TABLE I

PROPERTIES OF NEW ALKYLIODOSILANES

Compound	°C.	d^{20}_4	Mol. wt. (Dumas) Found	Calcd.	I, % Found	Calcd.	Distillation range °C., uncor.	Mm.
Et_4Si	153.7[a]	0.7662[b]	...	...	....		....	
Et_3SiI	193 ± 1	1.333	235	242	52.0, 52.8	52.4	191.5–192.5	760
Et_2SiI_2	221 ± 1	2.009	350	340	74.5, 74.9	74.6	149–150	102
$EtSiI_3$	251 ± 1	2.748	450	438	87.2, 86.3	86.9	112.5–113.5	10
SiI_4	290[c]	....	...		....		....	
$C_{12}H_{25}SiI_3$	389 ± 2	1.744	...		67.5	66.0	199–202	3

[a] R. N. Lewis and A. E. Newkirk, THIS JOURNAL, **69**, 701 (1947). Value listed. [b] F. C. Whitmore and others, *ibid.*, **68**, 475 (1946). [c] Value generally accepted.

of a special round-bottom flask of appropriate size, in which there was approximately double the theoretical equivalence of ethanolic sodium hydroxide solution; after closing the stopper, a special ground joint, the entire system was shaken most vigorously until the thin capsule holding the sample had shattered. In this method the excess of base reacted quite rapidly with the hydrogen iodide and thus prevented a reaction between ethanol and hydriodic acid. Thereupon the excess of base was titrated in the presence of a universal indicator, finally crushing the fragile soft glass tube completely just before the end-point. Because the alcoholysis product was insoluble in ethanol, the acidity from dodecyltriiodosilane could be approximated closely only after an extended period of extremely vigorous agitation.

Alkoxyiodosilanes.—Persistent attempts to convert methoxychlorosilanes or ethoxychlorosilanes by the Ruff method into the corresponding alkoxyiodosilanes never yielded any definite product which boiled at a fixed low pressure, such as 10 mm. Moreover, 100 g. of phosphorus triiodide and 40 g. of tetraethoxysilane upon heating furnished 15 g. of ethyl iodide, boiling at 72.5°, rather than an ethoxyiodosilane; triethoxyiodosilane should boil at approximately 200°. Despite all this, alkoxyiodosilanes may enjoy a limited stability at 30° or so.

Discussion

(1) Alkyliodosilanes are far more reactive toward water than are the alkylbromosilanes, alkylchlorosilanes and alkylfluorosilanes; this factor makes the handling and analysis of the iodine compounds the most difficult of all.

(2) Our boiling points for triethyliodosilane and diethyldiiodosilane are in good agreement with those of Eaborn, who lists 190.5° (744 mm.) and 220–221°, respectively.[7]

(3) All-in-all, the Ruff method[3] is probably the best for alkyltriiodosilanes and dialkyldiiodosilanes; it is shorter than the Eaborn process,[7] especially for dialkyldiiodosilanes.

(4) Other information regarding alkyliodosilanes has been submitted for publication. Alkylanilinosilanes are stable compounds; six are now (March, 1951) known, and will be described later. This information explains difficulties encountered in the Ruff process—especially with trialkylhalogenosilanes.

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[7] C. Eaborn, *J. Chem. Soc.*, 2760 (1949).

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[CONTRIBUTION FROM THE CARBIDE AND CARBON CHEMICALS COMPANY, A DIVISION OF UNION CARBIDE AND CARBON CORPORATION]

Preparation and Physical Properties of a Series of *n*-Alkanes

BY ARTHUR K. DOOLITTLE AND ROLAND H. PETERSON

Ten *n*-paraffin hydrocarbons covering a molecular weight range of 72 to 900 were prepared by conventional synthetic methods. Most of the preparations were of high purity and their freezing points, refractive indices and densities (the last over the temperature range −10 to 300°) were carefully determined as criteria of their purity. The viscosities of the hydrocarbons were measured with great precision from −10 to 300° for the purpose of testing the validity of certain viscosity relationships over a greater range of temperature and molecular weights than heretofore possible. The results of this analysis will be published elsewhere. The estimation of the errors in viscosity measurements is discussed and a maximum probable error assigned to each viscosity measurement.

The studies here described were undertaken to appraise certain viscosity relationships for liquids over ranges of temperature and of molecular weights (in homologous series) greater than have been possible with data heretofore available. In order to provide the simplest conditions for the study of Newtonian flow, as free as possible from complications due to association and from uncertainties in regard to molecular weight and molecular weight distribution, the study was made with pure members of the homologous series of normal paraffins. Ten members of this series ranging from *n*-pentane (m = 72) to *n*-tetrahexacontane (m = 900) were synthesized, and their viscosities and densities measured with great accuracy at atmospheric pressure over a range of temperatures between −10 and 300°.

Preparation of Hydrocarbons

n-Pentane was prepared by hydrogenolysis of pure hexanol-1 after the method of Adkins[1] wherein the alcohol is treated with hydrogen at 250° and 3000 p.s.i. in the presence of Raney nickel. In contrast to higher alcohols, very poor yields resulted unless an equal quantity of heptane was included in the bomb charge. Under these conditions 40% yields were realized. Distillation of several bomb charges yielded a liter of crude pentane which was refractionated after washing with concd. sulfuric acid. Heart cuts of identical densities (±0.00002 g./cm.^{3}) were retained for study.

