pendent of the frequency. When either polarization or the shunt effect are present and the bridge is balanced for the fundamental frequency it is not balanced for the first harmonic which will appear on the screen as a sine wave with twice the number of peaks as the fundamental. The harmonic can be made negligible by suitable tuning if desired. The precision of the balance is not affected by the appearance of the harmonic because even a slight unbalance of the fundamental frequency distorts the pure sine wave form of the harmonic and is therefore readily apparent. Since the harmonics cause less trouble when using the oscillograph than with a telephone it is less important to eliminate them by tuning. We do not know whether the harmonic comes solely from the oscillator or is also introduced as a result of the process of electrolysis in the cell, and therefore is one aspect of the complex phenomena called "polarization." At any rate it is clear that even if the harmonics are strong they will cause much less difficulty when using the oscillograph than with a telephone.

Summary

The utilization of the cathode-ray oscillograph instead of the telephone as a detector for precision measurements of conductance of electrolytes is described. The cathode-ray oscillograph has the following advantages over a telephone: (1) Visual observation is less tiresome and at least as precise as auditory observations. (2) The resistance and capacitance balance of the bridge can be made substantially independent. (3) Outside disturbances (pick-ups) are more readily traced to their source and eliminated, or more easily ignored if it is not feasible to eliminate them. (4) Measurements can be made over a greater range of frequency. (5) Harmonics and transients can be seen as such and are therefore less troublesome. (6) Progressive or periodic changes in conductance due to chemical reactions or variations in temperature can be followed more easily.

For the normal person the only advantage of the telephone is that it is less expensive than the oscillograph.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 11, 1940

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Vapor Pressures of Some Organic Compounds. I.[1]

BY JAMES M. STUCKEY[2] AND JOHN H. SAYLOR

A program of research on the solubilities of organic compounds has been in progress for several years in this Laboratory. The concept of vapor solubilities[3,4] has been of use in correlating the solubilities of various organic compounds.

The calculation of these vapor solubilities necessitates the knowledge of the vapor pressures of the organic compounds. Therefore it was decided to measure the vapor pressures of some of these compounds as there is considerable disagreement in the literature, particularly at low temperatures, and in some cases few or no measurements are to be found. The determinations were made between 0 and 75° because the solubilities determined in our laboratory have been within this temperature range.

Experimental

Method.—The method used was essentially the same as that devised by Ramsay and Young.[5] A diagram of the apparatus is shown in Fig. 1; it is very similar to that used by Linder.[6] The temperature was measured by means of a six-junction thermel constructed of no. 30 constantan wire and no. 36 copper wire and insulated with cellulose acetate. The e. m. f. measurements were made with a Leeds and Northrup type K-2 potentiometer and a Leeds and Northrup No. 2500-a galvanometer which had a sensitivity factor of 0.5 mmv./mm.

The thermel was calibrated in a well-stirred water-bath against a set of Goetze thermometers graduated in 0.02° which had been calibrated by the Physikalisch-Technische Reichsanstalt. The comparisons were made at intervals of about 5° ranging from 0 to 80°. In all measurements with the thermel the ice-bath was prepared in a manner similar to that described by Roper.[7] The data were fitted

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[1] This work was supported in part by a grant from the Research Council of Duke University.

[2] This paper was taken from the thesis submitted by James M. Stuckey to the Graduate School of Duke University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1940.

[3] Saylor, Stuckey and Gross, THIS JOURNAL, **60**, 373 (1938).

[4] Gross, Rintelen and Saylor, *J. Phys. Chem.*, **43**, 197 (1939).

[5] Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

[6] Linder, *J. Phys. Chem.*, **35**, 531 (1931).

[7] Roper, THIS JOURNAL, **60**, 866 (1938).

