.00394	446.5		
115.0				.00345	622.9		
123.0					809.6		

The rate of change of five of the physical properties (Table I) was found when plotted to deviate somewhat in the temperature range 40 to 60°. This is well shown also in the table where the calculated value of parachor decreases from 15 to 45° and then again increases. The value of Eötvös constant decreases from 1.83 to 1.37 and then increases to 2.20 above 65°. This would indicate a fairly normal liquid above 60° and association below this temperature. Judging from the other properties there is no reason to believe that there is a slow transformation from one to another form of the alcohol. But should it be a fact it is hoped to discover it when the specific heat of the alcohol is measured.

The physical constants of the other hexanol are being measured at present and their values will be reported in later communications.

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The Temperature-Composition Relations of the Binary System Magnesium Nitrate–Water

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Mention is made of several hydrates of magnesium nitrate in the literature:[1] namely, the ennea, hexa, tri, di and monohydrates and the anhydride. The purpose of this investigation was to establish definitely which of these forms actually occur in order that they might be prepared for calorimetric and vapor pressure measurements which are being made in this Laboratory. The existence of the ennea, the hexa, and the dihydrate and the anhydride has been confirmed and the conditions under which they exist are indicated by the accompanying data.

Experimental Method.—The freezing point method was used. An approximate preliminary freezing point was first determined outside the apparatus. The accurate freezing point was then determined in the apparatus, with only a fraction of a degree of supercooling. This was repeated until the accurate temperature was definitely established. The apparatus used has been described in a previous article.[2]

The following modifications were used. For temperatures below 0° a platinum resistance thermometer was used. The resistance was measured by means of a Mueller type temperature bridge made by Eppley Laboratory, Inc. The bath surrounding the freezing point tube consisted of alcohol cooled by means of solid carbon dioxide. For the higher temperatures the bath surrounding the freezing point tube consisted of oil. It contained a resistance coil extending from the top to the bottom of the oil. The oil was stirred by a stream of air bubbling through it.

C. P. magnesium nitrate was thrice recrystallized as hexahydrate from water. These crystals were dried over 60% sulfuric acid. The dihydrate was prepared by drying the hexahydrate over phosphorus pentoxide. It was possible to remove still more water by drying over phosphorus pentoxide at 110°.

The composition of the samples was determined by igniting to the oxide and weighing.

(1) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, Vol. IV, pp. 379–381, 1923.

(2) Ewing, Krey, Law and Lang, THIS JOURNAL, **49**, 1958 (1927).