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[1] H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, pp. 79–80.

The above and subsequently mentioned fractionations were all conducted in a 50 cm. high by 2.8 cm. internal diameter column packed with $^{3}/_{16}''$ glass helices. The column was well insulated and equipped with an electric heater. The fractionations were performed with an approximate reflux ratio of 10 to 1 although there was no precise control of this factor.

n-**Heptane** was obtained by refractionation of two liters of material meeting the Bureau of Standards specification for anti-knock standard. Heart cuts of identical densities were retained.

n-**Octane**.—Constant-density octanol-1 was obtained by fractionation of "Antifoam" LF (du Pont) and converted to 1-bromoöctane by saturation with anhydrous hydrogen bromide at 100°. To remove octanol, the distilled product was treated with octanoyl chloride and pyridine, the mixture washed and pure bromide separated from the octyl octanoate by distillation. The bromide was washed with concd. sulfuric acid and refractionated. Constant-density fractions (±0.0001 g./cm.^{3}) were converted to the Grignard reagent in the usual manner which was decomposed to octane by addition to dilute sulfuric acid (93% yield on bromooctane). The product was fractionated twice and final heart cuts of identical densities retained.

n-**Nonane**.—Decanol-1 of f.p. >6.5° was isolated by fractional distillation from the tails of a large amount of "Antifoam" LF and hydrogenated to nonane in 85% yield by the Adkins procedure. This product was fractionated twice and final heart cuts of identical densities retained.

n-**Undecane**.—Pure dodecanol-1 was obtained from "Lorol" (du Pont) by stirring with concd. aqueous potassium hydroxide at 100°, washing and fractionating. An Adkins hydrogenolysis of material f.p. 24.15° gave a 92% yield of undecane which was fractionated twice and final heart cuts of identical densities retained.

n-**Tridecane**.—Crude tetradecanol-1 was obtained from the tails of a large quantity of "Lorol," stirred with concd. aqueous potassium hydroxide at 100°, washed and fractionated. An Adkins hydrogenolysis of cuts f.p. 37.6° gave a 91% yield of tridecane. This was fractionated twice and final heart cuts of identical densities retained.

n-**Heptadecane**.—Pure octadecanol-1 was prepared from "Stenol" (du Pont) by stirring with concd. aqueous potassium hydroxide at 100°, washing with boiling water and fractionating. An Adkins hydrogenolysis of cuts f.p. 57.5° gave a 90% yield of heptadecane. This product was fractionated twice and final heart cuts of identical densities retained.

n-**Octacosane**.—Twenty grams purchased from Eastman Kodak Co. was recrystallized twice from hot, filtered, diisopropyl ether solutions (10%) (80% over-all recovery, f.p. 61.1°, capillary m.p. 61.2–61.4).

n-**Hexatriacontane** was obtained by the Wurtz reaction of 1-bromoöctadecane prepared by bromination of pure octadecanol with concd. sulfuric and hydrobromic acids after the method of Kamm and Marvel.[2] The crude product was treated with 2-ethylhexanoyl chloride and washed. The pure bromide (f.p. 27.7–27.9°) was separated from the octadecyl 2-ethylhexanoate by fractional distillation.

The Wurtz synthesis was conducted in a scrupulously dried apparatus by gradual addition of bromoöctadecane to 100% mole excess of sodium sand in absolute ether. Characteristic blue color and vigorous refluxing developed quickly. After eight hours of refluxing, the mixture was allowed to stand overnight. Excess sodium was destroyed with alcohol, the mixture shaken with an equal volume of water and the crude product filtered off. This material was melted, separated from water and sediment (84% yield, f.p. 73.6°) and recrystallized three times from filtered, boiling-hot diisopropyl ether solutions (20–25%) (83% recovery, f.p. 75.73°).

n-**Tetrahexacontane** was prepared by the Wurtz reaction of 1-bromodotriacontane prepared by bromination of dotriacontanol-1 isolated from carnauba wax.

One kg. of carnauba wax (f.p. 82°) was refluxed 24 hours with excess alcoholic potassium hydroxide containing enough benzene to render the mixture homogeneous. The dried residue was extracted with heptane in a soxhlet extractor. The crude alcohols obtained upon evaporating the solution were melted and some soap contaminants filtered off. The product was freed of hydrocarbons by solution in a small amount of hot heptane and precipitation with 30–60° petroleum ether. The product was acidified and recrystallized from several solvents in an unsuccessful effort to remove fatty acids. Conversion of these acids to alcohols by hydrogenation (isopropyl ether solution–Raney nickel, 100°) enabled removal of the lower molecular weight components by crystallization; (yield 134 g., f.p. 85.2°, brown melt).

The dotriacontanol-1 was brominated with anhyd. hydrogen bromide at 100° The dark-colored product was crystallized and then rendered virtually colorless by molecular distillation (180° at 0.001 mm.). Although repeated recrystallizations did not change the freezing point, analysis found 4.5% $C_{30}H_{61}OH$ present. The material was rebrominated as before with the extra addition of 1 ml. of phosphorus tribromide, and recrystallized twice (yield 74 g., f.p. 68.2°, Br, 14.88,[3] 2% $C_{30}H_{61}OH$). On basis of the analysis the pure bromide would contain 15.18% bromine which compares closely with that of bromodotriacontane (15.09%).

