

air in an enclosed space was corroborated several times by accident. While thiophosphoryl chlorofluorides and thiophosphoryl trichloride do not catch fire when brought in contact with air at room temperature, vapors of thiophosphoryl trichloride escaped on one occasion from a distilling flask and ignited spontaneously. This leads one to wonder whether the intermediate products would ignite spontaneously under the proper conditions.<sup>18</sup>

On cooling, thiophosphoryl monochlorodifluoride condenses to a colorless liquid that becomes more and more viscous until it sets as a glass. The glass quickly changes to an opaque crystalline mass when the Dewar jar of liquid air is removed from it. This might suggest two forms although there was no indication of them from the melting point studies and probably merely means unusually great supercooling.

(18) Since writing this, a storage balloon of 15 l. capacity containing  $\text{PSF}_2\text{Cl}$  at less than one atmosphere pressure developed a leak permitting entrance of air. Finally the balloon exploded violently with sufficient force to demolish a glass lamp reflector 20 feet away. Fortunately, no one was near. Apparently, despite the fact that the gas did not burn on escaping into the air during a previous test, at the right ratio of air to  $\text{PSF}_2\text{Cl}$  it constitutes a dangerous spontaneous explosive.

Thiophosphoryl dichloromonofluoride was distilled in a column open to dry air which it dissolved and held firmly. Considerable difficulty was encountered in removing all the air from the sample used in vapor pressure determinations. However, there was no sign of spontaneous combustion at the condensing point in the column.

### Summary

The fluorination of thiophosphoryl chloride by antimony trifluoride in the presence of antimony pentachloride as catalyst yields thiophosphoryl fluoride, and two new compounds, thiophosphoryl monochlorodifluoride and dichloromonofluoride. The physical and a few chemical properties of these three compounds have been determined. It was found that in the solid state thiophosphoryl chloride exists in two forms, the alpha freezing at  $-40.8^\circ$  and the beta with a freezing point of  $-36.2^\circ$ . The alpha form on warming tends to change to the beta form in the solid state. At certain concentrations in air  $\text{PSF}_2\text{Cl}$  is spontaneously explosive.

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## Thermodynamic Properties of the Hexyl Alcohols. V. 2,2-Dimethylbutanol-1 and 2-Ethylbutanol-1

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This paper represents the fifth<sup>1</sup> of a series of investigations being carried out in this Laboratory dealing with the relation between the structure and certain physical properties of the isomeric hexyl alcohols, and concerns the vapor pressure, viscosity, surface tension, density and refractive index of 2,2-dimethylbutanol-1 and 2-ethylbutanol-1.

### Experimental

**Preparation of Materials.**—2,2-Dimethylbutanol-1 was prepared from *t*-amyl chloride and formaldehyde by the Grignard synthesis. 2-Ethylbutanol-1 was obtained from Sharples Solvents Corporation and further purified.

**Purification.**—The fractionating column employed for the distillation of the alcohols has been described previously.<sup>1b</sup>

The alcohols were allowed to stand over Drierite for at least two weeks, filtered and then fractionally distilled.

(1) (a) Hovorka, Lankelma and Naujoks, *THIS JOURNAL*, **55**, 4820 (1933). (b) Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938). (c) Hovorka, Lankelma and Axelrod, *ibid.*, **62**, 187 (1940). (d) Hovorka, Lankelma and Schneider, *ibid.*, **62**, 1096 (1940).

A fraction boiling over a range of  $0.02^\circ$  was taken for the physical measurements.

**Apparatus and Procedure.**—The apparatus and the procedures used in this research have been described by Hovorka, Lankelma and Stanford.<sup>1b</sup>

The instruments used for the determination of density, surface tension and viscosity were recalibrated before the measurements were made.

### Discussion of Results

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

A summary of the values calculated from the vapor pressure data is given in Table II.

**Viscosity.**—The viscosity data are collected in Table I, column 3. A discussion of the various theories of viscosity advanced by Andrade,<sup>2</sup> Raman<sup>3</sup> and others has been given before.<sup>1b</sup> These theories need not be discussed further here.

In order to compare the hexanols under con-

(2) E. N. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

(3) C. V. Raman, *Nature*, **111**, 532 (1923).

