at 162–164°.[29] The benzyl benzoate fraction boiled at 145–151° (4 mm.). Benzyl trimethylacetate was obtained mixed with neopentyl benzoate as a fraction boiling at 113–118° (15 mm.). The amounts of each of the esters in this fraction were determined by saponification and determination of the quantities of the respective alcohols and acids. From the residues of the reaction of this ester a solid, which crystallized from alcohol in fine white needles, was obtained. Analytical data (Table III) indicated that this substance had the molecular formula $C_{11}H_{22}O$. No further work was done with this material.

Summary

A study of the reaction of various alkyl benzoates with the corresponding sodium alkoxides is reported. The simplest reaction occurs with the methyl ester and produces dimethyl ether and sodium benzoate. The reaction products from the other alkyl benzoates that were studied are explained by two general reaction courses: (1) a reverse Tischtschenko reaction that yields benzaldehyde and an aliphatic aldehyde (or ketone if the alkyl group is secondary); the resulting aldehydes then enter into further condensations such as forward Tischtschenko reactions to yield new esters or mixed aldol condensations to yield alkylphenylcarbinols and ketones. In the cases of the ethyl and isopropyl esters the ketones produced in the reaction yield 1,3-diketones by further condensation with the starting ester; (2) the condensation of an alcohol (or its ester) with the sodium alkoxide through the Guerbet reaction.

The relatively large quantities of sodium benzoate that are formed in each reaction are attributed to saponification of the starting esters by water produced in the various reactions which occur.

MADISON, WISCONSIN RECEIVED JANUARY 12, 1938

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[29] Samec, *Ann.*, **351**, 261 (1907).

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

Thermodynamic Properties of the Hexyl Alcohols. II. Hexanols-1, -2, -3 and 2-Methylpentanol-1 and -4

BY FRANK HOVORKA, HERMAN P. LANKELMA AND SPENCER C. STANFORD[1]

This paper represents the second[2] of a series of investigations being carried out in this Laboratory on the relations between the physical properties and the chemical constitution of the hexyl alcohols, and concerns the viscosity, vapor pressure, surface tension, density and refractive index of hexanols-1, -2, -3, and 2-methylpentanols-1 and -4.

Preparation of Materials.—Satisfactory methods of preparation are described in the literature for each of the alcohols concerned. Each alcohol, with the exception of 2-methylpentanol-4, was made by the Grignard synthesis, as follows: hexanol-1 from *n*-butyl bromide and ethylene oxide,[3] hexanol-2 from *n*-butyl bromide and acetaldehyde,[4] and hexanol-3 from *n*-propyl bromide and propionaldehyde. Pickard and Kenyon[5] prepared hexanol-3 from *n*-propyl chloride and propionaldehyde. 2-Methylpentanol-1 was prepared from formaldehyde and 2-chloropentane.[6] 2-Methylpentanol-4 was prepared by the reduction of methyl isobutyl ketone with sodium in ethyl alcohol according to the directions given by Neely.[7]

Purification.—The preliminary fractional distillations were carried out using a column 40 cm. long filled with glass beads. This column was equipped with a liquid divider still head and was heated externally by means of a nichrome wire heater.

The final fractional distillations were performed in a similar column, 70 cm. long equipped throughout with Pyrex ground glass joints.

Aluminum amalgam was used as the drying agent.[8] It proved satisfactory for all the alcohols except hexanol-2. When used with this alcohol there apparently was some decomposition to the corresponding olefin, as evidenced by a decided decrease in the boiling point with time. The final fractional distillation of this substance was, therefore, carried out in the absence of the drying agent.

The temperature ranges were read on a Beckmann thermometer which was suspended inside the column. The alcohols were considered to be sufficiently pure when the boiling point range did not exceed 0.04°.

Apparatus. Temperature Control.—The temperature was controlled to ±0.01° up to about 55°. At the highest temperatures used (150–160°) the maximum variation was not over ±0.05°, and such variations were not of long duration, hence the control was of the order of ±0.02° up to the highest temperature measured.

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[1] This article represents a part of a dissertation submitted by Spencer C. Stanford to the Graduate School, Western Reserve University, May, 1935, in partial fulfilment of the degree of Doctor of Philosophy.

[2] Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).

[3] Dreger, *Org. Syntheses*, **6**, 54 (1926).

[4] Norris and Cortese, THIS JOURNAL, **49**, 2640 (1927).

[5] Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1923 (1913).

[6] Przewalski, *J. Russ. Phys.-Chem. Soc.*, **40**, 1105 (1908).

[7] Neely, unpublished Master's Thesis, Western Reserve University, 1931.

[8] Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 561 (1921).