The Wurtz reaction was conducted as in the preparation of hexatriacontane except that a diisopropyl ether medium was required because of the insolubility of the bromide in ethyl ether. However, no evidence of reaction was noted until some ethyl ether was added to the mixture. After refluxing ten hours, excess sodium was destroyed and the mixture acidified and extracted three times with boiling benzene. Crude tetrahexacontane crystallized on cooling (m.p. 92.5–96.5°). This was recrystallized from heptane and benzene (yield 16 g., m.p. 101.9–102.2°). The product undoubtedly was not pure since it was tan-colored when molten. Carnauba wax is not an entirely satisfactory raw material for the synthesis since it contains a mixture of higher alcohols[4] and their complete separation is unlikely.[5]

Determination of Physical Properties

Refractive Indices.—Refractive indices were determined at the D spectral line with a Pulfrich refractometer. A General Electric "Lab-Arc" sodium lamp was used for illumination. The prisms and sample were thermostated to ±0.05° by water circulating through the jackets. All values were determined at 20°, except in the cases where the hydrocarbons were solids at this temperature. For these cases, values were obtained near the melting point.

The operations of cleaning and filling the sample cell were made at room temperature to avoid possible condensation of moisture. A rubber gasket between the cell rim and thermostating cup assured air-tightness during measurements. For the determinations at elevated temperatures it was necessary to surround the sample cell with a thick layer of cotton batting to prevent local freezing and to attain uniform temperature. The instrument zero correction was determined and applied to each measurement. Correction for the changed refractive index of the prism glass at the elevated temperatures was made according to the manufacturer's directions. Table I lists the values obtained and some values from the literature for comparison.

Freezing Points.—With two exceptions, the freezing points were measured with a platinum resistance thermometer of Leeds and Northrup manufacture and calibrated by the National Bureau of Standards. Its resistance was determined with an L. and N. Mueller bridge. A sensitive L. and N. table-type galvanometer with the usual light and scale determined the null point.

The freezing-point cell consisted of a 125-ml. glass tube centered within a steel jacket by means of a ground joint at the top of the assembly. A steel jacket was purposely chosen to eliminate the danger of a liquid air explosion with those hydrocarbons requiring such a coolant. The surfaces of the enclosed air space were covered with bright aluminum foil and provision made for evacuation of the space when desired. The glass tube was closed with a rubber stopper through which passed the thermometer, reciprocating stirrer and sample entry tube. A rubber bellows about the exterior portion of the stirrer prevented aspiration of moisture into the cell during operation. Before use, the cell was

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[2] O. Kamm and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Editors, John Wiley and Sons Inc., New York, N. Y., 1941, p. 25.

[3] By method of W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937) (Found: Br, 14.93, 14.93, 14.77).

[4] S. D. Koonce and J. B. Brown, *Oil and Soap*, **21**, 167 (1944).

[5] F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (*London*), **A128**, 214 (1930).

TABLE I

FREEZING POINTS AND REFRACTIVE INDICES OF *n*-PARAFFINS

						Literature	
Compound	Formula	Mol. wt.	F.p., °C.[a]	n_D[b]	Purity[c]	F.p., °C.	n_D[b]
Pentane	C_5H_{12}	72.15	−129.75	1.3572	99.87	−129.721[e]	1.35748[e]
Heptane	C_7H_{16}	100.20	− 90.66	1.3876	99.74	− 90.601[e]	1.38765[e]
Octane	C_8H_{18}	114.22	− 56.89	1.3976	99.51	− 56.798[e]	1.39743[e]
Nonane	C_9H_{20}	128.25	− 53.54	1.4051	...	− 53.535[e]	1.40542[e]
Undecane	$C_{11}H_{24}$	156.30	− 25.61	1.4170	...	− 25.60[e]	1.41716[e]
Tridecane	$C_{13}H_{28}$	184.35	− 5.42	1.4254	...	− 5.3[e]	1.4256[e]
Heptadecane	$C_{17}H_{36}$	240.46	21.95	1.4358(22.0°)	...	21.8[e]	1.4368[e]
Octacosane	$C_{28}H_{58}$	394.74	61.2–61.4[d]	1.4359(62.0°)	...	61.6[f]	1.4368(61.6°)[f]
Hexatriacontane	$C_{36}H_{74}$	506.95	75.73	1.4360(77.0°)	...	76[f]	1.4341(82°)[g]
Tetrahexacontane	$C_{64}H_{130}$	899.68	101.9–102.2[d]	1.4363(104.0°)	...	102[f]	....

[a] Highest temperature observed during freezing. Average of several determinations. [b] At 20° unless otherwise noted. [c] Mole per cent. Calculated after manner of A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945), using constants from "Selected Values of Properties of Hydrocarbons," Circ. C461, Nat. Bur. Standards, Tables 1z 2z 3z, U. S. Govt. Printing Office, Washington, D. C. Values somewhat lower than actual since experimental freezing points are not corrected to zero freezing time. [d] Melting points. See text. [e] American Petroleum Institute Research Project 44, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons," Table 20a, June 30, 1948. [f] G. Egloff, "Physical Constants of Hydrocarbons," Vol. 1, Reinhold Publ. Co., New York, N. Y., 1939. [g] M. P. Doss, "Physical Constants of Principal Hydrocarbons," The Texas Co., New York, N. Y., 1943.

