Summary

1. The electrical conductance and density of solutions of potassium bromide from 0.00025 to 3.75 molar and of lanthanum chloride from 0.00025 to 1.0 molar have been determined at both 0° and 25°.

2. The densities may be expressed by equations having the form suggested by Root throughout the range of concentration studied.

3. The Shedlovsky conductance equation fits the data for potassium bromide up to 0.1 N better than any other equation, but this equation is not applicable to the data on lanthanum chloride.

4. The Jones and Dole equation fits the data on both salts and at both temperatures up to high concentrations better than any known equation. This equation gives higher values for Λ_0 than either the Onsager or Shedlovsky method of extrapolation and a greater limiting slope than is predicted by the Onsager equation.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 22, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

Derivatives of Normal Pentane and Normal Heptane. III. Dipole Moments of the Bromoethoxy and the Dibromo Derivatives

BY MARY L. SHERRILL, MARTHA E. SMITH AND DOROTHY D. THOMPSON[1]

Previously one of the authors[1a] has measured the dielectric constants and determined the electric moments of a series of derivatives of normal heptane. The dielectric constant and moment were found to be considerably smaller for the halogen derivatives with the substituent in the 1-position than for those with the substituent in the 2-, 3- or 4-positions. The moments of the latter are the same although the dielectric constants of these differ somewhat from each other.

In connection with an investigation of unsaturated hydrocarbons, a series of bromoethoxy derivatives and the corresponding dibromo derivatives of *n*-pentane and *n*-heptane have been prepared and their physical constants determined. It seemed that an accumulation of dielectric constant and electric moment data covering parallel series of compounds should ultimately be valuable in the field of molecular structure and their dielectric constants have been measured. The boiling points, refractive indices and densities of the compounds, including the density of the benzene solutions used in the dielectric constant measurements, were determined by methods given in a previous paper.[2] The dielectric constants were determined by the resonance method. The apparatus consisted of two heterodyne oscillators, connected by a resistance-coupled amplifier and a calibrated condenser. The capacity measurements of the pure compounds were of a precision of 1 part in 500. The condenser used for the capacity measurements of the benzene solutions at 25 ± 1° was a Type 222-S Precision Condenser (General Radio Company). The calibration of this condenser was accurate to one-tenth of a micro-microfarad. The wave length was 100 meters. The condenser used for measuring the capacity of the liquids is a nickel cell with an adjustable plate. The probable error in the dielectric constant is 0.5%.

Experimental

Preparation of Compounds

β-Ethoxyalkyl Bromides, $RCHBrCHOC_2H_5R'$.—These compounds have been synthesized according to the method used by Boord and co-workers.[3] The method involved the synthesis of the α-chloroalkyl ethyl ether, the bromination of the ether and the reaction of the α,β-dibromoalkyl ethyl ether thus formed with a Grignard reagent, $R'MgX$. The best yields of both crude and purified β-ethoxyalkyl bromides were obtained when an excess (0.5 mole) of the Grignard reagent was used. The repeated distillation of the bromo ethers with alkali, suggested by Boord and co-workers, while removing any excess of the dibromo ether has been found to form some of the unsaturated ether, $RCH{=}COC_2H_5R'$.[4] Therefore the bromo ethers were purified by distillation in vacuo until products of constant densities and refractive indices were obtained. The positions of the bromine and the ethoxy groups were confirmed by the transformation of each bromo ether into the corresponding olefin.

---

(1) Holder of a Skinner Fellowship, Mount Holyoke College, 1931–1932.

(1a) Jacques Errera and Mary L. Sherrill, THIS JOURNAL, **52**, 1993 (1930).

(2) Mary L. Sherrill, *ibid.*, **52**, 1982 (1930).

(3) Swallen and Boord, *ibid.*, **52**, 651 (1930); Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); Shoemaker and Boord, *ibid.*, **53**, 1505 (1931).

(4) Lauer and Spielman, *ibid.*, **53**, 1533 (1931); Soday and Boord, *ibid.*, **55**, 3293 (1933).

Dibromo Derivatives of *n*-Pentane and *n*-Heptane.—The 1,2- and 2,3-dibromopentanes and the 1,2-, 2,3- and 3,4-dibromoheptanes were prepared by the addition of bromine dissolved in carbon tetrachloride to a solution of the corresponding olefin in the same solvent at −5° and with light excluded. After the solvent was completely removed the dibromides were purified by distillation in vacuo until products of constant densities and refractive indices were obtained.

Benzene.—Benzene (Kahlbaum, for Molecular Weight Determinations, b. p. 80.0°) was dried over and fractionally distilled from phosphorus pentoxide. Previous work had shown that recrystallization was not necessary.

