interpreted on the basis that vinylidene chloride serves as a moderately unreactive diluent for the more reactive styrene and that the vinylidene chloride cannot polymerize by itself because the vinylidene chloride-type radicals are quickly converted to styrene-type radicals by their preferred reaction with styrene. However, there is no close relation between the rates of polymerization of two monomers by themselves and their relative tendencies to react with free radicals and enter a copolymer. Quantitative study of such relations (including those between the different standards in Table III) must await development of a method for measuring, estimating, or comparing very low concentrations of free radicals in solution.

Other Problems in Copolymerization.—The copolymerization equation is the most useful tool now available for comparing the behavior of monomers in copolymerizations. Its development assumed that the reactions of the growing radicals with monomers depend only on the monomer units which form the free radical ends of the growing chains and on the relative monomer concentrations. The usual small spread in monomer reactivity ratios over a wide range of feed ratios shows that these assumptions are excellent approximations, at least within experimental error. However, as our techniques have improved, we occasionally find instances where the discrepancy among the three pairs of solutions to three equations is beyond our expected experimental error. Some of these effects now seem to be associated with the size of the monomer unit adjacent to the terminal radical units in the growing chains, others with an actual or incipient precipitation of the polymer. Since the effects have become noticeable only with the most careful work, their investigation is difficult. Finally, the effects of temperature on some monomer reactivity ratios give some insight into the manner in which substituents affect reactivity. We have made substantial progress in investigating most of the problems mentioned and we hope to report some of our results in the near future.

Summary

The copolymerizations of acrylonitrile, methyl methacrylate, styrene and vinylidene chloride, taking two monomers at a time, have been studied at 60° with benzoyl peroxide as catalyst. The good correlation of the experimental data by the copolymerization equation which was previously developed indicates that the assumptions made about the chain growth process are substantially correct.

The relative reactivities of the four kinds of monomers with the four kinds of free radicals are compared. The results show clearly that reactions of free radicals with double bonds are specific, that both the ratio and the order of reactivities of a monomer series change as the radical is changed. There is no simple relation between the relative tendencies of two monomers to enter a copolymer and their rates of polymerization alone.

The copolymerization equation is a useful tool for pointing out and measuring the factors which govern copolymerization reactions. Investigation of several of these factors is in progress.

Difficulties in the analysis of certain polymers are discussed.

PASSAIC, NEW JERSEY RECEIVED JUNE 13, 1945

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, RESEARCH AND DEVELOPMENT DEPARTMENT]

Physical Properties of Thiophene[1]

BY FRANK S. FAWCETT AND HERBERT E. RASMUSSEN

In a new process for the production of thiophene, a product has been obtained which has consistently had physical properties differing somewhat from data appearing in the literature. A consideration of the literature data summarized in Table I shows that, while the reported properties have been in general agreement from the time of the earliest observer, the properties of no one sample agree in all respects with a critical average of the data of the several investigators. The melting point especially is in doubt. With larger quantities than have previously been available, it seemed desirable to carry out extensive purification of thiophene and to redetermine its physical properties.

Purification of Thiophene

Four liters of the pilot plant product, obtained as a constant boiling distillate from a 15-theoretical plate column, was washed successively with dilute hydrochloric acid, sodium hydroxide, and distilled water and dried over calcium chloride. Approximately two liters was distilled at atmospheric pressure with a reflux ratio of 50:1 using a rectifying column having the following characteristics: rectifying section, 18 mm. i. d., 235 cm. length; packing, 2.4 mm. o. d. 1.25-turn helices of no. 30 B. & S. gage stainless steel wire; head, total condensation variable take-off; temperature measurement, 1-junction iron–constantan thermocouple with a Leeds and Northrup No. 8662 potentiometer. The product was collected as several fractions substantially all boil-

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[1] Presented at the Spring Meeting, Philadelphia Section of the American Chemical Society, Philadelphia, June 13 1945.