TABLE I

BOILING POINTS, FREEZING POINTS AND CONSTANTS OF THE VAPOR PRESSURE EQUATIONS

Substance	B. p. range, °C.	Previously obsd. B. p., °C.		Refs.	Constants of the equations $\log P = \frac{-A}{T - C} + B$ A	B	C
Benzene	80.06–09	80.09		10	1323.06	7.12491	41.23
o-Chlorotoluene	158.93–97	159.4	159.15	11, 12	1701.60	7.29547	45.42
m-Chlorotoluene	161.74–75	162.0		11	1887.31	7.62515	33.40
o-Bromotoluene	181.37–43	180.65	181.75	11, 13	1913.46	7.50879	38.34
m-Bromotoluene	184.00–02	183.9		11	2049.14	7.75409	31.44
Methylcyclohexane	101.10–25	100.3	101.20	14, 15	1336.93	6.95423	45.52
Methyl amyl ketone	150.18–32	150.2		16	1650.47	7.36537	54.48
					$\log P = \frac{-A}{T} - 5 \log T + B$		
o-Xylene	144.39–41	144.0	144.4	14, 17	2908.07	22.95279	
m-Xylene	139.20–26	139.3	139.15	12, 17	2870.38	22.92341	
p-Xylene	138.33–38	138.4		15, 17	2851.90	22.88436	
	13.20–12.95 (F.P.)	13.20 (F.P.)		15			
Mesitylene	164.54–66	164.6		14	3122.45	23.23680	
Ethylbenzene	136.32 ± .02	136.15	136.28	18, 19	2847.75	22.90283	
p-Chlorotoluene	161.98–99	162.4		11	3041.02	23.07210	
	7.30–15 (F.P.)	7.4 (F.P.)		20			

by the method of averages to a cubic equation. The mean deviation for all the temperatures calculated from the equation and those noted on the thermometers was 0.013°.

Two different manometers were used to measure the pressures. For pressures above 10 mm. of mercury an improved mercury U-gage, E, Fig. 1, designed by Zimmerli[8] was used. An oil manometer F, Fig. 1, designed by Hickman[9] was used to measure all pressures below 10 mm. of mercury. The *n*-dibutyl phthalate used in this gage was purified by the method described by Hickman. Its density referred to water at 4° was determined in duplicate at 10, 30 and 50° and found to be 1.0546, 1.0381 and 1.02175 g./ml., respectively.

The manometers were read by means of a cathetometer which was calibrated against a standard meter bar and could be read to 0.05 mm. Every pressure recorded was the average of several readings which could be repeated to 0.1 mm. of mercury on the U-gage and 0.01 mm. of mercury on the oil manometer. The cathetometer readings were reduced to mm. of mercury at 0°C., 45° latitude and sea level.

In making the measurements, the thin-walled end of the thermel well A, Fig. 1, was wrapped with a little cotton wool and immersed in the organic liquid to be measured. This liquid was always preheated to a temperature above that at which the measurements were being made. The ground-glass joint bearing the well was then quickly placed in tube B, the pump started and the pressure in the system reduced to approximately that desired.

The exposed part of the thermel and the thermel well were wrapped with aluminum foil to within a few mm. of the cotton. The exposed part of the thermel was further protected from the radiation of the flame used to heat the bath by means of the asbestos shield N, Fig. 1. Thermal contact between the thermel and its well was made by the use of mercury. It was found necessary to have sufficient mercury in the well to cover the thermel one to two centimeters deep. The bath around tube B was always 20 to 40° above the temperature at which the determination was made.

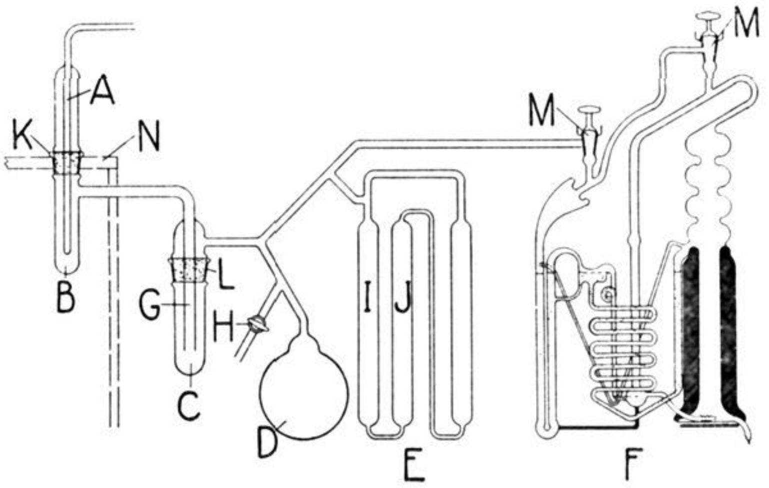

Fig. 1.—The vapor pressure apparatus: A, thermel well; B, outer tube; C, G, trap; D, 3-liter flask; E, mercury manometer; F, oil manometer; H, pump connection; I, J, reading limbs; K, L, ground-glass joints; M, mercury-seal stopcocks; N, asbestos shield.

After the system was pumped down, e. m. f. measurements were made every minute or so until the temperature changed only slightly, in most cases only a few hundredths of a degree. The pressure in the system was read at inter-

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(8) Zimmerli, *Ind. Eng. Chem., Anal. Ed.*, **10**, 283 (1938).

(9) Hickman, *Rev. Sci. Instruments*, **5**. 161 (1934).

(10) Smith and Matheson, *Bur. Standards J. Research*, **20**, 641 (1938).