TABLE I

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

Temp., °C.	Surface tension, dynes	Av. viscosity	Abs. density	Vapor press., mm.	Index of refraction	Parachor	Eötvös constant	Total surf. energy, ergs.
A. 2,2-Dimethylbutanol-1								
5.0	26.01	0.32120	0.84103	...	...	274.2	1.78	47.14
15.0	25.25	.16143	.83239	...	1.4229	275.0	1.80	49.45
25.0	24.41	.09039	.82429	3.5	1.4188	275.4	1.82	50.04
35.0	23.55	.05425	.81622	6.3	1.4147	275.6	1.82	49.43
45.0	22.71	.03526	.80792	12.5	1.4101	275.9	1.84	47.84
55.0	21.92	.02438	.79949	23.6		276.4	1.87	49.81
65.0	21.07	.01773	.79099	41.0		276.6	1.88	48.47
75.0	20.23	.01336	.78205	62.0		277.0	1.90	50.51
85.0	19.36	.01041	.77304	108.7		277.2	1.91	50.05
95.0	18.50	.00832	.76388	168.5		277.5	1.93	49.42
105.0	17.66	.00685	.75432	251.6		277.9	1.97	50.55
115.0	16.79	.00573	.74440	366.2		278.3	2.01	49.00
125.0	15.96	.00486	.73440	516.3		278.6	2.19	54.18
135.0	15.00	.00450	.72404	720.3		278.6	..	...
140.0	...	.....	.....	839.3		...	..	...
142.8	...	.....	.....	912.1		...	..	...
B. 2-Ethylbutanol-1								
5.0	25.90	0.14559	0.84506	...	...	272.4	1.55	49.26
15.0	25.06	.08021	.83735	...	1.4243	272.8	1.55	46.38
25.0	24.32	.05892	.82955	3.8	1.4205	273.4	1.56	47.87
35.0	23.53	.03965	.82205	5.0	1.4166	273.6	1.55	49.10
45.0	22.70	.02765	.81413	8.6	1.4126	273.8	1.54	43.38
55.0	22.05	.02018	.80595	15.1		274.6	1.61	43.38
65.0	21.40	.01593	.79740	26.3		275.5	1.61	42.36
75.0	20.78	.01177	.78920	43.7		276.3	1.67	43.41
85.0	20.13	.00929	.78053	71.3		277.2	1.73	41.26
95.0	19.54	.00752	.77141	113.2		278.5	1.85	43.83
105.0	18.88	.00622	.76233	173.8		279.5	1.98	53.29
115.0	17.97	.00528	.75249	257.5		279.8	1.99	50.18
125.0	17.14	.00448	.74289	370.0		280.2	2.08	54.56
135.0	16.20	.00386	.73276	526.5		280.4	2.05	53.34
140.0	...	.00361	.....	622.5		...	..	...
145.0	15.29	.....	.72231	731.0		280.6	..	...
150.0	...	.....	.....	853.0		...	..	...
153.0	...	.....	.....	932.5		...	..	...

TABLE II

SUMMARY OF VALUES CALCULATED FROM VAPOR PRESSURE DATA

$$\log p = A/T + B \log T + C$$

Substance	A	B	C	Max. devn., %		Av. devn.	Heat of vapn. <sup>a</sup>	Boiling point, °C. <sup>b</sup>	Trouton constant
				+	-				
2,2-Dimethylbutanol-1	-4849.3	-14.701	53.1187	4.8	0.26	+0.83	10,430	136.69° ± 0.02	25.4
2-Ethylbutanol-1	-3780.1	-7.6641	31.9952	1.5	.50	+ .15	10,322	146.27° ± .02	24.4

<sup>a</sup> These values are calculated from the slope of the curve obtained by plotting log p against 1/T. <sup>b</sup> Boiling point values were obtained by interpolation from the vapor pressure curves.

sideration with those previously studied, the viscosity values for the former have been calculated using both Andrade's and Raman's equations. The constants A and B of Raman's equation and A and C of Andrade's equation were calculated by the method of least squares. The constants and the deviation of the calculated from the observed viscosities are given in Table III.