TABLE I

PHYSICAL CONSTANTS OF THE BROMOETHOXY DERIVATIVES OF *n*-PENTANE AND *n*-HEPTANE

Derivative, ethoxypentane	B. p., °C.	Press., mm.	d^t_4		n^{20}_D	Molecular refraction Found	Calcd.
1-Bromo-2-	75.4– 76.0	22	1.1798/20°	1.1856/15°	1.4462	44.07	43.93
2-Bromo-3-	70.0– 70.2	24.5	1.1754/20°	1.1698/25°	1.4448	44.16	43.93
3-Bromo-2-	70.6– 70.8	22.5	1.1831/20°	1.1888/15°	1.4471	44.06	43.93
Ethoxyheptane							
1-Bromo-2-	101.2–101.6	19.5	1.1054/20°	1.1092/15°	1.4483	54.08	53.17
2-Bromo-3-	97.6– 97.8	21	1.0621/20°	1.0556/25°	1.4455	55.94	53.17
3-Bromo-4-	84.0– 84.2	12	1.0983/20°	1.1034/15°	1.4483	54.41	53.17

TABLE II

DIBROMOPENTANES AND DIBROMOHEPTANES

Compound	B. p., °C.	Press., mm.	d^{20}_4	n^{20}_D	Molecular refraction Found	Calcd.
1,2-Dibromopentane	81.6– 82.0	27	1.6722	1.5063	40.87	40.82
2,3-Dibromopentane	52.6– 52.8 71.1– 71.3 178 –179	9 20 746	1.6789	1.5079	40.72	40.82
1,2-Dibromoheptane	110.1–110.2	19	1.5086	1.4986	50.17	50.05
2,3-Dibromoheptane	101.0–101.2	17	1.5139	1.4992	50.03	50.05
3,4-Dibromoheptane	107.2–107.4	24	1.5182	1.5010	50.07	50.05

TABLE III

POLARIZATION AND ELECTRIC MOMENTS OF DERIVATIVES OF *n*-PENTANE AND *n*-HEPTANE AT 25°

Derivative	d^t_t	ϵ	P	P_∞	P_E	$\mu \times 10^{18}$
1-Bromo-2-ethoxypentane	1.1740	6.45	106.6	155	44.28	2.30
1-Bromo-2-ethoxyheptane (20°)	1.1054	5.48	121	162	54.05	2.27
2-Bromo-3-ethoxypentane	1.1698	6.40	107.2	134	44.16	2.05
2-Bromo-3-ethoxyheptane	1.1056	5.22	124.0	146	55.97	2.08
3-Bromo-2-ethoxypentane	1.1774	8.24	117.2	138	44.06	2.13
3-Bromo-4-ethoxyheptane	1.0932	6.24	129.5	148	54.40	2.11
1.2-Dibromopentane	1.6650	4.39	73.03	105	40.89	1.75
1.2-Dibromoheptane	1.5022	3.77	82.48	115	50.17	1.76
2.3-Dibromopentane	1.6720	5.43	81.72	135	40.85	2.12
2.3-Dibromoheptane	1.5082	5.08	98.60	144	50.03	2.13
3.4-Dibromoheptane	1.5120	4.70	98.86	144	50.07	2.13

Discussion of Results

A detailed interpretation of the electric moments of these bromoethoxy and dibromo derivatives is not within the scope of this paper but merely a correlation of these data with the data previously obtained for aliphatic ethers, mono- and di-halogen aliphatic compounds is given.

In the case of ethers it has been found that the moment of methyl ethers (1.29 or 1.32 × 10^{-18})[5] is greater than that of ethyl ether with a moment[5a,6] of 1.12 × 10^{-18} and that there is a further decrease in propyl ether with a moment of 0.85 × 10^{-18}.[6c] The diisoamyl ether, however, has a moment[6a] of 1.0 × 10^{-18}, practically equal to that of ethyl ether and the more unsymmetrical ethyl isoamyl ether has a moment slightly higher than either (1.2 × 10^{-18}).[6a] It would therefore seem probable that the more unsymmetrical secondary ethyl ethers, methylpropylmethyl ethyl ether, methylamylmethyl ethyl ether, diethyl-

---

(5) (a) Stuart, *Z. Physik*, **51**, 490 (1928); (b) Parts, *Z. physik. Chem.*, **12B**, 323 (1931).