Vapor Pressure.—The method used in measuring vapor pressure was that described by Booth, Elsey and Burchfield,[9] except that in the present work the cathetometer telescope was used to observe the levels in the two arms of the "Isoteniscope." The observed values for vapor pressure are corrected for the vapor pressure of mercury and expressed in mm. of mercury at 0°. These values are accurate to 0.5 mm.

Surface Tension.—The capillary rise method was employed. The apparatus was similar to that used by Richards and Coombs.[10] The large tube had a diameter of 39 mm. and the capillary had a radius of 0.01813 cm. This radius was determined by calibration with a mercury thread, whose length was measured by means of a very accurate measuring microscope. Calculations showed that the radius did not change appreciably over the temperature range used. All of the determinations were performed *in vacuo*, to eliminate the possibility of a contact angle and also to procure better wetting of the capillary. The capillary rise was measured with a cathetometer having a reproducible accuracy of 0.02 mm.

The values for the surface tension were calculated from the customary equation

$$\gamma = 0.5r(h + r/3)(d_1 - d_v)g$$

where the symbols have the usual meaning. The value of g used was 980.24 cm./sec.^{2}. The values of d_v were determined from the vapor pressure data. The values for γ are accurate to ±0.02 dyne.

Density.—The dilatometric method was used. The dilatometer was calibrated carefully with redistilled mercury. The density of each alcohol was determined under the vapor pressure of the liquid. This was done by evacuating and then sealing the dilatometer before it was placed in the bath. This technique is similar to that of Maass and Wright.[11] The height of the liquid in the dilatometer was determined with the cathetometer.

The working volume of the dilatometer was from 4.4 to 4.9 cc. The smallest volume that could be read was equivalent to 0.0001 g. of the alcohol at 5°. Thus the method is accurate to about 1 part in 35,000 since the density of the alcohols is approximately 0.8. The accuracy becomes greater at the higher temperatures due to the decreased density of the alcohols.

Viscosity.—The viscosimeter used was made according to the specifications of Bingham.[12] The apparatus is shown in Fig. 1. B is a three-way stopcock, connected to a water pump by means of a heavy rubber tube; C and C′ are three-way stopcocks; D and D′ are barium oxide drying tubes; E and E′ are five-gallon (20-liter) reservoirs packed in asbestos. The reservoirs prevented sudden temperature changes from affecting the pressure and minimized errors due to change in volume of the system as the liquid passed through the viscosimeter and smoothed out the surging effect due to the applied pressure. The manometer F is filled with water. The apparatus was connected to the air line at X″ and to the pressure control at Y.

The pressure control was of the conventional relay-sounder type and was activated by means of a dilute sulfuric acid manometer with sealed in electrodes. The air was allowed to escape through a small rubber tubing which could be pinched off by the sounder arm. With this simple device pressures constant to 0.5 mm. of water were maintained easily.

A typical run was made as follows. The viscosimeter was connected to the pressure apparatus at X, X′ being left open. The liquid was introduced by means of a pipet and the connection made at X′. The desired pressure was attained. C was turned to the higher pressure, and C′ to the lower pressure side of the system. B was opened and the volume of the liquid in the viscosimeter was adjusted by suction. B was then opened to the system, and the time of flow determined. To determine the time of flow in the opposite direction stopcocks C and C′ were reversed.

The viscosity results were calculated from Bingham's formula

$$n = CPt - C'd/t$$

where the symbols have the usual meaning. The values of P were corrected by use of the tables given by Bingham and Jackson.[12b] The pressures used were of the order of 75–76 g./sq. cm. and were read to 0.5 mm. of water. The time was measured with a stop-watch accurate to 0.1 second. From these values it is apparent that the accuracy is about 0.1% over the entire range.

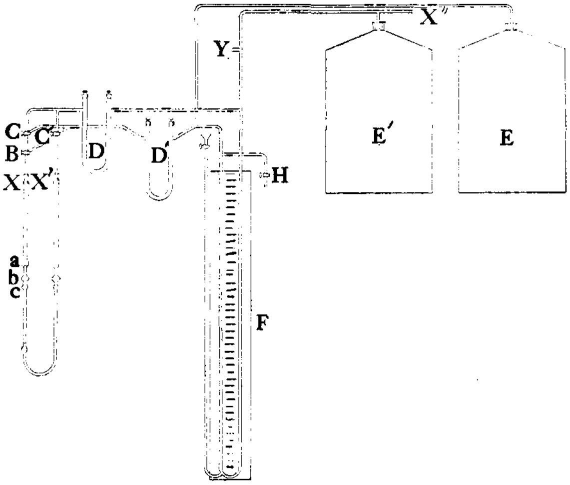

Fig. 1.

