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

Thermodynamic Properties of the Hexyl Alcohols. III. 2-Methylpentanol-3 and 3-Methylpentanol-3

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This paper represents the third[1,2] of a series of investigations being carried out in this Laboratory dealing with the relation between the physical properties and chemical constitution of the hexyl alcohols, and concerns the vapor pressure, viscosity, surface tension, density and refractive index of 2-methylpentanol-3 and 3-methylpentanol-3.

Experimental

Preparation of Materials.—2-Methylpentanol-3 was prepared from ethyl bromide and isobutyraldehyde by the Grignard synthesis.[3] 3-Methylpentanol-3 was obtained from the Eastman Kodak Co. and further purified.

Purification.—The fractionating columns employed for the initial and final distillations have been described previously.

"Drierite"[4] was used as the drying agent for both alcohols. The alcohols were allowed to stand over the "Drierite" for two weeks, filtered, and then fractionally distilled.

The alcohols were considered pure when the final boiling point range did not exceed 0.02°.

Apparatus and Procedure for Determining Physical Constants.—The apparatus and the procedures used in this research are those described by Hovorka, Lankelma and Stanford.[2]

All of the instruments used in the surface tension, density, and viscosity measurements were recalibrated before determinations were made.

Discussion of Results

Vapor Pressure.—The vapor pressure data are tabulated in Table I, column 5.

The summary of the values calculated from the vapor pressure data is given in Table II. The constants of the Rankine equation are designated as A, B, and C. The vapor pressures calculated from the Rankine equation agree quite closely with the observed values.

The values of the Trouton constant are considerably higher than the normal value of 21 and indicate varying degrees of association. These high values correspond with those found by Hovorka, *et al.*,[1,2] for the hexanols thus far reported.

Viscosity.—The viscosity data are collected in Table I, column III. The relationship between chemical structure and viscosity is an obscure one since the curves of viscosity *vs.* temperature possess different slopes and even tend to cross each other. This fact has been noted previously. It is significant to observe, however, that the temperature *vs.* viscosity curves for the two hexanols under observation tend to approach the same value at 60° and that from 60 to 130°, the two hexanols have practically the same viscosity values. This behavior may be interpreted by assuming that the molecular aggregation of the alcohols is the same in the temperature interval 60–130°.

Stewart[5] has shown that there are two types of association found among alcohols. According to his theory, both of the hexanols under investigation are associated side by side, the spacing corresponding to one molecular length. Assuming that association takes place through the hydroxyl group, the shielding effect upon the association forces should be approximately the same in both cases. This observation is borne out by the fact that the slopes of the viscosity *vs.* temperature and the density *vs.* temperature curves are practically the same in the temperature interval 60–130°, thus pointing to the fact that the breakdown of these association complexes with temperature is approximately the same for both hexanols.

Plots of Raman's equation[6] and Andrade's[7] equation for 2-methylpentanol-3 yielded perfectly symmetrical curves instead of the straight lines which are to be expected if the equations held. In the case of 3-methylpentanol-3, the plot of the Andrade equation showed a decided break in the higher temperature range. A similar break occurs in the same temperature range when the specific volumes of 3-methylpentanol-3 are plotted against temperature. The constants

(1) Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).
(2) Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938).
(3) Pickard and Kenyon, *J. Chem. Soc.*, **101**, 620 (1912).
(4) Hammond and Withrow, *Ind. Eng. Chem.*, **25**, 1112 (1933).
(5) Stewart, *Phys. Rev.*, **24**, 919 (1927).
(6) C. V. Raman, *Nature*, **111**, 532 (1923).
(7) E. N. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

TABLE I

SURFACE TENSION, VISCOSITY, DENSITY, VAPOR PRESSURE, AND REFRACTIVE INDEX

Temp., °C.	Surface tension, dynes	Abs. viscosity	Abs. density	Vapor press., mm.	Index of refraction	Parachor	Eötvös constant	Total surface energy, ergs
			A. 2-Methylpentanol-3					
5.0	25.72	0.10174	0.83713	...	....	274.7	..	...
15.0	24.95	.05768	.82911	...	1.4189	275.2	1.58	47.14
25.0	24.14	.03640	.82064	6.0	1.4148	275.8	1.59	49.49
35.0	23.33	.02400	.81182	10.5	1.4100	276.4	1.81	47.99
45.0	22.45	.01675	.80300	20.0	1.4049	276.8	1.84	50.76
55.0	21.55	.01230	.79346	36.0		277.3	1.88	50.76
65.0	20.64	.00928	.78380	63.0		277.9	2.01	51.41
75.0	19.70	.00729	.77362	103.8		278.1	2.14	52.77
85.0	18.72	.00589	.76295	163.0		278.6	2.10	54.50
95.0	17.69	.00485	.75173	247.0		279.1	2.07	53.78
105.0	16.75	.00409	.73987	364.0		279.9	2.38	53.05
115.0	15.70	.00355	.72787	520.0		280.0	2.47	56.84
125.0	14.61	.00315	.71860	719.0		280.1	2.42	57.62
126.0	...	...	...	744.2		...	..	...
128.0	...	...	...	790.0		...	..	...
			B. 3-METHYLPENTANOL-3					
5.0	24.63	0.07341	0.83861	...	....	271.2	..	...
15.0	23.93	.04565	.82866	...	1.4123	272.5	1.20	44.14
25.0	23.27	.03040	.81903	18.0	1.4079	273.6	1.32	42.94
35.0	22.55	.02150	.80911	23.8	1.4038	275.0	1.57	44.43
45.0	21.74	.01545	.79864	38.0	1.3990	276.1	1.78	47.51
55.0	20.85	.01175	.78808	61.0		276.9	1.82	49.73
65.0	19.95	.00920	.77705	92.0		277.8	2.00	50.39
75.0	19.00	.00731	.76588	139.5		278.5	2.07	52.40
85.0	18.02	.00600	.75447	211.0		279.3	2.02	52.41
95.0	17.03	.00498	.74265	310.8		280.0	2.59	51.68
105.0	15.97	.00425	.73057	450.5		280.0	2.49	59.05
115.0	14.87	.00366	.71860	632.0		279.9	2.54	57.53
120.0	...	...	...	740.0		...	..	...
121.0	...	...	...	762.8		...	..	...
123.0	...	...	...	810.0		...	..	...