ing in a temperature range of 0.2°. The first and last 25% portions of this distillate were rejected, while central fractions having refractive indices (n^{20}D) equal to 1.5288 ± 0.0001 were combined for use. Fractions adjacent (before and after) to those retained had freezing points differing by not more than 0.2°. By means of the distillation and refractive index data benzene was not detected, and the material was further processed assuming its absence in the central portion retained. Later in the work, however, analyses were obtained by means of the mass spectrometer. This method, capable of detecting one part of benzene in 7000 parts of thiophene (and *vice versa*), showed the benzene content of the first distillation fraction to be 0.37 mole per cent. The combined central portion, amounting to 1 liter, was treated by fractional crystallization in which the entire product contained in an Erlenmeyer flask was slowly cooled with constant swirling in an acetone-bath cooled with Dry Ice until about 90% was frozen, at which point the liquid was decanted and rejected. The refractive index of the product after the fourth and sixth successive stages agreed within 0.00005 and the freezing point within 0.05°. The material (550 ml.) after the final (sixth) crystallization was transferred to a vacuum system; it was then frozen with Dry Ice, evacuated, and melted three successive times to remove gases. It was finally distilled at 30 to 50° into several Pyrex vessels previously cleaned and warmed with a flame while being evacuated. Three ampoules, one of which was later used for the freezing point determination, were sealed under reduced pressure. Mass spectrometer analysis of the product at this stage showed benzene, the only impurity detected, to be present to the extent of 0.06 mole per cent.

A sample of thiophene rejected from the crystallization process was treated with mercuric chloride in alcohol–sodium acetate solution according to the procedure of Volhard as given by Steinkopf.[2] The 2-chloromercurithiophene thus obtained (m. p. 182.2–182.8°) was heated under reflux with dilute hydrochloric acid and the regenerated thiophene extracted from the cooled water mixture with *n*-pentane. The pentane solution was dried over calcium chloride and distilled with a 28-theoretical plate column of the twisted wire gauze type.[3] The properties of the 30 ml. of thiophene obtained were: n^{20}D 1.5285, d^{20}_4 1.0644, f. p. −38.5°, η_{20} 0.664 centipoise. Thus the chemical and physical methods of purification gave products having essentially the same properties (see Table II). The physical method is preferable since in the chemical method inconveniently large quantities of reagents are required and consequently contamination is likely.

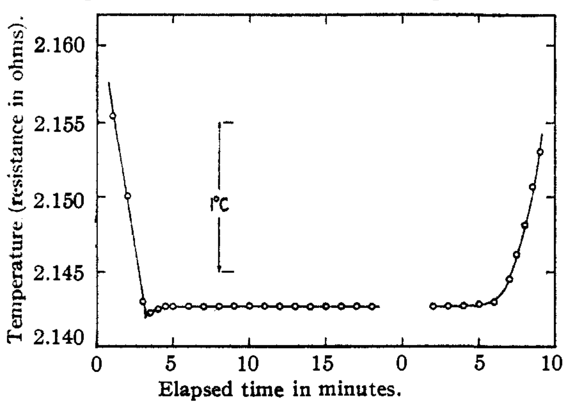

Fig. 1.—Time–temperature freezing and melting curves for thiophene.

Experimental

Determination of Properties

Freezing Point.—The apparatus and procedure used were essentially as described by Mair, Glasgow and Rossini[4] for use with hydrocarbons. The 2.5-ohm (at the ice point) platinum resistance thermometer had been standardized by the National Bureau of Standards and was checked during this work at the ice and steam points. The more recent value of the ice point resistance and the Bureau of Standards fundamental interval were used in the calculations. The Mueller bridge used was a Leeds and Northrup type G-1. This equipment was used as the temperature standard for the various measurements throughout the work. Vertical mechanical stirring was provided. The 40-ml. sample was cooled in a Dry Ice-bath and readings of the thermometer resistance taken at one minute intervals, or one-half minute intervals at critical points. When the stirrer began to labor, after a large fraction of the sample had frozen, the Dry Ice-bath was replaced by an ice–water-bath and the melting observed. The same sample was then frozen a second time and the two freezing and the melting temperatures were all in agreement within ±0.01° (Fig. 1).