TABLE II

DENSITIES OF *n*-PARAFFINS (CORRECTED TO VACUUM)

		Temperatures, °C.							
Compound	Mol. wt.	−10°	20°	50°	100°[e]	150°	200°	250°	300°
Pentane	72.15	0.6548	0.6263						
Heptane	100.20	.7087	.6839	0.6582	0.6119				
Octane	114.22	.7265	.7026	.6782	.6350				
Nonane	128.25	.7408	.7177	.6942	.6532	0.6086			
Undecane	156.30	.7623	.7402	.7180	.6800	.6393	0.5947		
Tridecane	184.35	.7778[a]	.7563	.7349	.6985	.6604	.6201		
Heptadecane	240.46		.7780[b]	.7575	.7232	.6880	.6512	0.6119	0.5687
Octacosane	394.74			.7876[c]	.7555	.7235	.6910	.6578	.6226
Hexatriacontane	506.95				.7667	.7357	.7048	.6730	.6399
Tetrahexacontane	899.68				.7878[d]	.7579	.7283	.6981	.6680

[a] Extrapolated from 0.7745 at −5.4°; 0.7706 at 0°. [b] Extrapolated from 0.7766 at 22°; 0.7732 at 27°. [c] Extrapolated from 0.7799 at 62°. [d] Extrapolated from 0.7818 at 110°. [e] Values for 100° and above calculated from determinations made within a few degrees of stated temperature.

thoroughly dried by passing dry air (liquid air trap) through it. Then 40–50 ml. of hydrocarbon were pipetted into the cell with dry air still flowing out of the sample entry tube. After closing, a slight positive pressure (2–4 cm.) of dry air was maintained within the apparatus to prevent entrance of moisture during determination of the freezing point.

The cell was cooled by immersion in a bath appropriate to the hydrocarbon. Pentane and heptane required liquid air; octane, nonane and undecane required Dry Ice and acetone. Tridecane, heptadecane and hexatriacontane were frozen in conventional thermostats maintained a few degrees below the freezing points. With liquid air and Dry Ice coolants the cooling rate was retarded at the freezing point by evacuation of the air space surrounding the sample.

The freezing points of octacosane and tetrahexacontane could not be determined as above because of the small quantities available. Accordingly, the usual capillary tube melting points were determined in well-stirred oil-baths whose temperatures were very carefully controlled near the melting point. Accurate thermometers were used.

The values determined with the platinum resistance thermometer are deemed accurate to 0,01°. They were reproducible to less than this figure and were quite constant for extended periods of freezing. The values are listed in Table I with some values from the literature for comparison.

Densities.—A high-accuracy pycnometer used for determinations up to 100° consisted of a single capillary attached to a 25-ml. erlenmeyer flask. The capillary was enclosed by a stoppered chamber which served as an overflow reservoir.

This pycnometer was filled from a separate reservoir attached to the capillary by means of a ground joint smooth enough to be virtually vacuum tight when wet with liquid. The liquid was introduced into the pycnometer by repeated partial evacuations of the assembly. The pycnometer was thermostated with the filling reservoir still attached to it. When thermostated, suction was applied to the reservoir and the ground joint parted with the pycnometer in an inverted position. The resultant rush of air through the ground joint swept it free of liquid. Final adjustment of liquid volume was made after returning pycnometer to the thermostat. When equilibrium was established the pycnometer was wiped and weighed by a standard procedure.

Above 100°, densities were determined with a pycnometer consisting of a 7-ml. bulb attached to a long graduated and calibrated capillary. In filling, the capillary was sealed into the mouth of a test-tube with a rubber stopper and the assembly evacuated *via* a side arm. Thrusting the pycnometer orifice into the liquid and then releasing the vacuum nearly filled the pycnometer. The residual bubble was driven out upon thermostating at the elevated temperatures. After noting the equilibrium position of the meniscus in the capillary the pycnometer was cooled, rinsed with solvent, wiped and weighed by the standard procedure.

For solids, the pycnometer had to be filled in an oven. In addition, it was necessary to place an electrically heated loop of wire in the capillary during transfer to the thermostat to prevent freezing and consequent bursting when the pycnometer contents expanded in the thermostat.

The thermostating media for the density determinations were the same as those used for the viscosity determinations and are described later under that subject.

The pycnometer volumes were determined at 20° with distilled water. Volumes at all other temperatures were calculated from the expansion coefficient of the glass (Pyrex). The densities determined are listed in Table II.

Viscosities.—Measurements were made in accurate thermostats. A large water-bath constant to ±0.02° was used in the range 5–40°. Small baths constant to ±0.05° were used for temperatures below 5° and between 40 and 100°.

For temperatures of 100° and above, a condensing-vapor thermostat was successfully employed. It consisted simply of a Dewar-type chamber encasing the viscometer and possessing an air condenser at the top and a flask at the bottom for boiling the various liquids. A narrow window in the silvering permitted observation of the viscometer and thermometer. A bellows throat relieved the stresses arising from differential expansion of the inner and outer walls. For all vapors other than steam, constant temperatures were readily maintained in the working space when the vapor level was held slightly above the vacuum jacket. For constant temperatures with steam it was necessary for the steam to completely fill the apparatus and vent steadily at the top.

It was possible to find suitable liquids boiling within a few degrees of all desired temperatures. Although the use of a manostat would have enabled the indefinite maintenance of the exact desired temperatures, its use was unnecessary since barometric pressures were usually constant for the period of a viscosity determination and the values obtained could be accurately corrected over small temperature ranges.