Discussion of Results

Vapor Pressure.—The vapor pressure data are given in Table I. The temperature variation of the vapor pressure was found to agree very closely with values calculated from the Rankine equation. The constants for this equation are listed in columns 2, 3, and 4, and maximum positive and negative deviations are given in columns 5 and 6 of Table II. The average values for the heat of vaporization (see Table II), were calculated from the slope of the curve obtained by plotting log P against $1/T$. The values for

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[9] Booth, Elsey and Burchfield, THIS JOURNAL, **57**, 2064 (1935).

[10] Richards and Coombs, *ibid.*, **37**, 1654 (1915).

[11] Maass and Wright, *ibid.*, **43**, 1098 (1921).

[12] (a) Bingham, *J. Ind. Eng. Chem.*, **6**, 233 (1914); (b) Bingham and Jackson, *Bur. Standards Sci. Paper*, No. **298**.

the boiling points (Table II) were interpolated from the vapor pressure curves.

Viscosity.—The data which are tabulated in Table I, column 3, and plotted in Fig. 2 show that there must be relations of a complex nature between the structure of the alcohol and its viscosity behavior. These are generally explained by the association of the alcohol.

TABLE I

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

Temp., °C.	Surface tension, dynes	Absolute viscosity	Absolute density	Vapor pressure, mm.	Index of refraction	Parachor	Eötvös constant
			A. 2-METHYLPENTANOL-4				
5.0	24.20	0.11304	0.81909	...	....	276.7	..
15.0	23.39	.06564	.81120	...	1.4131	277.1	1.65
25.0	22.63	.04074	.80306	8.2	1.4091	277.6	1.53
35.0	21.87	.02715	.79484	12.0	1.4046	278.1	1.53
45.0	21.02	.01915	.78639	21.0	1.4000	278.3	1.80
55.0	20.17	.01404	.77771	32.6	1.3951	278.5	1.78
65.0	19.34	.01070	.76897	52.2		278.8	1.78
75.0	18.49	.00844	.75989	83.5		279.0	1.83
85.0	17.71	.00682	.74962	131.1		279.3	1.62
95.0	16.85	.00562	.73997	201.2		280.2	1.86
105.0	16.08	.00472	.73014	299.0		280.7	1.60
115.0	15.25	.00404	.72003	432.5		281.2	2.03
125.0	14.34	.00349	.71014	609.0		280.9	2.10
130.0	...	.....	.....	719.8		...	..
132.0	13.65	.....	.70210	...		281.1	2.29
133.0	...	.....	.....	796.7		...	..
			B. HEXANOL-3				
5.0	25.74	0.17007	0.83098	...	....	276.8	..
15.0	24.94	.08654	.82275	...	1.4179	277.3	1.57
25.0	24.04	.04880	.81428	7.2	1.4139	277.7	1.82
35.0	23.17	.03038	.80582	10.0	1.4093	278.0	1.78
45.0	22.36	.02042	.79699	16.1	1.4043	278.7	1.63
55.0	21.50	.01450	.78812	26.8	1.3992	279.0	1.78
65.0	20.60	.01081	.77908	44.0		279.3	1.89
75.0	19.75	.00838	.76974	71.5		279.8	1.77
85.0	18.81	.00669	.75971	115.0		280.1	2.01
95.0	17.90	.00547	.75042	175.6		280.2	2.02
105.0	17.06	.00458	.74015	264.0		280.8	1.91
115.0	16.11	.00390	.73036	380.7		280.7	2.15
125.0	15.16	.00338	.71920	537.8		281.1	2.13
135.0	...	.....	.....	746.5		...	..
136.0	14.14	.....	.70708	...		281.4	2.13
138.0	...	.....	.....	820.5		...	..
			C. HEXANOL-2				
5.0	25.90	0.10746	0.82582	...	....	279.0	..
15.0	25.07	.06549	.81814	...	1.4165	279.3	1.66
25.0	24.25	.04221	.81036	3.3	1.4128	279.6	1.72
35.0	23.41	.02873	.80223	5.4	1.4084	280.0	1.67
45.0	22.57	.02051	.79403	10.0	1.4038	280.3	1.74
55.0	21.68	.01520	.78549	18.8	1.3992	280.5	1.86
65.0	20.89	.01165	.77676	33.0		281.1	1.64
75.0	20.02	.00921	.76778	53.0		281.4	1.83
85.0	19.09	.00746	.75803	86.0		281.6	2.02
95.0	18.23	.00616	.74928	140.0		281.9	1.84
105.0	17.34	.00518	.73897	216.3		282.3	1.95
115.0	16.45	.00442	.72882	320.5		282.7	1.96
125.0	15.53	.00383	.71845	455.0		282.9	2.07
135.0	14.59	.00335	.70774	647.2		283.0	2.17
140.0	14.15	.....	.70224	760.5		283.2	2.11
142.0	...	.....	.....	811.5		...	..

