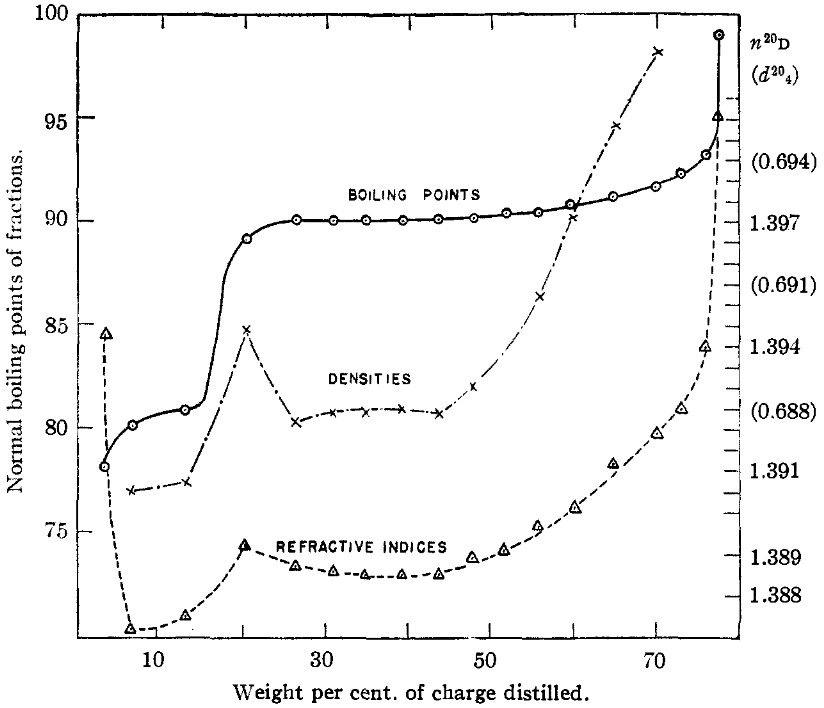

Fig. 4.—Distillation of C_7 hydrocarbons from dimethyldichlorosilane hydrolyzates.

0.6870. No azeotrope is formed between this material and dimethyldichlorosilane.

GENERAL ELECTRIC RESEARCH LABORATORY
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RECEIVED MAY 17, 1948

Azeotropes of Trimethylchlorosilane and Silicon Tetrachloride

BY ROBERT O. SAUER AND E. M. HADSELL

In the course of identifying some of the less abundant products[1] of the reaction of methyl chloride with silicon[2] a constant-boiling material (b.p. 54.7°) was obtained which proved to be a mixture of silicon tetrachloride (b.p. 57.6°) and trimethylchlorosilane (b.p. 57.7°). We thought it might be of some interest to describe our characterization of this material and to summarize (Tables I and II) the properties of several other azeotropes of these two substances. These latter azeotropes were characterized in our attempts to discover azeotroping agents for resolving the $(CH_3)_3SiCl-SiCl_4$ binary. Both acetonitrile and acrylonitrile were found to be suitable for this purpose.[3]

TABLE I

AZEOTROPES WITH TRIMETHYLCHOLOROSILANE (A-COMPONENT)

B-Component	B. p. (B), °C.	B. p. (azeo), °C.	Wt. % A
Silicon tetrachloride	57.6	54.7	35.2
2-Methylpentane[1]	60.3	56.4	*ca.* 70
3-Methylpentane[1]	63.2	57.3	*ca.* 75
Acetonitrile	82	56.0	92.6
Acrylonitrile	79	57.0	93
Ethylidene chloride[1]	57.4	*ca.* 56	?

TABLE II

AZEOTROPES WITH SILICON TETRACHLORIDE (A-COMPONENT)

B-Component	B. p. (B), °C.	B. p. (azeo), °C.	Wt. % A
Trimethylchlorosilane	57.7	54.7	64.8
Ethylidene chloride[1]	57.4	53	63.5
Acetonitrile	82	49.0	90.6
Acrylonitrile	79	51.2	89
Propionitrile	97	55.6	92
Nitromethane	101	53.8	94
Chloroform[1]	61.3	56	*ca.* 70

Experimental

The first isolation of the $(CH_3)_3SiCl-SiCl_4$ binary was accomplished in a 90 cm., 19 mm. diameter vacuum-jacketed Stedman column.[4] The material then obtained possessed the following properties: b. p. 54.6 ± 0.1° (755 mm.), 65.57 ± 0.05% Cl, mol. wt. (vapor density extrapolated to zero pressure) 140–145, mol. wt. (f. p. depression in cyclohexane) 245–250, vapor pressure at 0° 86 ± 0.5 mm. A portion of the mixture upon treatment[5] with ethylene oxide (Method A) yielded a mixture of trimethyl-2-chloroethoxysilane and tetrakis-2-chloroethyl silicate containing 45 mole per cent. of the former (46 mole per cent. would be required for a $(CH_3)_3SiCl-SiCl_4$ mixture with 65.6% Cl).