The following liquids were used in this work to attain approximately the temperatures given:

Water	100°
n-Nonane	150°
Methyl benzoate	200°
n-Butyl benzoate	250°
Diphenylamine	300°

The thermal stability of these liquids was sufficient for our purposes. That of water need not be discussed. *n*-Nonane was unaffected by weeks of continuous refluxing, which agrees with the observations of Shepard, *et al.*,[6] on the thermal and oxidation stability of hydrocarbons at the boiling point. Hurd[7] mentions methyl benzoate as being thermally stable to 430°. However, it did discolor upon prolonged refluxing, probably because of oxidation. No change in boiling point was observed but, as a precaution, used material was occasionally replaced. Other alkyl benzoates are less stable than the methyl ester[10] but we found pure butyl benzoate quite stable at its boiling point[8] although Whitmore[9] states that it decomposes to butene and benzoic acid. It did discolor fairly readily due to oxidation as also did the diphenylamine. These substances were also replaced with fresh material from time to time as a matter of precaution.

The diphenylamine was obtained from Eastman Kodak Company and was fractionated twice under vacuum. The other materials were prepared in this Laboratory and purified by fractional distillation under vacuum. Their freezing points are listed below as criteria of their purity.

n-Nonane	−53.54°
Methyl benzoate	−12.73°
n-Butyl benzoate	−12.46°
Diphenylamine	52.88°

The temperatures of the water-baths were determined with thermometers calibrated against Bureau of Standards thermometers. Temperatures in the large bath were read with an accuracy of 0.01°, in the other baths of 0.02°. Temperatures in the vapor baths were determined by two methods. In the cases of water and nonane the temperature was calculated from the observed pressure. The values of Shepard, *et al.*,[9] for the normal boiling point of nonane and its change with pressure were used. The temperatures of the other vapors were determined with short-range thermometers attached to the viscometer. The thermometers were graduated to 0.2° and estimated to 0.02° by means of a telescope. These latter thermometers were calibrated when the work was begun by comparison with standard mercury-in-glass thermometers. At the conclusion of the work they were recalibrated by comparison with a platinum resistance thermometer. Both the standard mercury-in-glass thermometers, and the platinum resistance thermometer were calibrated by the National Bureau of Standards. The extreme difference in the thermometer corrections by the two calibrations was 0.25°. The temperatures stated are those based upon the first calibration and are assumed to be correct within ±0.3°.

Of the many methods of measuring viscosity, only the method of capillary flow was deemed practical for this work. The Ubbelohde relative viscometer was selected as the best capillary instrument because of its manipulative ease and high accuracy. However, the procurement of well-constructed instruments proved to be difficult because of the war. Initial calibrations with water at different temperatures showed that available instruments exhibited a variable kinetic energy constant. This appeared to be due to improper construction of the suspended level which according to Ubbelohde[10] must be of exact dimensions and shape. The coöperation of the Fish–Schurman Corporation enabled us to examine and calibrate many instruments until satisfactory ones were found.

The selected No. 1 capillary instrument was calibrated with water at 5, 10, 15, 20 and 25°, and the two constants in equation (1) below, determined by simultaneous solution of four pairs of equations (5–10°, 10–15°, 15–20°, 20–25°). The viscosities of water as determined by Bingham and Jackson[11] were used in the calculations. The constants by all four solutions showed remarkable agreement. The instrument constant (C) of 0.009963 varied by only ±0.000002 and the kinetic energy constant (B) of 1.89 varied by only ±0.05.

A superstructure was added to the viscometer for the purpose of easy operation in the vapor thermostat, filtration of samples within the viscometer and maintenance of a nitrogen atmosphere in the viscometer to prevent oxidation at high temperatures.

Prior to a viscosity determination the completely clean viscometer was purged of oxygen with dry, oxygen-free nitrogen. The filter chamber in the superstructure then was opened and the hydrocarbon inserted while the flow of nitrogen passing out the opening prevented admission of air. After closing the viscometer, the sample was filtered into the viscometer proper by application of nitrogen pressure to the filter chamber.

The viscometer was placed in the thermostat with the capillary plumb. When thermostated, the liquid was raised above the upper timing mark by nitrogen pressure and the fall of the meniscus timed between the marks with an accurate stopwatch. Six to twelve values were averaged for each viscosity determination.

The viscosities were calculated by means of the following equation

$$\eta = (\rho_l - \rho_v)(Ct - B/t) \qquad (1)$$

(η = viscosity in centipoises, ρ_l = liquid density in g./cc., ρ_v = vapor density in g./cc., t = flow time in seconds, B and C, instrument constants.)

The constant, C, was assumed to be constant over the entire range of temperatures, since mathematical treatment of the Poiseuille equation for capillary flow indicates that such is the case if expansion of the viscometer glass is linear with temperature. This assumption was verified experimentally in the range of 20–100° by calibration of the viscometer with water at 20° and 50°, with one N.B.S. viscosity standard at 20°, 50° and 100°, and with another N.B.S. viscosity standard at 50 and 100°. The constants calculated from all determinations agreed within ±0.1%.

The observed viscosities of the *n*-paraffins are listed in Table III along with the experimental data of average flow time and temperature of measurement. The per cent. deviation measure for the flow times is also included in the table as an index of the precision of the determinations. The logarithms of the observed viscosities are plotted

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[6] A. F. Shepard, A. L. Henne and T. Midgley, Jr., THIS JOURNAL, **53**, 1948 (1931).