TABLE I (*Concluded*)

D. 2-METHYLPENTANOL-1

Temp., °C.	Surface tension, dynes	Absolute viscosity	Absolute density	Vapor pressure, mm.	Index of refraction	Parachor	Eötvös constant
5.0	26.45	0.13274	0.83472	...	....	276.5	..
15.0	25.66	.08407	.82801	...	1.4208	277.6	1.46
25.0	24.94	.05553	.82065	2.6	1.4172	278.0	1.42
35.0	24.09	.03805	.81309	4.2	1.4131	278.2	1.61
45.0	23.37	.02711	.80550	7.8	1.4089	278.7	1.59
55.0	22.57	.01988	.79757	13.5	1.4049	279.1	1.62
65.0	21.69	.01502	.78952	22.6		279.4	1.88
75.0	20.86	.01171	.78121	38.8		279.7	1.74
85.0	20.05	.00933	.77271	64.3		280.1	1.70
95.0	19.26	.00761	.76415	103.5		280.6	1.68
105.0	18.44	.00631	.75479	160.0		280.9	1.76
115.0	17.60	.00532	.74536	237.0		280.0	1.82
125.0	16.68	.00455	.73571	347.5		281.3	2.05
135.0	15.79	.00393	.72576	494.2		...	1.99
140.0	...	.00368	.....	...		...	..
145.0	...	.....	.....	688.5		...	..
148.0	14.63	.....	.71252	...		281.4	2.06
150.0	...	.....	.....	806.4		...	..

E. HEXANOL-1

Temp., °C.	Surface tension, dynes	Absolute viscosity	Absolute density	Vapor pressure, mm.	Index of refraction	Parachor	Eötvös constant
5.0	27.27	0.08921	0.82985	...	....	281.1	..
15.0	26.55	.06293	.82269	...	1.4198	281.7	1.40
25.0	25.80	.04592	.81556	...	1.4158	282.2	1.50
35.0	25.04	.03415	.80836	2.0	1.4121	282.6	1.52
45.0	24.24	.02596	.80105	4.4	1.4081	282.9	1.64
55.0	23.50	.02007	.79358	7.8	1.4041	283.3	1.50
65.0	22.65	.01583	.78536	14.0		283.7	1.76
75.0	21.89	.01268	.77822	25.9		283.8	1.61
85.0	21.04	.01031	.77024	43.3		284.0	1.82
95.0	20.25	.00852	.76214	71.4		284.3	1.68
105.0	19.41	.00714	.75341	112.7		284.7	1.81
115.0	18.59	.00605	.74462	171.0		285.0	1.78
125.0	17.75	.00519	.73550	251.0		285.4	1.84
135.0	16.87	.00448	.72602	367.0		285.6	1.97
145.0	15.96	.00391	.71618	516.5		285.8	2.07
155.0	...	.00345	.....	714.0		...	..
159.0	14.69	.....	.70211	...		285.9	2.10
160.0	...	.....	.....	833.4		...	..

TABLE II

SUMMARY OF VALUES CALCULATED FROM VAPOR PRESSURE DATA

Substance[a]	*A*	*B*	*C*	Maximum deviation +	Maximum deviation −	Average deviation	Heat of vaporization	Boiling point, °C.
1	−4719.0	−12.1075	45.7376	0.9	0.8	−0.07	12,100	157.04 ± 0.02
2	−5345.9	−16.7380	59.6096	1.0	2.5	− .53	11,890	139.90 ± .02
3	−3479.0	− 6.5863	28.5950	1.4	1.2	+ .25	11,080	135.52 ± .02
2–1	−4165.7	− 9.4847	37.6419	1.6	1.4	+ .13	12,000	147.93 ± .03
2–4	−3223.2	− 5.3212	24.7167	3.1	0.9	+ .55	10,900	131.60 ± .04

[a] The numerals refer to the numerical coefficients of the alcohols.

In order to examine this matter further we may consider the modern kinetic theory of viscosity which has been developed by several authors[13-16] who assume some kind of definite arrangement of the molecules in the liquid state. These authors have arrived at a formula of the general type

$$n = Ae^{b/T}$$

where A stands for the viscosity of the ideal liquid[17] and b is a term involving the energy difference between single molecules and those

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[13] C. V. Raman, *Nature*, **111**, 428, 532, 600 (1923).

[14] (a) E. N. da C. Andrade, *ibid.*, **125**, 309, 580 (1930); **128**, 835 (1931); (b) *Phil. Mag.*, **17**, 497, 698 (1930).

[15] S. E. Sheppard, *Nature*, **125**, 498 (1930); *J. Rheol.*, **1**, 299, 349 (1930). This later article contains an excellent account of the work done to date on the kinetic theory of viscosity. The reader is referred to it for much of the theory.