A solution of 1.15 mole per cent. carbon disulfide (Baker Analyzed, n^{20}D 1.6276, d^{20}_4 1.2629) in thiophene had a f. p. of −39.31°; the freezing curve showed slight undercooling and was concave downward. The heat of fusion calculated from these data is 1,250 cal./mole. Jacobs and Parks[5] give an experimentally determined value of 1,185 cal./mole.

Refractive Index.—A Bausch and Lomb Precision Oil Refractometer, Abbe type, was used for the D-line values (see Table II and Fig. 2). Circulating water from a thermostat maintained the temperature to ±0.02° at the instrument for the 20° readings. At 25 and 30° the thermostat heater was operated manually to maintain an instrument temperature to ±0.05°. With each set of readings a reading was made for a sample of toluene, the index of which was certified by the Bureau of Standards, and a correction of about 0.0001 at most applied where necessary. A Zeiss Pulfrich instrument with similar temperature control and standardization was used for the F- and C-line determinations.

Density.—A 20-ml. pycnometer was used, the liquid level being adjusted to the mark with the aid of a magnifier until no further change in the level occurred, while the pycnometer was immersed in a water-bath maintained to ±0.015°. The volume of the pycnometer was determined at each temperature with water which had been distilled and then redistilled from potassium permanganate. Weighings were made using a tare pycnometer which received the same external treatment as the operating one; the weights used had been compared with a set

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[2] Steinkopf, "Die Chemie des Thiophens," Theodor Steinkopff, Dresden and Leipzig, 1941, p. 109.

[3] Bower and Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

[4] Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

[5] Jacobs and Parks, THIS JOURNAL, **56**, 1513 (1934).

TABLE I

PHYSICAL PROPERTIES OF THIOPHENE (LITERATURE DATA)

B. p., °C. at 760 mm.	M. p., °C.	d^{20}_4	n^{20}_D	Ref.
84	.....	1.064^b	.....	6
84.2–84.3^a	.....	1.0649^c	.....	7
..	.....	1.0647	1.5286^d	8
84	.....	1.0654^b	1.5301^d	9
84.0	.....	1.0639	.....	10
84.5–85.5^a	.....	1.0646^b	1.5289^d	11
..	–37.1	.....	.....	25-b
..	.....	.....	1.5273^d	12
86.6^a	−29.8^e	1.0633^b	.....	13
84.0	.....	1.0615	.....	14
84.3	.....	1.0638^b	.....	22
..	−39.5^f	.....	.....	5
84	.....	1.0617	1.5246	15
..	.....	1.0638	1.5283	16
83.8–84.2^a	−39.82 to −39.62	1.0629	1.5287^d	17
84.12	−38.30	1.0644	1.5287	18

^{a} Adjusted to 760 mm. by means of $\Delta t/\Delta p = 0.043°/$mm. ^{b} Adjusted to 20° by means of $\Delta d_4/\Delta t = 0.0012/°$. ^{c} Adjusted to 20° by graphical interpolation. ^{d} Adjusted to 20° by means of $\Delta n_D/\Delta t = 0.00064/°$. ^{e} Steinkopf and Boëtius[17] state "probably a typographical error." ^{f} Stated to have shown "considerable premelting."

TABLE II

OBSERVED PHYSICAL PROPERTIES OF THIOPHENE

Boiling point, °C. at	500 mm.	71.0
	600 mm.	76.6
	700 mm.	81.45
	760 mm.	84.12
	800 mm.	85.8
	900 mm.	89.7
(dt/dp) at 760 mm., °/mm.		0.043
Freezing point in air, °C.		−38.30
Density, g./ml. at	20°	1.0644
	25°	1.0583
	30°	1.0524
Index of refraction, n^t_D at	20°	1.5287
	25°	1.5256
	30°	1.5223
Specific dispersion, $10^4(n_F - n_C)/d$ at 20°		162.6
Absolute viscosity, centipoise at	20°	0.662
	25°	0.621
	30°	0.584
Molecular refraction at 20°		24.365

certified by the Bureau of Standards. All weights were corrected for the buoyant effect of air (Table II and Fig. 2).