[7] C. D. Hurd, "The Pyrolysis of Carbon Compounds," Chem. Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 537.

[8] Three hours refluxing in air produced only 0.03% benzoic acid.

[9] F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, p. 810.

[10] L. Ubbelohde, *J. Inst. Petroleum Technol.*, **23**, 427–451 (1937).

[11] E. C. Bingham and R. F. Jackson, *Bull. Bur. Stands.*, **14**, 75 (1918).

TABLE III

VISCOSITY OF n-PARAFFINS (OBSERVED EXPERIMENTAL DATA)[a]

Compound		C_5	C_7	C_8	C_9	C_{11}	C_{13}		C_{17}		C_{28}	C_{36}	C_{64}
Mol. wt.		72.15	100.20	114.22	128.25	156.30	184.35		240.46		394.74	506.95	899.68
−10.10°	Av. flow, sec.	51.56	87.52	116.70[d]	157.54	287.09	447.8[e]	388.23[f]					
	Deviation, %[b]	0.03	0.01	0.01	0.01	0.01	0.02	0.00					
	Viscosity, cp.	.3117	.6016	.8314[d]	1.1518	2.1717	3.446[e]	2.971[f]					
	Accuracy, %[c]	.4	.2	.2	0.2	0.2	0.2	0.2					
20.00°	Av. flow, sec.	43.01	64.40	80.76	102.23	162.18	251.10		518.25[g]	458.83[h]			
	Deviation, %	0.02	0.01	0.02	0.01	0.01	0.1		0.00	0.00			
	Viscosity, cp.	.2404	.4180	.5479	.7165	1.1855	1.8834		4.000[g]	3.526[h]			
	Accuracy, %	.4	.2	.2	.1	0.1	0.1		0.2	0.2			
50.00°	Av. flow, sec.		51.07	61.32	74.49	108.28	154.11		288.55		768.93[i]		
	Deviation, %		0.01	0.02	0.01	0.00	0.01		0.01		0.02		
	Viscosity, cp.		.3100	.3928	.4968	.7609	1.1177		2.1696		5.965[i]		
	Accuracy, %		.4	.3	.3	.2	0.2		0.2		1.2		
Near 100°	Obsd. temp., °C.		99.97	99.50	99.76	99.74	99.72		99.71		99.43	99.91	110.08
	Av. flow, sec.		39.30	44.78	51.28	67.74	88.71		143.23		385.76	641.43	1844.1
	Deviation, %		0.02	0.02	0.01	0.01	0.01		0.01		0.00	0.01	0.02
	Viscosity, cp.		.2099	.2563	.3093	.4395	.6019		1.0215		2.898	4.892	14.346
	Accuracy, %		.5	.5	.4	.3	.2		0.2		1.4	1.5	1.3
Near 150°	Obsd. temp., °C.				150.02	150.05	150.06		149.97		149.92	150.01	150.04
	Av. flow, sec.				40.02	49.33	60.40		89.55		203.94	316.74	946.8
	Deviation, %				0.03	0.02	0.02		0.02		0.01	0.00	0.01
	Viscosity, cp.				.2136	.2893	.3763		.5986		1.4615	2.315	7.140
	Accuracy, %				.5	.5	.4		.3		1.3	1.4	1.5
Near 200°	Obsd. temp., °C.					201.16	201.31		201.26		201.42	201.04	201.28
	Av. flow, sec.					39.25	46.19		63.27		128.76	190.91	512.0
	Deviation, %					0.04	0.02		0.02		0.01	0.01	0.03
	Viscosity, cp.					.2033	.2592		.3900		.8743	1.3309	3.705
	Accuracy, %					.6	.6		.5		1.2	1.4	1.6
Near 250°	Obsd. temp., °C.								248.46		248.32	247.94	248.25
	Av. flow, sec.								49.90		93.43	133.87	334.76
	Deviation, %								0.2		0.01	0.01	0.01
	Viscosity, cp.								.2813		.5994	.8889	2.326
	Accuracy, %								.6		1.3	1.4	1.5
Near 300°	Obsd. temp., °C.								300.60		300.66	300.39	300.60
	Av. flow, sec.								40.47		69.84	97.26	229.46
	Deviation, %								0.03		0.02	0.01	0.01
	Viscosity, cp.								.2023		.4156	.6068	1.5193
	Accuracy, %								.8		1.5	1.5	1.5

[a] No. 1 Ubbelohde viscometer used for all determinations. [b] % Deviation measure $= \frac{100}{\sqrt{n.t}} \cdot \frac{\Sigma(d)}{n}$ where d = deviation, t = average flow time, n = number of observations. [c] Maximum probable error as described in text. [d] At −10.00°. [e] At −5.48°. [f] At 0.00°. [g] At 22.00°. [h] At 27.00°. [i] At 62.00°.

vs. reciprocal absolute temperature in Fig. 1. It will be noted that the data do not define straight lines for those compounds measured over a wide temperature range. The significance of this observation will be discussed in subsequent papers.