[16] Daniel Silverman, *Trans. Faraday Soc.*, **29**, 1285 (1933).

[17] R. E. Burk, *Science*, **81**, 344 (1935).

existing in groups. This definite arrangement of the molecules in the liquid state has been demonstrated by several methods. Perhaps the most convincing of these is the X-ray evidence obtained by Stewart and others.[18] They found diffraction patterns pointing to a special arrangement of molecules in the liquid. This grouping is called the "Cybotactic State." In a later paper Stewart[19] called attention to a fairly well defined relation between the "perfection of grouping" of the molecules and the viscosity of 22 liquid octyl alcohols, thus furnishing further evidence that a kinetic theory of the viscosity of liquids must take into account molecular arrangements.

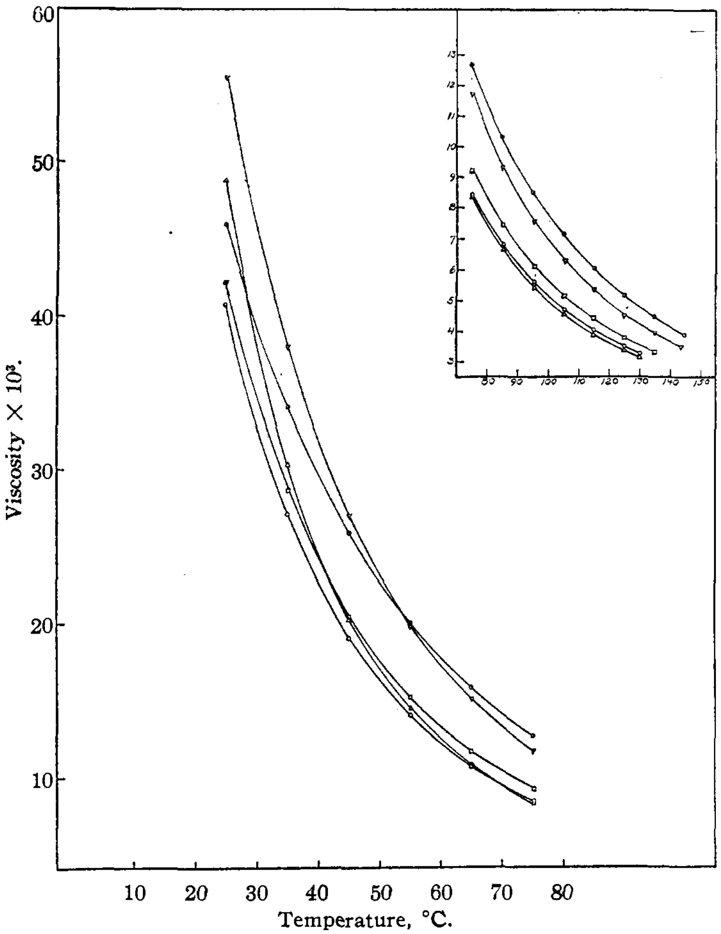

Fig. 2.—○, 2-Methylpentanol-4; □, hexanol-2; ▽, 2-methylpentanol-1; ⊙, hexanol-1; △, hexanol-3.

Andrade[14b] modified his original equation to account for the variation of the volume of the liquid with temperature. His final equation is of the form

$$nv^{1/3} = Ae^{c/vT}$$

where A is proportional to the frequency of vibration of the molecules. The term c/v is an energy term which represents the mutual potential energy which the molecules must have at extreme libration for transfer of momentum to occur. This potential energy term was evaluated by means of the van der Waals equation.

Preliminary plots of our observed data of both Raman's equation and Andrade's modified equation showed that the resulting curves were not straight lines as these equations would require. The curves were symmetrical, showing that the equations need modification. The constants for the equations were determined by the method of least squares and are listed in Table III.

Since the checks are so poor (Table IV), it is doubtful whether definite conclusions can be drawn from the results. It is interesting to note, however, that a steady decrease in the value of the energy constant in the exponential term occurs as the hydroxyl group is changed from the 3-position to the 1-position. The same decrease occurs when the hydroxyl group is changed from the 2- to the 1-position in 2-methylpentane. The constant A changes in the opposite direction, that is, A increases as the position of the hydroxyl group changes from the 3- to the 1-position.

Some of the values calculated from the equations are given in Table IV. The symmetrical nature of the deviations mentioned above is well shown by the data for 2-methylpentanol-1. Since the deviations are of similar nature for the other alcohols studied, only the maximum positive and negative deviations are given.

Although neither equation fits the observed data very closely, the Raman equation applies better at higher temperatures and the Andrade equation at lower temperatures. The behavior of hexanol-1 is an exception.