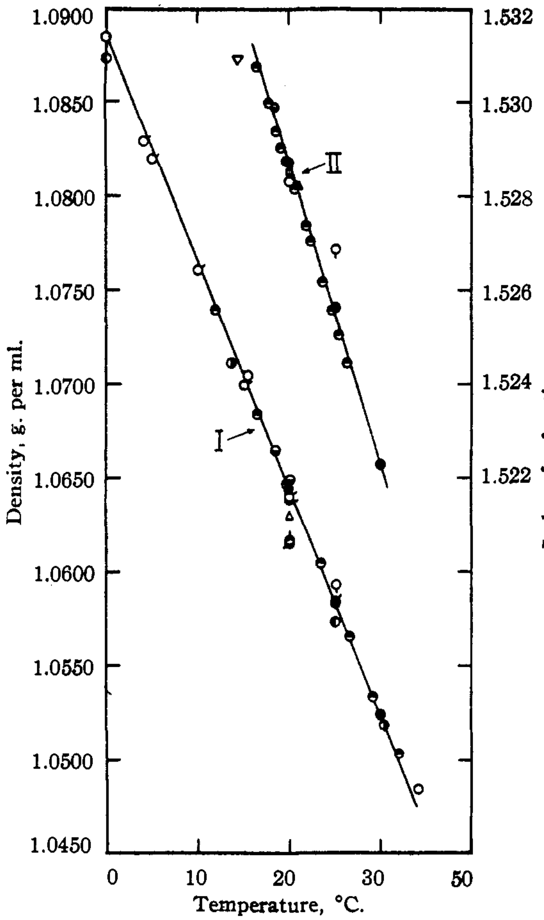

Fig. 2.—Density (I) and index of refraction (II) of thiophene at various temperatures: ○, ref. 7; ◓, 8; ♀, 9; ∝, 10; ◒, 11; ∇, 12; ◐, 13; ⚲, 14; ◑, 22; ȯ, 15; ○-, 16; Δ, 17; ●, this investigation.

Viscosity.—Data on viscosity of thiophene have previously been reported.[19]

A Cannon[20] viscometer for non-viscous fluids was used which had an efflux time for water at 20° of 274.0 seconds. A charge of 2.0 ml. was added from a pipet. The instrument was made vertical in the thermostat used for density measurements by means of a small plumb bob. At least two consecutive efflux times agreeing to 0.1 second were obtained with a Precision Scientific Company electric chronometer. The viscometer was calibrated at each temperature with the water used for density measurements using the viscosity data for water as listed by Dorsey,[21] and was also checked with *n*-heptane and with methylcyclohexane (Table II).

Boiling Points and Vapor Pressures.—Vapor pressure data over the range 20° to the normal boiling point

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(6) Meyer, *Ber.*, **16**, 1471 (1883).

(7) Schiff, *ibid.*, **18**, 1601 (1885).

(8) Knops, *Ann.*, **248**, 204 (1888).

(9) Nasini and co-workers, in Beilstein's "Handbuch der organischen Chemie," Vol. XVII, 4th ed., Julius Springer, Berlin, 1933, p. 30.

(10) Perkin, *J. Chem. Soc.*, **69**, 1204, 1251 (1896).

(11) Brühl, *Z. physik. Chem.*, **22**, 376, 388 (1897).

(12) Cotton and Mouton, *Ann. chim. phys.*, [8] **28**, 220 (1913).

(13) Jaeger, *Z. anorg. Chem.*, **101**, 155 (1917); *Chem. Zentr.*, **89**, I, 325 (1918).

(14) Peel and Robinson, *J. Chem. Soc.*, 2068, (1928).

(15) Jurjew, *Ber.*, **69B**, 440 (1936).

(16) Moore, Renquist and Parks, THIS JOURNAL, **62**, 1505 (1940).

(17) Steinkopf and Boëtius, *Ann.*, **546**, 208 (1941).