(6) (a) Estermann, *Z. physik. Chem.*, **1B**, 134 (1928); (b) Williams, THIS JOURNAL, **50**, 2350 (1928); (c) Sänger and Steiger, *Helv. Phys. Acta*, **2**, 136 (1929); (d) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, pp. 87–89 and bibliography.

methyl ethyl ether, dipropylmethyl ethyl ether and ethylbutylmethyl ethyl ether, would have moments higher than that of isoamyl ethyl ether.

A bromine substituted in these ethers on a carbon adjacent to the ether group brings into the molecule a second polar group and the moment obtained should be a resultant of the two effects, the magnitude depending on the distortion of the molecule due to induction, on the repulsion between the two polar groups, and also on the rotation about the C–C, C–O and C–Br bonds.[7] The dipole moments of primary, secondary and tertiary aliphatic halides have been shown by Parts[8] to increase from the primary to the secondary to the tertiary halide. It has also been found[9] that the moment induced by the polar group is transmitted through the first two carbons of the chain in *n*-alkyl halides while the atoms beyond these two do not have appreciable moments induced in them. This is evidenced by the fact that the *n*-butyl and isobutyl halides[8a] have the same moments, the branching of the chain being too far away from the principal doublet to have any marked effect in isobutyl compounds. The secondary butyl halides, however, have a higher moment and the tertiary still higher.

The moments of the heptyl halides[1,10] indicate the same effect, when the halogen is moved from the end of the chain to the second carbon atom, the moment rises due to induction in these two, but when the halogen is moved farther along the chain there is no change in the moment.

In view of these facts it seems significant that the values of the moments of the bromoethoxypentanes and the corresponding bromoethoxyheptanes are so nearly identical. The moment 2.3×10^{-18} of the 1-bromo-2-ethoxy derivatives, while much higher than either the unsymmetrical isoamyl ether or the monobromoheptanes, seems satisfactory as compared with the values for dihydroxy derivatives, for example glycol with a moment of 2.28×10^{-18} and 1,2-dihydroxypropane with a moment of 2.25×10^{-18}, as reported by Smyth and Walls.[11] The lower and practically identical values of the 2-bromo-3-ethoxy and the 3-bromo-4-ethoxy derivatives ($\mu = 2.12 \times 10^{-18}$) may be due to the fact that these molecules are more symmetrical.

The effect of two halogen substituents has been studied in the case of some di-halogen derivatives of methane, ethane and propane. When the two halogens are on the same carbon atom it has been found that the moment increases from methylene chloride to 1,1-dichloropropane and that 2,2-dichloropropane has a still higher moment.[12] Also when the two halogens are on adjacent carbons there is practically no difference between the derivatives of ethane and propane.

The moments of the dibromides of longer chain aliphatics in which the bromine atoms are separated by varying lengths of carbon chain, 2, 3, 4, 5, 6, 9 and 10 carbon atoms,[13] increase as the bromine atoms are separated from each other; for example, the moment of ethylene bromide is 1.50×10^{-18} and that for decamethylene bromide is 2.54×10^{-18}.

The moments of the dibromopentanes and heptanes obtained in this work correspond very favorably with the values to be expected based on those reported for the halides of ethane and propane. The moment of ethyl bromide is 1.86×10^{-18}, of dibromoethane 1.52×10^{-18}, the moment of propyl chloride is 2.00×10^{-18} and that of 1,2-dichloropropane is 1.85×10^{-18}. Also the values for ethylene chloride and 1,1-dichloropropane are practically identical. Moreover, in correspondence with the fact that when the halogen is substituted in the one position (1-bromoheptane, μ is 1.85×10^{-18}) the moment is smaller than when it is substituted in other positions in the chain (2-bromoheptane, μ is 2.05×10^{-18}) the present data give a moment of 1.75×10^{-18} for 1,2-derivatives and a moment of 2.12×10^{-18} for 2,3- or 3,4-bromo derivatives.

Summary

1. The bromoethoxy and dibromo derivatives of *n*-pentane and *n*-heptane have been prepared.

2. The physical constants of these compounds have been determined.

---

(7) Smyth, Ref. 6d, pp. 64–83 and bibliography; Smyth, THIS JOURNAL, **46**, 2151 (1924); *Phil. Mag.*, **50**, 361 (1925); *J. Chem. Physics*, **1**, 190 (1933); Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4243 (1931); Williams, *Z. physik. Chem.*, **138A**, 75 (1928); Meyer, *ibid.*, **8B**, 27 (1930); Smallwood and Herzfeld, THIS JOURNAL, **52**, 1919 (1930).

(8) (a) Parts, *Z. physik. Chem.*, **7B**, 327 (1930); (b) **12B**, 312 (1931).

(9) Smyth, Ref. 6d, pp. 101–102.