(11) Feitler, *Z. physik. Chem.*, **4**, 66 (1889).

(12) Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).

(13) Timmermans, *Bull. soc. chim. Belg.*, **27**, 334 (1913).

(14) Timmermans, *ibid.*, **30**, 62 (1921).

(15) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926).

(16) Park and Hofmann, *Ind. Eng. Chem.*, **24**, 132 (1932).

(17) White and Rose, *Bur. Standards J. Research*, **9**, 711 (1932).

(18) Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911).

(19) White and Rose, *Bur. Standards J. Research*, **10**, 639 (1933).

(20) "International Critical Tables," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1926.

vals. It was found to remain constant throughout a determination.

Materials.—The three xylenes, ethylbenzene, the three chlorotoluenes, the *o*-bromotoluene and *m*-bromotoluene were Eastman Kodak Co. best grade. With the exception of ethylbenzene these compounds were purified by fractional distillation in a 50-cm. Widmer column using calibrated thermometers. The best boiling fraction of *p*-xylene was further purified by fractional crystallization. The ethylbenzene was treated with sulfuric acid, washed with dilute alkali and water, dried and then fractionated. The benzene and mesitylene were portions of some material which had been purified by Dr. A. A. Maryott and Mr. Horace Russell for use in dielectric constant measurements. The methylcyclohexane and methyl amyl ketone were purified by Mr. V. J. Baxt. The methylcyclohexane was refluxed with a nitrating mixture, washed with dilute alkali and water, dried and fractionated. The methyl amyl ketone was shaken with several portions of ammoniacal silver nitrate, washed, dried and fractionated. Water was obtained from the laboratory supply of distilled water.

All boiling points were corrected to 760 mm. by means of Craft's rule when dp/dt was not available. The boiling points and freezing points when determined are given in Table I together with the values reported in the literature.

Results

The method was tested by making twenty-three measurements of the vapor pressure of water at temperatures ranging from 4.96 to 59.65°. These pressures were compared with those calculated from an equation given by Osborn and Meyers[21] and a mean deviation of 2.2 parts per 1000 was found. As an additional check on the method the vapor pressures of benzene were determined at twenty-seven different temperatures ranging from 0.97 to 53.49°. In all other cases between twenty and thirty individual measurements were made on each compound at temperatures ranging from about 4 to 75°.

The data were fitted by the method of least squares to the following types of equations.

$$\log P = \frac{-A}{T - C} + \mathrm{B} \qquad (1)$$

$$\log P = \frac{-A}{T} - 5 \log T + B \qquad (2)$$

In these equations 0°C. = 273.16 K. The second equation has been employed by Kassel[22] to express experimentally observed vapor pressures of the xylenes and mesitylene. The equation used in each particular case was the one which best expressed the experimental data. The mean deviations between the observed pressures and those calculated from the equation varied from 1 part per 1000 for *m*-xylene to 7 parts per 1000 for mesitylene with an average of about 4 parts per 1000. The constants of the vapor pressure equation used for each substance are given in Table I. In Table II the vapor pressures of benzene calculated for even temperatures are compared with those of other investigators.

TABLE II

THE VAPOR PRESSURES OF BENZENE COMPARED WITH PREVIOUS VALUES

Temp., °C.	Press., mm.				
		Young[23]	Regnault[24]	Radulescu[25]	Scatchard[26]
0	26.32	26.54	25.31	26.32	
10	45.30	45.43	45.25	45.35	
20	74.7	74.66	75.65	75.47	
30	118.5	118.24	120.24		119.16
40	181.8	181.08	183.62		182.70
50	270.4	268.97	271.37		271.34

The vapor pressures of *m*-xylene agree well with those determined by Kassel.[22] The agreement is not so good for *o*-xylene, *p*-xylene and mesitylene. Kassel pointed out that the accuracy of his data is limited both by the method employed and by the fact that he did not purify his materials. The values obtained by Linder[6] for the hydrocarbons at 0° do not agree with those obtained in the present investigation or with those obtained by Kassel. The data of Vvendenski[27] for methylcyclohexane check fairly well with our results while those for ethylbenzene do not. The values for ethylbenzene given by Maess and Müffling[28] do not check ours. Our values agree fairly well with those given by Rechenberg.[29] A few previous determinations[30] made in this Laboratory of the vapor pressures of the hydrocarbons agree with the present data as well as could be expected in view of the limited precision of the previous method. It has been pointed out several times that the data of Woringer used in the "International Critical Tables" are obviously wrong with the possible exception *m*-xylene.