(18) This investigation.

(19) Thorpe and Rodgers, *Trans. Roy. Soc.* (London), **A185**, 397 (1895).

(20) Cannon and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

(21) Dorsey, "Properties of Ordinary Water-Substance," Reinhold Publishing Corporation, New York, N. Y., 1940, p. 183; "International Critical Tables," Vol. V. McGraw-Hill Book Co., New York N. Y., 1929, p. 10.

have been reported.[22] The comparative dynamic method[23] was employed using Cottrell ebulliometers. An atmosphere of nitrogen was maintained in the system and temperatures were measured with a single junction copper–constantan thermocouple and a Leeds and Northrup Type K-2 potentiometer. Benzene purified by crystallization was used as the reference liquid. The temperatures as measured were constant to at least 0.01° but the calibration of the thermocouple limits their certainty to 0.1°. The data listed in Table II were obtained from a plot of the observed corresponding boiling points (Table III) and the data of Smith[24] for benzene. The data of Table III when plotted according to the Dühring rule give a linear relationship; since the difference in the boiling points is essentially constant, 4.0°, the slope of the line is unity. A direct measurement of the difference between the boiling temperatures of the two liquids at atmospheric pressure was also made using the "cold" junction in the benzene ebulliometer, the value of Δt being 4.02°. The heat of vaporization calculated from the data of Table II is 7,760 cal./mole. The possibility of mutual contamination of the boiling liquids by diffusion was checked by mass spectrometer analysis after the measurements, and such effect was found negligible. From these data and the cited data for benzene the value of α, the vapor pressure ratio, was calculated as 1.13 in the range 80 to 85°.

TABLE III

CORRESPONDING BOILING POINTS OF THIOPHENE AND BENZENE IN DEGREES CENTIGRADE

Thiophene	Benzene	Thiophene	Benzene
69.48	65.47	84.36	80.32
72.41	68.48	85.09	81.04
74.85	70.91	86.02	81.99
78.81	74.78	87.13	83.08
81.16	77.18	87.36	83.31
83.53	79.51	88.45	84.43
84.01	79.99	89.28	85.31
84.13	80.13		

The System Thiophene–Benzene

Since thiophene and benzene are so closely associated it seemed of interest to determine some properties for this system. J. T. Baker Analyzed thiophene-free benzene was crystallized three times as described above for thiophene using a salt–ice mixture for cooling. The properties of the final product were measured along with the corresponding properties of the thiophene so that a close comparison was kept throughout. The data for benzene were: f. p. 5.5°; n^{20}_D 1.5011, n^{25}_D 1.4979, n^{30}_D 1.4946; d^{20}_4 0.8790, d^{25}_4 0.8735, d^{30}_4 0.8683; $10^4 (n_F - n_C)/d$ at 20° 189.6; η_{20} 0.650, η_{25} 0.605, η_{30} 0.564 centipoise. Mass spectrometer analysis showed the presence of less than 0.015 mole per cent. of thiophene in the final product. Ten mixtures were prepared by weighing the thiophene and benzene into small Pyrex ampoules which were kept sealed when not in use. Mole fractions were calculated from the weights *in vacuo* of the components added using the molecular weight of thiophene as 84.13 and of benzene as 78.11. The density of each mixture was determined as described above with the exception that a 6-ml. pycnometer was used. Refractive indices and viscosities were obtained just as described for the thiophene. The data obtained are given in Table IV. The density and refractive index are very nearly linear functions of volume composition, whereas the kinematic fluidity (reciprocal of kinematic viscosity) is a linear function of molar composition. The deviations of experimental data from the values calculated by means of straight line equations derived from the values for the pure components are given in Table V together with the derived equations. The density and viscosity relationships are straight line functions within experimental error, whereas the refractive index deviates in an orderly manner from the straight line, corresponding more nearly to a simple second degree function. The freezing point for each mixture was determined by a procedure similar to the one mentioned but on a smaller scale (15-ml. sample), using a 1-junction copper–constantan thermocouple with the type K-2 potentiometer. The thermocouple was calibrated at the freezing point of mercury and the ice point and was checked at two temperatures as