Due to the success in representing vapor pressure by an equation of the Rankine type, it was decided to use an equation similar to that used by Dunn[20] to represent the change in fluidity with

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[18] (a) Stewart and Morrow, *Phys. Rev.*, **22**, 919 (1927); (b) Stewart, *Chem. Rev.*, **6**, 483 (1929). Summary of work to date.

[19] Stewart and Edwards, *Phys. Rev.*, **38**, 1575 (1931).

[20] J. S. Dunn, *Trans. Faraday Soc.*, **22**, 401 (1926).

TABLE III

CONSTANTS FOR THE EQUATION

$\text{Log } n = A/T + B \log T + C$

	A	B	C
Hexanol-1	1726.5	4.036	−17.116
Hexanol-2	3433.1	14.780	−49.461
Hexanol-3	4598.2	21.614	−70.215
2-Methylpentanol-1	3020.0	11.584	−40.049
2-Methylpentanol-4	3605.7	15.688	−52.305

Constants for the Andrade Equation

	c	$A \times 10^5$
Hexanol-1	2406	6.693
Hexanol-2	2699	2.942
Hexanol-3	3115	1.104
2-Methylpentanol-1	2786	2.739
2-Methylpentanol-4	2816	2.252

Constants for the Raman Equation $n = Ae^{W/RT}$

	W	$A \times 10^6$
Hexanol-1	5136	7.791
Hexanol-2	5406	4.171
Hexanol-3	6205	1.260
2-Methylpentanol-1	5528	4.365
2-Methylpentanol-4	5581	3.006

TABLE IV

COMPARISON OF VISCOSITY EQUATIONS

A. 2-METHYLPENTANOL-4

	Andrade		Raman		Dunn	
T, °C.	+	−	+	−	+	−
5.0	..	25.4	..	29.8	...	11.4
15.0	..	11.0	..	21.2	...	4.7
25.0	1.3	..	..	6.8	...	0.3
35.0	9.9	..	3.4	..	1.9	..
45.0	14.7	..	7.7	..	2.4	..
55.0	16.9	..	12.1	..	2.1	..
65.0	16.6	..	14.1	..	1.5	..
75.0	13.6	..	11.1	..	0.7	..
85.0	9.0	..	12.7	..	...	0.4
95.0	4.1	..	10.4	..	...	.7
105.0	..	3.5	7.4	..	...	.8
115.0	..	4.7	3.4	..	...	.8
125.0	..	12.6	0.0	..	...	.3
130.0	..	16.5	..	2.6	...	.6

SUMMARY OF MAXIMUM POSITIVE AND NEGATIVE DEVIATIONS

	Maximum positive and negative deviations					
	• Andrade		Ramam		Dunn	
Substance	+	−	+	−	+	−
Hexanol-1	5.3	8.7	3.3	5.1	1.2	0.6
Hexanol-2	14.3	22.4	12.4	31.0	3.3	·4.8
Hexanol-3	24.2	32.8	20.4	43.8	4.6	17.2
2-Methylpentanol-1	12.7	16.8	10.8	27.1	1.1	0.6
2-Methylpentanol-4	16.9	25.4	14.1	29.8	2.4	11.4

temperature. The constants were evaluated by the use of simultaneous equations. No attempt was made to use least squares since the equation is empirical. The values of the constants thus found are listed in Table III and the deviations from the experimental results are given in Table IV. Since the equation contains three constants the checks are much better than in the case of either Raman's or Andrade's equation; in fact the agreement in the case of hexanol-1 is excellent. The fact that with this equation the deviations are not symmetrical is perhaps significant, reminding one of the behavior in the case of vapor pressure, although the deviations are greater for the viscosities.

It is interesting to note that the radically different slopes of the viscosity temperature curves for hexanol-1 and hexanol-3 may be explained in terms of different types of association. Stewart[18b] has shown that alcohols having the hydroxyl group on the first or second carbon atom exhibit end to end pairing, whereas if it is on the third carbon atom end to end pairing is excluded, but a side to side grouping is possible. In fact, Iyer[21] has made this latter assumption and uses it to explain the higher viscosity found in such alcohols.

Figure 2 shows that hexanol-1 has a small temperature coefficient of viscosity as compared with the other alcohols. This would imply either very slight association or the existence of a complex which is quite stable thermally. The former assumption is contrary to the findings of Bingham.[22,23] On the other hand, Girard[24] has obtained evidence which points to fairly stable complexes for certain primary alcohols. This is further supported by the fact that hexanol-1 shows the least variation in density with temperature (Fig. 3).