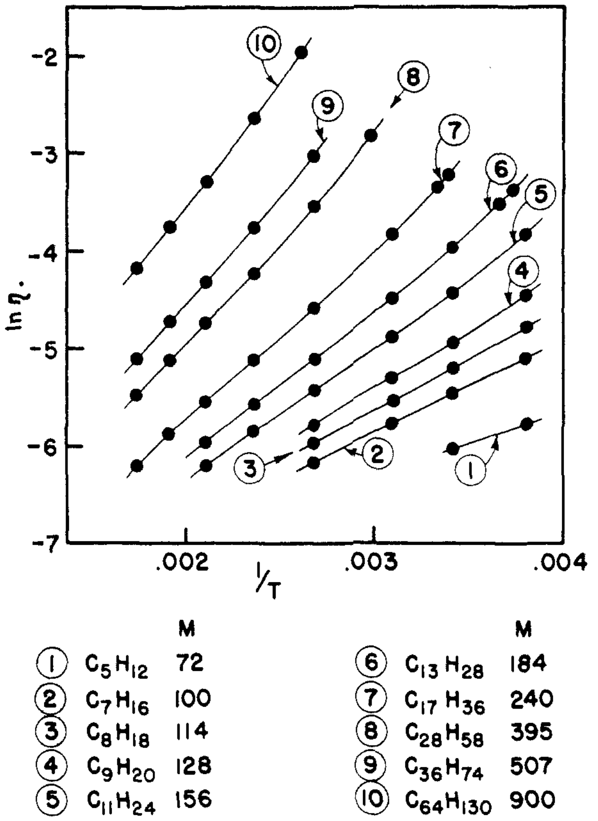

Fig. 1.—Viscosity of *n*-paraffins.

Accuracy of the Viscosity Data

The accuracy of the viscosity values reported here depends directly upon the accuracy of the timing, of the density measurements and of the viscometer constants. In addition, these values are subject to further error to the extent that the temperatures are inexact and the compounds impure. The errors contributed by each of these factors are by no means constant over the entire range of temperatures and molecular weights.

The stopwatch used in this study could be read to ±0.01 second and comparison of it with a standard watch showed no divergence for either short or long time intervals. Hence real timing errors were chiefly personal. Apparent timing errors could be introduced by temperature fluctuations and suspended particles in the liquid. The deviation measures of Table III show that all of these influences were very small. The combined errors of timing and density are judged to be no greater than ±0.1% for any determination.

Assuming Bingham and Jackson's[14] values for the absolute viscosities of water to be correct, the viscometer constant C is believed accurate to ±0.02% and constant B to ±2.5%. From equation (1) it is seen that inaccuracy in B has a variable effect on the accuracy of the viscosity. Thus for a flow time of 40 seconds the above error in B causes an error of ±0.4% in the viscosity. For a flow time of 75 seconds the error in the viscosity is ±0.1% and for longer times the effect rapidly vanishes. Although the viscometer constant C should not change with temperature, an error of 0.1% per 100° from the calibration temperature is assumed, nevertheless, in order to allow for possible unknown effects.

Since viscosity is a property of liquids that possesses a very large temperature coefficient, it is obvious that temperature inaccuracies will cause considerable error in the viscosity values. Equation (2), with the proper value of A, provides a ready way to assess the viscosity error resulting from a temperature error dT.

$$\frac{d \ln \eta}{dT} = -\frac{500 \ln \eta + 4023 + A(T - 373)}{T^2} \quad (2)$$

where η is the viscosity in poises, T is absolute temperature. The value of A is substantially constant at 4.54 for molecular weights 72 through 240, but is represented by $A \cong -(2 \ln \eta + 0.0125\ T)$ for molecular weights above 240. Equation 2 will be developed in a later paper. It will be noted that the absolute value of this differential increases with viscosity for any given temperature. Hence, maximum error in viscosity for unit temperature inaccuracy occurs with the most viscous compound at any stated temperature. In Table IV below, errors are calculated on this basis for the estimated temperature errors.

Table IV

Error in Viscosity Due to Temperature Inaccuracy

t, °C.	Δt	Compound	Error in η, %
−10	±0.04	Undecane	∓0.09
20	± .02	Heptadecane[a]	∓ .05
50	± .04	Heptadecane	∓ .07
100	± .05	Hexatriacontane	∓ .08
150	± .1	Tetrahexacontane	∓ .15
200	± .3	Tetrahexacontane	∓ .34
250	± .3	Tetrahexacontane	∓ .26
300	± .3	Tetrahexacontane	∓ .22

[a] Measured at 22°.

The presence of impurities in the compounds also will alter their viscosity—the exact alteration depending upon the nature and amounts of the contaminants. The chief impurities to be expected in this series of paraffins would be paraffins of slightly different molecular weight and/or isomers. Conceivably, proper distribution of impurities above and below the chief component could result in an unaltered viscosity. However, it is necessary to consider the most unfavorable situation—that where the impurities all are of either higher or lower molecular weight. Judging from their freezing points and densities upon fractionation, it is believed that the hydrocarbons up through heptadecane are extremely pure. The higher paraffins, especially tetrahexacontane, are probably somewhat impure.

An empirical molecular weight relationship, to be developed in a subsequent paper, enables a quantitative estimate of the error caused by such impurities. The results of such a calculation are given in Table V for what seems a probable kind and amount of impurity.