TABLE IV

DATA FOR THIOPHENE–BENZENE SOLUTIONS

Thiophene, % Mol.	Thiophene, % Vol.[a]	d^{20}_4	n^{20}_D	F. p., °C.	Viscosity at 20° Kinematic[b]	Viscosity at 20° Abs.[c]	M. R. at 20°
0	0	0.8790	1.5011	+ 5.5	0.740	0.650	26.185
9.54	8.58	.8947	1.5033	+ 1.3	.726	.650	26.011
19.84	18.04	.9123	1.5058	− 3.5	.712	.650	25.818
29.99	27.59	.9300	1.5084	− 8.6	.699	.650	25.632
39.93	37.16	.9477	1.5110	−13.0	.688	.652	25.451
46.04	43.15	.9590	1.5127	−17.02	.680	.652	25.337
55.73	52.82	.9768	1.5154	−22.8	.672	.656	25.166
59.89	57.04	.9848	1.5165	−24.8	.664	.654	25.083
69.73	67.20	1.0036	1.5194	−28.8	.654	.656	24.908
80.13	78.20	1.0240	1.5225	−32.5	.643	.658	24.721
90.20	89.11	1.0444	1.5257	−35.6	.631	.659	24.541
100.0	100.0	1.0644	1.5287	−38.30	.622	.662	24.365

[a] From volumes of components added. [b] Centistoke. [c] Centipoise.

TABLE V

DEVIATIONS OF DATA OF TABLE IV FROM LINEAR FUNCTIONS (1), (2) AND (3)

(1) $d^{20}_4 = 0.001854$ (vol. % thiophene) $+ 0.8790$

(2) $n^{20}_D = 0.000276$ (vol. % thiophene) $+ 1.5011$

(3) Kinematic fluidity = 1/(Kinematic viscosity) = 0.00256 (Mole % thiophene) + 1.352.

Thiophene, % Mole	Thiophene, % Vol.	(1) $10^4 \Delta$	(2) $10^4 \Delta$	(3) $10^3 \Delta$
0	0	...	...	...
9.54	8.58	−2	−1	+1
19.84	18.04	−2	−3	+2
29.99	27.59	−2	−3	+2
39.93	37.16	−2	−4	−2
46.04	43.15	0	−3	0
55.73	52.82	−1	−3	−6
59.89	57.04	0	−3	0
69.73	67.20	0	−2	0
80.13	78.20	0	−2	−1
90.20	89.11	+2	0	+3
100	100	...	...	...

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(22) Nasini, *Proc. Roy. Soc.* (London), **A123**, 711 (1929).

(23) Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945.

(24) Smith, *J. Research Natl. Bur. Standards*, **26**, 129 (1941).

determined by the resistance thermometer, *viz.*, the freezing points of pure thiophene and of a 50–50 mixture of thiophene and benzene. Undercooling was observed in all cases and the curves except for the pure compounds were concave downward. The pure compounds froze into rigid masses adhering to the walls of the freezing tube, while their mixtures always froze into a soft, mushy slurry. As previously observed,[25] these data show the existence of solid solutions; no eutectic was observed, the addition of benzene always raising the freezing point of thiophene even at concentrations of about 1 mole per cent. The freezing point data are given in Table IV and Fig. 3.

Acknowledgment.—The authors wish to express their appreciation for the assistance given by Mr. David Christison of this Laboratory who worked out the procedure for and ran the mass spectrometer analyses.

Summary

1. A sample of thiophene large enough to assure good working quantities has been purified by distillation and crystallization to give a product which froze at a temperature constant to 0.01°.