Deviations of the experimental viscosity values

TABLE III

CONSTANTS FOR THE EQUATION OF ANDRADE,  $\eta v^{1/3} = A e^{C/V T}$

	A × 10 <sup>-3</sup>	C	Maximum deviation
2,2-Dimethylbutanol-1	9.2442	3350.8	+23.7-45.7
2-Ethylbutanol-1	25.327	2792.9	+11.8-19.7

CONSTANTS FOR THE EQUATION OF RAMAN,  $\eta = A e^{B/T}$

	A × 10 <sup>-7</sup>	B	Maximum deviation
2,2-Dimethylbutanol-1	3.6736	3707.1	+21.6-29.6
2-Ethylbutanol-1	18.380	3083.06	+ 9.7-17.6

from the calculated values are observed. This deviation depends both upon the position of the hydroxyl group in the carbon chain and the degree of branching of the chain. The observed data conform most closely to the values required by Andrade's equation in the case of hexanol-1. As the hydroxyl group is moved away from the end of the chain and as the carbon chain becomes more branched the calculated results deviate more from the experimental. Of the thirteen hexyl alcohols studied, 2,2-dimethylbutanol-1 shows the greatest deviation, namely, 45.7%.

Bingham<sup>4,5</sup> and co-workers, on the supposition that fluidity is an additive property, have proposed methods for calculating the degree of association of liquids at temperatures of equal fluidity. The association factors of 2,2-dimethylbutanol-1 and 2-ethylbutanol-1 have been calculated from Bingham's "atomic temperature" constants and are given in Table IV.

TABLE IV

CALCULATION OF ASSOCIATION FROM FLUIDITY					
Temp., °A., at 100 rhes		X	Temp., °A., at 200 rhes		X
Calcd.	Obsd.		Calcd.	Obsd.	
2,2-Dimethylbutanol-1					
226.2	359.6	1.59	271.1	396.4	1.46
2-Ethylbutanol-1					
226.2	355.4	1.57	271.1	391.7	1.44

The values of X are the same as those obtained previously<sup>1d</sup> for 3-methylpentanol-1 and 2-methylpentanol-5 showing that these alcohols are associated to approximately the same degree. The values of 1.48 at 100 rhes and 1.36 at 200 rhes obtained for 2-methylpentanol-3 and 3-methylpentanol-3 show these alcohols to be less associated than those studied by Schneider<sup>1d</sup> and those of the present study.

The degree of association calculated from Trouton's constant and by Bingham's method are not in close agreement.

**Surface Tension.**—The surface tension data are collected in Table I, column 2. The values of the Eötvös constant, parachor and total surface energy have been calculated over the entire temperature range and are given in Table I. The calculated values of the parachor for all the hexanols studied are lower than the theoretical value

(4) Bingham and Spooner, *J. Rheol.*, **3**, 228 (1932).

(5) Bingham and Darrall, *ibid.*, **1-2**, 174 (1929-1931).

of 288.2. These values increase gradually with increase in temperature due probably to diminished association. The critical temperatures have been calculated from the Ramsey-Shields equation and are given in Table V. A large decrease in the values with increase in temperature is readily apparent.

TABLE V

Substance	CRITICAL TEMPERATURES			
	T	°C. <sup>a</sup>	T	°C.
2,2-Dimethylbutanol-1	364.5	(25-35)	336.6	(115-125)
2-Ethylbutanol-1	418.9	(25-35)	350.4	(115-125)

<sup>a</sup> The values in parentheses show the two temperatures used to calculate the critical temperature in question.

**Refractive Index.**—Using the values given by Eisenlohr<sup>6</sup> for the atomic refractive constants of carbon, hydrogen and oxygen, we have calculated the molecular refractive power of the hexanols. This value is compared with those calculated from the Lorenz-Lorentz equation in Table VI.

TABLE VI

MOLECULAR REFRACTIVE POWER: SUMMATION OF ATOMIC CONSTANTS = 31.44			
T, °C.	Calculated from Lorenz-Lorentz equation		
	2,2-Dimethylbutanol-1	2-Ethylbutanol-1	
15	30.91	31.14	
25	30.96	31.18	
35	31.00	31.21	
45	31.00	31.24	

### Summary

1. The preparation and purification of the two hexyl alcohols, 2,2-dimethylbutanol-1 and 2-ethylbutanol-1, have been described.

2. The vapor pressure, viscosity, density, and surface tension 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, Trouton constant and the constants of the Rankine equation have been calculated from the vapor pressure data.

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

5. The degree of association of these hexanols has been calculated from the viscosity data.

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