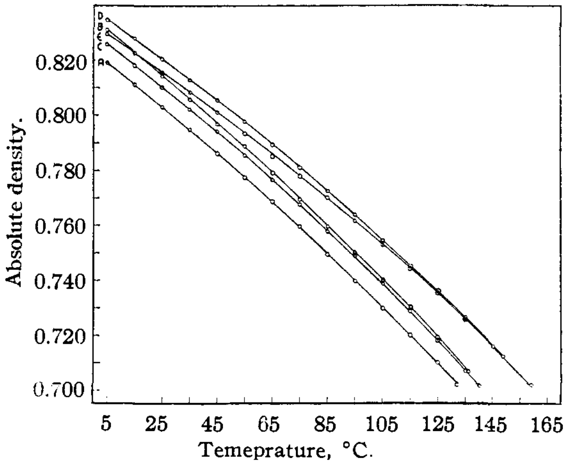

Fig. 3.—A, 2-Methylpentanol-4; B, hexanol-3; C, hexanol-2; D, 2-methylpentanol-1; E, hexanol-1.

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(21) Iyer, *Ind. J. Physics*, **5**, 371 (1930).

(22) Bingham and Spooner, *Physics*, **4**, 387 (1933).

(23) Bingham and Damall, *J. Rheol.*, **1**, 174 (1930).

(24) Girard, *Trans. Faraday Soc.*, **30**, 763 (1934).

Figure 2 shows, on the other hand, that at the lower temperatures hexanol-3 has the highest viscosity of the alcohols studied and that it also has the highest temperature coefficient of viscosity. The high viscosity is explained[21] by the fact that the effective distance through which the momentum is transferred is increased due to side to side pairing. The high temperature coefficient of viscosity may be expected in this type of pairing since the forces causing association would be less, due to the greater shielding effect of the alkyl groups.

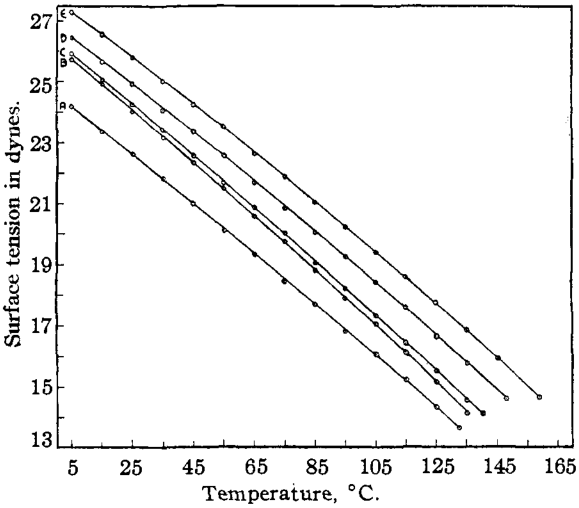

Fig. 4.—A, 2-Methylpentanol-4; B, hexanol-3; C, hexanol-2; D, 2-methylpentanol-1; E, hexanol-1.

These results show that an appropriate equation for the variation of viscosity of liquids with temperature awaits more exact knowledge of the laws governing the forces acting between liquid molecules. The exponential term, if it has somewhat the significance of a heat of fusion, must express the energy required to break the forces holding the molecules in the "cybotactic" groups, as well as the energy required to break up the associated molecules. It is possible, as suggested by Iyer,[21] that this term may involve certain orientations of the molecules necessary for transfer of momentum to occur. It is also logical to believe that each of these energies would vary with temperature just as does the heat of vaporization.[17] Also if the qualitative explanations found above hold true for other cases to be studied, it is possible that the energy term will have to be modified to take into account different types of association.

Surface Tension.—The surface tension data are collected in Table I, column 2. The data when plotted show that all the curves have essentially the same slope, and that the surface tension increases with the boiling point. Some trouble was experienced in the determination of the surface tension of hexanol-1 due to the improper wetting of the glass.

Eötvös constants were calculated for each of the alcohols over the entire temperature range employed. The values, Table I, column 8, are typical of associated compounds, being lower than the normal value of 2.12 and increasing with temperature.

If the value 2.12 indicates an unassociated molecule, there is then a contradiction between the conclusions drawn from the Eötvös constant and the parachor, because with all the alcohols the value of the Eötvös constant exceeds or very nearly reaches the normal value, whereas the value of the parachor does not. This is shown by the parachor values given in Table I, column 7. The normal value of the parachor for the hexyl alcohols is 288.2.

Mumford and Phillips[25] consider that "strain constants" should be assigned to the parachors, dependent on the position of the different groups in the molecule. If such strain constants have actual existence there must be some compensating factor in certain cases, for the parachors for 2-methylpentanol-4, 2-methylpentanol-1 and hexanol-3 are approximately the same.

The critical constants were calculated by means of the Ramsay and Shields equation. The values are given in Table V. The values in parentheses show the two temperatures used to calculate the critical temperature in question.