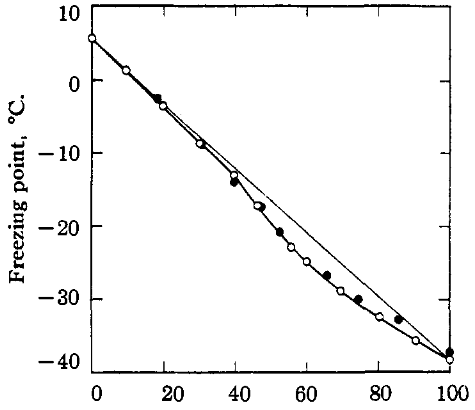

Fig. 3.—Freezing point–composition diagram for thiophene–benzene: ○, this investigation; ●, literature data (25b).

2. The following properties have been determined for the purified sample: f. p., b. p. over the range 500–900 mm., n_D, d_4 and η at 20, 25 and 30°, specific dispersion at 20° and some derived constants.

3. For the system thiophene–benzene the following properties have been determined as a function of composition: $n^{20}{}_D$, $d^{20}{}_4$, η_{20} and f. p.

PAULSBORO, NEW JERSEY RECEIVED JUNE 25, 1945

(25) (a) Beckmann, *Z. physik. Chem.*, **22**, 609 (1897); (b) Tsakalotos and Guye, *J. chim. phys.*, **8**, 340–357 (1910); *B. C. A.*, **98**, II, 826 (1910).

[CONTRIBUTION FROM RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Polyethyleneammonium Chlorocuproates[1]

BY HANS B. JONASSEN,[2] THOMAS B. CRUMPLER AND THOMAS D. O'BRIEN

Grossman and Schueck[3] have previously reported the preparation of the chlorocuproate of ethylenediamine ("en"). This paper reports the repetition of the preparation of this substance and also the attempt to prepare and study the corresponding chlorocuproates of diethylenetriamine ("dien"), triethylenetetramine ("trien"), and tetraethylenepentamine ("tetren").

Experimental

Materials.—The tetraethylenepentamine was generously provided by the Carbide and Carbon Chemicals Corporation. The other polyethyleneamines were obtained from the Eastman Kodak Company. The ethylenediamine in 60% aqueous solution was used without further treatment. The others were refluxed for several hours over metallic sodium and were then distilled *in vacuo* over sodium. The fractions collected had the boiling ranges: dien, 78–79° at 3 mm.; trien, 128–131° at 3 mm.; and tetren, 152–154° at 1 mm.

Procedure.—One-tenth mole of cupric chloride ($CuCl_2 \cdot 2H_2O$) was dissolved at room temperature in about 50 ml. of absolute methanol and the amine was added in small portions until 0.1 mole had been added or until a thick paste was produced. The reaction mixture was cooled in an ice-bath before being filtered by suction, following which the precipitate was washed with absolute methanol until the washings were colorless. The precipitate, which contained yellow, green, and blue particles, was washed at room temperature first with a few small portions of acetone and then with ether and finally dried for about three minutes at 100°.

The dry solid was mixed with sufficient concentrated hydrochloric acid to convert it to a homogeneous yellow residue and then a few milliliters in excess was added. The yellow residue was filtered by suction and washed with ethyl alcohol until the washings were free of acid. This residue was dissolved in the minimum volume of water at room temperature and upon addition of an equal volume of concentrated hydrochloric acid a distinctly crystalline, yellow precipitate formed. At least four such reprecipitations were effected in each instance. The physical properties, freezing-point depressions, and analyses of these compounds are given in Table I.

Discussion

In color these compounds resemble the solid chlorocuproate salts of various monoamines reported previously[4] and of ethylenediamine.[3] To

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[1] Based on M.S. thesis of H. B. Jonassen, 1944.

[2] Present address: Graduate School, University of Illinois.

[3] H. Grossman and B. Schueck, *Z. anorg. Chem.*, **50**, 1 (1906).

[4] H. Topsoe, *Dansk. Videns.*, 17 (1882); W. M. Dehn, THIS JOURNAL, **48**, 275 (1926); Y. Michaelenko, *J. Russ. Phys.-Chem. Soc.*, **61**, 2253 (1929); H. Remy and G. Laves, *Ber.*, **66B**, 401 (1933); J. Amiel, *Compt. rend.*, **201**, 964 (1935); **201**, 1383 (1935).