(10) Errera and Sherrill, "Leipziger Vorträge," 1929, p. 41.

(11) Smyth and Walls, THIS JOURNAL, **53**, 2115 (1931).

(12) Gross, *Z. physik. Chem.*, **6B**, 215 (1929); Sack, *Ergebnisse exakten Naturwissenschaften*, **8**, 307 (1929); Müller and Sack, *Physik. Z.*, **31**, 815 (1930); Smyth and Rogers, THIS JOURNAL, **52**, 2227 (1930); Smyth, Ref. 6d, p. 103.

(13) Smyth and Kamerling, THIS JOURNAL, **53**, 2988 (1931); Smyth and Walls, *ibid.*, **54**, 2261 (1932); *J. Chem. Physics*, **1**, 200 (1933).

3. The dielectric constant of each compound, pure and in benzene solution, has been measured. From these data the electric moments of the compounds have been determined.

4. These moments are compared with those of aliphatic ethers and with mono-substituted and di-substituted aliphatic halides.

SOUTH HADLEY, MASS. RECEIVED NOVEMBER 27, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Vapor Pressure of Fluorine

BY WILLIAM H. CLAUSSEN

Introduction

The vapor pressure of liquid fluorine has been measured before in this Laboratory by Cady and Hildebrand.[1] We decided to repeat this work because several possibilities for increased accuracy seemed to exist. In the first place, the different runs in the earlier investigation were all made upon one sample of fluorine and it seemed desirable to have some check upon purity. Second, the inclusion of glass parts in the system suggests the possibility of contamination that could be avoided by an all metal apparatus. Third, the use of a diaphragm gage in place of the constant level mercury manometer, and the use of the vapor pressure of pure oxygen as the thermometer in place of the thermocouple used earlier appeared to offer prospects for more accurate work.

Experimental

The fluorine used was generated by the electrolysis of fused potassium bifluoride in the generator used by Cady and Hildebrand.[1] Electrolysis was carried out for several hours before collecting any fluorine to decompose any water present in the electrolyte. The additional precaution was taken of keeping the electrolyte at 150° between runs to prevent water from condensing on the salt. The fluorine was passed through a copper trap cooled with liquid oxygen to remove hydrogen fluoride, carbon tetrafluoride, and oxygen fluoride. The fluorine was always passed through the apparatus for one hour to drive out the air. The volume of fluorine passed through was approximately 60 times the volume of the apparatus. The apparatus was then closed by means of a Monel metal needle valve and cooled with liquid air to condense the gas being generated at the rate of about five grams per hour. After collecting from 10 to 15 g. of liquid, the apparatus was closed off from the generator by means of another Monel metal needle valve.

The fluorine was contained in an annular cell of thin Monel metal in the center of which was a second cell for liquid oxygen that was condensed there at the same time fluorine was condensed in the outer cell. About 8 g. of electrolytic distilled oxygen was used. This fluorine–oxygen cell was surrounded by a calorimeter block of the design used by Giauque and Wiebe.[2] The whole was then surrounded by a Monel metal can which could be filled with pure hydrogen at a pressure of about 10 mm. during condensation of the liquids and subsequent cooling by evaporation of the liquid air under 5 cm. pressure. The apparatus was contained in a 90 cm. Dewar vessel fitted with a vacuum-tight top through which all tubes from the apparatus passed. After cooling to about 68°K. the hydrogen was pumped down to a pressure of 10^{-5} mm. The temperature was obtained by reading the vapor pressure of the liquid oxygen on a mercury manometer and using the Leiden equation for the vapor pressure.[3] The temperature rose about 0.2° per hour because of the heat leak through the Monel metal tubes leading to the cell, the calorimeter block being kept 0.1 to 0.5° above the cell temperature by means of a constantan heating coil to prevent distillation. The temperature difference was measured with a copper–constantan differential thermocouple and a type K potentiometer.

The fluorine vapor pressure was taken as the air pressure needed to balance a metal null instrument that was constructed of a thin (0.12 mm.) hard German silver diaphragm 7.6 cm. in diameter fitted with an ordinary lever arrangement and a mirror from which was reflected a spot of light that fell on a scale one meter away. The instrument was sensitive to a difference of pressure of 0.1 mm. The pressures of the oxygen and fluorine

---

[1] Cady and Hildebrand, THIS JOURNAL, **52**, 3839 (1930).

[2] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

[3] Cath, *Comm. Phys. Lab. Univ. Leiden*, **152*d*** (1918). The equation is $\log_{10} P(\text{atm.}) = -419.31/T + 5.2365 - 0.00648\, T$.