TABLE II

SUMMARY OF VALUES CALCULATED FROM VAPOR PRESSURE DATA

Substance	A	B	C	Max. devn. +	Max. devn. −	Av. devn.	Heat of vapn.[a]
2-Methylpentanol-3	−5078.0	−16.9262	59.6217	0.28	1.4	−0.40	10,624
3-Methylpentanol-3	−2013.4	− 1.0840	5.1802	1.15	2.14	− .03	10,057

	Boiling point, °C.[b]	Trouton's constant
2-Methylpentanol-3	126.68° ± 0.02	26.6
3-Methylpentanol-3	120.91° ± .02	25.5

[a] These are average values calculated from the slope of the curve obtained by plotting log P against $1/T$. [b] Boiling point values were obtained by interpolation from the vapor pressure curves.

of the Andrade equation were evaluated by the method of least squares and the viscosities calculated. The constants and the deviations of the calculated from the observed viscosities are given in Table III. The symmetrical nature of these deviations is very evident. The above observations are in accordance with those previously found.

TABLE III

CONSTANTS FOR THE EQUATION $mv^{1/3} = Ae^{c/VT}$

	$A \times 10^{-6}$	C	Maximum deviation +	Maximum deviation −
2-Methylpentanol-3	17.34	2804	15.2	25.6
3-Methylpentanol-3	36.12	2493	13.3	14.6

Bingham and co-workers[8,9] have proposed various methods for the calculation of the degree of association of liquids which are based upon the premise that fluidities are additive and that, accordingly, liquids should be compared at temperatures of equal fluidity. The association

(8) Bingham and Spooner, *J. Rheol.*, **3**, 228 (1932).
(9) Bingham and Darral, *ibid.*, **1-2**, 174 (1929-31).

factors of 2-methylpentanol-3 and 3-methylpentanol-3 have been calculated from Bingham's "atomic constants" and are given in Table IV.

Refractive Index.—Using the values given by Eisenlohr[10] for the atomic refractive constants of carbon, hydrogen and oxygen, we have calculated the molecular refractive power of 2-methylpentanol-3 and 3-methylpentanol-3. These values are compared in Table V with those calculated from the Lorenz–Lorentz formula.

TABLE IV

CALCULATION OF ASSOCIATION FROM FLUIDITY

200 rhes			300 rhes		
Calcd. temp., °A.	Obsd. temp., °A.	X	Calcd. temp., °A.	Obsd. temp., °A.	X
2-Methylpentanol-3					
271.1	367.0	1.36	305.5	393.0	1.28
3-Methylpentanol-3					
271.1	369	1.37	305.5	396.0	1.29

TABLE V

MOLECULAR REFRACTIVE POWER

	Lorenz–Lorentz equation	Summation of atomic constants
3-Methylpentanol-3	30.74	31.44
2-Methylpentanol-3	31.15	31.44

Surface Tension.—The surface tension data are collected in Table I, column 2.

The values of the Eötvös constant, parachor, and total surface energy were calculated over the entire temperature range and are tabulated in Table I. The general trend of these values is the same as that found by Hovorka, Lankelma and Stanford.[2] In all cases the values are those of associated substances.

(10) F. Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911).

If, according to Sidgwick, the parachor is to be used as a criterion for the degree of association, it is seen that 3-methylpentanol-3 is slightly more associated than 2-methylpentanol-3 at the lower temperature, and that both hexanols are more associated than those previously studied.

The critical constants have been calculated from the Ramsay–Shields equation and are given in Table VI. A large decrease in the values with increase in temperature is readily apparent.

TABLE VI

CRITICAL TEMPERATURES

Alcohol	T	°C.	T	°C.
2-Methylpentanol-3	364.7	(25–35)[a]	296.6	(115–125)
3-Methylpentanol-3	402.4	(25–35)	283.4	(105–115)

[a] The values in parentheses show the two temperatures used to calculate the critical temperatures in question.

Summary

1. The preparation and purification of two hexyl alcohols, 2-methylpentanol-3 and 3-methylpentanol-3, have been described.

2. The surface tension, density, viscosity and vapor pressure have been determined over the temperature range from 5° to the boiling point. The refractive index has been determined from 15 to 45°.

3. The average heat of vaporization and the constants for Rankine's equation have been calculated from vapor pressure data.

4. The parachor, Eötvös constant, total surface energy, and critical constants have been calculated from surface tension data.

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