The values obtained by Rechenberg[29] for the three chlorotoluenes, *o*-bromotoluene and *m*-bromotoluene agree quite well with those ob-

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(21) Osborn and Meyers. *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

(22) Kassel, THIS JOURNAL, **58**, 670 (1936).

(23) Young, *J. Chem. Soc.*, **55**, 486 (1889).

(24) Regnault, *Mem. de Paris*, **26**, 339 (1862).

(25) Radulescu and Alexa, *Bull. soc. chim. Romania*, **20**, 89 (1938).

(26) Scatchard, Wood and Mochel, THIS JOURNAL, **61**, 3206 (1939).

(27) Vvendenski, *J. Gen. Chem.* (U. S. S. R.), **2**, 826 (1932).

(28) Maess and Müffling, *Z. angew. Chem.*, **50**, 759 (1937).

(29) Rechenberg, "Einfache und Frakionerte Destillation," Schimmel und Co., Leipzig, 1923.

(30) Rintelen, Saylor and Gross, THIS JOURNAL, **59**, 1129 (1937).

tained in this investigation. Rechenberg's values were calculated from the measurements of Feitler[11] made from around 90° to the boiling points of the compounds.

The vapor pressures of methyl amyl ketone have been measured by Park and Hofmann.[16] The agreement with the present work seems to be fair although their data are given in the form of a small logarithmic plot.

Acknowledgment.—We wish to express our gratitude to Dr. Paul Gross for numerous helpful suggestions made during the course of this investigation.

Summary

The vapor pressures of the xylenes, ethylbenzene, mesitylene, the chlorotoluenes, *o*-bromotoluene, *m*-bromotoluene, cyclohexane and methyl amyl ketone have been measured at temperatures ranging from about 4 to 75°.

The data have been fitted to suitable equations by the method of least squares.

DURHAM, NORTH CAROLINA RECEIVED JULY 17, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF ANATOMY AND INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

Studies on Pituitary Lactogenic Hormone. II. A Comparison of the Electrophoretic Behavior of the Lactogenic Hormone as Prepared from Beef and from Sheep Pituitaries

BY CHOH HAO LI, WILLIAM R. LYONS AND HERBERT M. EVANS

Introduction

Our preparations of pituitary lactogenic hormone have recently been shown to consist in each instance of a single protein, using both electrophoresis[1] and solubility[2] criteria. By the latter technique we have demonstrated that the hormone prepared from sheep pituitaries has a solubility which differs from that obtained from beef. Certain immunological methods had failed to distinguish one from the other.[3] The present report deals with an electrophoretic study of preparations obtained from beef pituitaries as well as further studies on sheep preparations. Sufficient data are now at hand to allow us to make a preliminary comparison of preparations made from the two species.

Experimental

The lactogenic hormone L 287 was prepared from beef pituitaries in essentially the same manner as has been published previously.[4] It has approximately 30 International Units per milligram.

The electrophoresis experiments were carried out with the Tiselius apparatus, with the technique described previously.[1] The migration of the boundary was observed by the schlieren method. The hydrogen ion concentration of the solution was measured with the glass electrode and its conductance with the usual Wheatstone bridge type of circuit and a Washburn conductivity cell. All experiments were conducted at 1.5°.

Fig. 1.—Schlieren band of lactogenic hormone (beef). Exposure was made after passing current for 80 minutes.

Results

In electrophoresis, Preparation L 287 showed a sharp boundary and migrated as a homogeneous substance. Figure 1 represents a typical schlieren photograph which was taken after exposing to the current for eighty minutes a 0.5% solution of the hormone in *p*H 4.19 acetate buffer. On scanning the whole field, there appeared no indications of a second boundary. The mobility of the preparation in different hydrogen ion concentrations is summarized in Table I. Each value[5] was calculated from at least three observations during an experiment. A typical series of readings is shown in Table II. In this experiment

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(1) Li, Lyons and Evans, *Science*, **90**, 622 (1939); *J. Gen. Physiol.*, **23**, 433 (1940).

(2) Li, Lyons and Evans, *ibid.*, in press.

(3) Bischoff and Lyons, *Endocrinology*, **25**, 17 (1939).

(4) Lyons, *Cold Spring Harbor Symposia Quant. Biol.* **5**, 198 (1937).

(5) Shortly after we had finished our study using a mean value $(U_d + U_a)/2$ for the calculation of mobility, Longsworth and MacInnes [THIS JOURNAL, **62**, 705–711 (1940)] suggested that the descending boundaries yield correct values of the mobility. Since the concentration of the protein used in our experiments was below 0.5%, the mean value $(U_d + U_a)/2$ is only slightly higher than the correct value U_d. The conclusions drawn from our data therefore remain unchanged.