TABLE V

CRITICAL TEMPERATURES

Alcohol	T, °C.	T, °C.
2-Methylpentanol-4	405.4 (25–35)	317.3 (115–125)
Hexanol-3	370.8 (25–35)	324.3 (125–135)
Hexanol-2	398.3 (25–35)	325.8 (125–135)
2-Methylpentanol-1	387.6 (25–35)	348.9 (135–148)
Hexanol-1	452.0 (25–35)	359.0 (145–159)

In conclusion it may be stated that we hope that further generalizations may be found when the data on all seventeen of the alcohols are obtained and that some of the results in the present paper may be made clearer. We plan in the future to determine in addition such properties as dielectric constants and specific heats and to obtain the X-ray diffraction pattern of the alcohols, in

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(25) Mumford and Phillips, *J. Chem. Soc.*, 155 (1928).

order to correlate these properties whose relation to molecular structure is known with the properties studied in this investigation. In this way it is hoped to arrive at a better correlation between the physical properties and the molecular structure.

Summary

An improved apparatus for the determination of viscosity of liquids has been described.

The viscosity, surface tension, vapor pressure and density of hexanols-1, -2 and -3, and 2-methylpentanol-1 and -4 have been determined at temperatures from 5° to their boiling points.

The boiling points, heats of vaporization and Rankine equation constants have been calculated from the vapor pressure measurements. They have been found to follow the Rankine equation closely.

The viscosity results have been discussed from the standpoint of the kinetic theory of viscosity. No quantitative results were obtained, but it has been found possible to give a qualitative explanation of the results in terms of different types of association.

The parachor, Eötvös constant, and critical temperature of each alcohol were calculated from the surface tension data. It has been found that no general conclusions could be drawn from the surface tension measurements.

Plans for further study have been outlined briefly.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF BRITISH COLUMBIA]

Mutual Solubilities of Hydrocarbons. II. The Freezing Point Curves of Dotriacontane (Dicetyl) in Dodecane, Decane, Octane, Hexane, Cyclohexane and Benzene

BY W. F. SEYER

It has been mentioned in a previous communication[1] that a quantitative study of the solubility relationships among simple hydrocarbon systems was highly desirable both from the theoretical and technical points of view. In this second paper on the subject there are given the freezing point data of six separate systems of dicetyl with some low molecular weight hydrocarbon. The hydrocarbons used were as follows: dodecane, decane, octane, hexane, cyclohexane and benzene. The purpose of investigating the last two was to find out whether ring structure would affect seriously the solubility of the dicetyl compared with that, say, of hexane.

Materials.—The dodecane, decane and hexane were obtained from the Eastman Kodak Co., and no other purification outside of drying over sodium was attempted. The dicetyl was prepared in the same manner as described previously except that the hydrocarbon was first recrystallized out of acetic acid and then out of ether.

It was found that in nearly all cases, if the dicetyl was first dissolved in glacial acetic acid, the acid became colored. This color could be removed readily by filtration through bone black. It would thus appear that in the treatment of the cetyl alcohol with hydrogen iodide as recommended by Kraft[2] some side reactions take place and that the products formed reacted with the glacial acetic acid, for it was found possible to raise the melting point of several samples of dicetyl which had been recrystallized only from ether by almost 0.2° by recrystallizing out of glacial acetic acid and then out of ether. For the preparation of the hydrocarbon two lots of cetyl alcohol from Eastman Kodak Co. were used. While in each case constant melting points were obtained, yet they differed by about 0.15° even after five recrystallizations from acetic acid and four from ethyl ether. The melting points were 70.0–70.1° for the first, and 70.1 to 70.2° for the second lot, both differing from that given by S. H. Piper and others[3] by about 0.6°. They give the transition point as 65.2–65.4° and state that it is a better criterion for indicating the purity of a paraffin than the melting points. Assuming this to be correct, it would indicate that our material was not pure but contained, calculated on the basis of their figures, about 5% of the next higher homolog.

In view of these findings, and that the long chain hydrocarbons separate out together to form mixed crystals, it becomes a question whether it is possible to prepare the pure hydrocarbon at all from cetyl alcohol, as it is probable that the lower member of the alcohol series will be present as well as the next higher.

The octane was prepared by the reaction as described by Lewis, Hendricks and Yohe.[4] The material had a refractive index $n^{20}{}_{\mathrm{D}}$ 1.3973, whereas the "International Critical Tables" give 1.3975. The cyclohexane was part

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[1] Seyer, THIS JOURNAL, **58**, 2029 (1936).

[2] Kraft, *Ber.*, **40**, 4783 (1907).

[3] Piper, Chibnall, Hopkins, Pollard, Smith and Williams, *Biochem. J.*, **25**, 2072 (1931).

[4] Lewis, Hendrick and Yohe, THIS JOURNAL, **50**, 1993 (1928).