TABLE V

ERROR IN VISCOSITY DUE TO IMPURITIES

Compound	Assumed impurity, %		Δm	t, °C.	Error in η, %
Heptadecane	0.2	$C_{15}H_{32}$	−0.06	22	−0.04
Octacosane	5	$C_{24}H_{50}$	−2.8	62	−1.0
Hexatriacontane	5	$C_{32}H_{66}$	−2.8	100	−0.7
Tetrahexacontane	10	$C_{60}H_{122}$	−5.6	110	−0.9

The maximum probable error in each viscosity measurement (listed in Table III under "Accuracy, %") was calculated on the basis of the foregoing considerations, and it is felt almost certain that the correct values lie within the region of the assigned error. It should be noted that the assigned error values are many times the degree of precision (reproducibility) obtainable with the apparatus. In several cases values were redetermined later using repurified samples and measuring the temperatures with the standard platinum resistance thermometer. The new values in these cases checked the original ones to ±0.1–0.2%.

A discussion of the results of these measurements will be published elsewhere.

S. CHARLESTON 3, W. VA. RECEIVED SEPTEMBER 15, 1950

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Dipole Moments of Some Acid Amides and the Structure of the Amide Group[1]

BY W. W. BATES[2] AND MARCUS E. HOBBS

The structure, association and direction of the group moment of acid amides have been studied by means of dipole moment measurements on a series of aliphatic and aromatic amides in dilute benzene and dioxane solutions. The group moment is found to be directed at an angle of about 70° to the C–C axis in the aromatic compounds. Association of amide molecules is found to occur in quite dilute benzene solutions and seems to be influenced quite significantly by the nature of the hydrocarbon fraction of the molecule. The structure of the amide group, as determined from dipole moment measurements, seems consistent with the keto form and does not require significant contributions from the highly polar resonance form usually associated with this group.

A knowledge of the details of the structure of the amide group is of considerable importance because of the role this group plays in many physiologically active compounds and in fibers. The information that might be made available on this problem through the measurement of the dipole moments of the amides has been limited to only a few studies.[3] In view of this the systematic investigation of the dipole moments of a series of quite pure aliphatic and aromatic acid amides was undertaken in the attempt (1) to establish the magnitude and direction of the amide group moment, (2) to study the relation of association of the amides in dilute solutions to the geometry of the molecule and (3) to furnish data for a critical examination of the possible relations between the electric moment values and the structure of the amide group. The particular compounds investigated in dilute benzene and dilute dioxane solutions were formamide, acetamide, propionamide, *n*-butyramide, isobutyramide, benzamide, *m*- and *p*-chlorobenzamide and *m*- and *p*-bromobenzamide. In addition approximate values of the dipole moments of oxamide and malonamide were determined from measurements in very dilute dioxane solutions.

Experimental

Materials and Methods.—Jones and Laughlin reagent grade benzene was dried over sodium wire for several days, refluxed over fresh sodium wire and finally distilled from fresh sodium through a 180 cm. Dufton column. The middle fraction was then redistilled in the same manner before use. Some benzene was recovered from measurements and used again. The recovery consisted in a simple distillation, followed by refluxing with 20% potassium hydroxide solution, drying with potassium hydroxide and finally refluxing over sodium wire. Two subsequent distillations over sodium yielded a product indistinguishable, by means of the dielectric constant, from the best benzene. The average b.p. and density of all benzene used is given in Table I. The benzene used in a particular measurement boiled over an average range 0.01°. The dioxane used was obtained from the Carbide and Carbon Chemical Corp. The purification procedure followed was storage over pellets of potassium hydroxide for several weeks, followed by siphoning off of the clear liquid. Three liters of this product was then mixed with 300 ml. of 1.0 *N* sulfuric acid and refluxed 12 hours with air bubbling through the liquid. The product so obtained was distilled from potassium hydroxide pellets and then refluxed with fresh sodium wire until the sodium remained bright. This refluxing was followed by distillation from sodium wire through a 180 cm. Dufton column. The middle fraction was stored and distilled over sodium just prior to use. Dioxane was recovered from measurements by refluxing over sodium until corrosion ceased, then carrying out a simple distillation. This recovered product was then treated in the same manner as the middle fractions of the originally purified material. Physical constants for the average of all samples of dioxane used are given in Table I. The average range in boiling point of any particular sample of dioxane used in a measurement was 0.03°.

The freezing points of all solutes are collected in Table I along with literature reference values. The freezing points were determined with calibrated thermometers by the cooling curve method and generally were constant for one-half frozen to better than 0.02°, or the product was further purified. The temperature limits shown in Table I are an estimate of the accuracy of the freezing temperature. When fractional freezing was used in the purifications, procedures, apparatus and technique similar to those of the cylindrical tube method of Schwab and Wichers[4] were employed.

Formamide.—Eastman Kodak Co. best grade of formamide was dried over anhydrous sodium sulfate and then vacuum distilled. The middle fraction from the distillation was then fractionally crystallized three times in the absence of moisture. Essentially one-half of the product was discarded in each crystallization.

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(1) Part of the thesis of W. W. Bates submitted in partial fulfillment of the requirements of the Ph.D. degree in chemistry at Duke University.

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(3) (a) C. T. Zahn, *Physik. Z.*, **33**, 515 (1933); (b) G. Devoto, *Gazz. chim. ital.*, **63**, 495 (1933); (c) Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934); (d) Davis, Bridge and Svirbely, *ibid.*, **65**, 857 (1943).

(4) Schwab and Wichers, *J. Research Natl. Bur. Standards*, **32**, 253 (1944).