Sauer and Reed[3] have reported the resolution of this azeotrope with inert components such as acetonitrile and acrylonitrile which behave as azeotropizing agents. With

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[1] Sauer, Scheiber and Hadsell, THIS JOURNAL, **70**, 4254 (1948).

[2] Rochow, *ibid.*, **67**, 963 (1945).

[3] Sauer and Reed, U. S. Patent 2,388,575 (Nov. 6, 1945).

[4] Bragg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 283 (1939).

[5] Patnode and Sauer, THIS JOURNAL, **67**, 1548 (1945).

acetonitrile, silicon tetrachloride forms a minimum-boiling binary boiling at 49.0° at 760 mm. whereas the azeotrope of trimethylchlorosilane and acetonitrile distils at about 56° at 760 mm. Acrylonitrile also forms new azeotropes with both components but the boiling point depressions are somewhat less. In addition silicon tetrachloride forms minimum boiling binaries with propionitrile and with nitromethane. No azeotrope is formed by trimethylchlorosilane with these latter two compounds.

Synthetic mixtures of pure silicon tetrachloride, b. p. 57.2–57.3°, 83.53% Cl (calcd., 83.48% Cl) and pure trimethylchlorosilane (the several fractions used gave individual analyses between 32.65 and 32.69% Cl (calcd., 32.64% Cl)) were prepared later and distilled in a 2.2 m., 9.5 mm. diameter Stedman column at a 100:1 reflux ratio. From a distillation using excess trimethylchlorosilane four successive 30–40 ml. fractions distilling at 54.9° (770 mm.) were obtained; these gave the following percentages of hydrolyzable chlorine: 65.77, 65.73, 65.80, 65.86 (av., 65.79). A similar distillation using excess silicon tetrachloride yielded six successive fractions having the following analyses: 65.82, 65.79, 65.78, 65.76, 65.78, 65.74% (av., 65.78%) hydrolyzable chlorine. Fractions 3 and 5 gave the specific gravities (24.7/25.0): 1.173, 1.173, respectively, which reduce to $d^{25}{}_4$ 1.170. The density ($d^{25}{}_4$) of the mixture may be calculated on the assumptions: (a) no change in volume on mixing, (b) the weight fraction of trimethylchlorosilane is 0.35 (corresponding to 65.69% Cl), and (c) the densities ($d^{25}{}_4$) of silicon tetrachloride and trimethylchlorosilane are 1.4745[6] and 0.8531[7], respectively; the value thus obtained is 1.176. Hence, there is a slight increase in volume on mixing. Approximately equal volumes of the two pure components when mixed at room temperature produce a temperature decrease of about 1.5°. These facts are in accord with the generalization that a positive deviation from Raoult's law is accompanied by an absorption of heat and an increase in volume on mixing.[8]

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(6) Robinson and Smith, *J. Chem. Soc.*, 1262 (1926); *Nature*, **118**, 303 (1926); Hölemann, *Z. physik. Chem.*, **B32**, 353 (1936).

(7) Gilliam and Sauer, THIS JOURNAL, **66**, 1793 (1944).

(8) J. H. Hildebrand, "Solubility of Non-Electrolytes," A. C. S. Monograph 17, Ed. 2, New York, Reinhold Publishing Corp., New York, N. Y., 1936, pp. 56–59.

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Cation Exchange Studies on the Barium Citrate Complex and Related Equilibria[1]

BY JACK SCHUBERT[2] AND JOHN W. RICHTER[3]

Recently it has been shown how ion exchange reactions, in combination with radiotracers, can be used to measure the dissociation constants of complex ions.[4,5]

Such investigations are of particular interest inasmuch as the remarkable separations of cations obtained with cation exchangers depend on the equilibria existing among the cations, the complexing anions and the cation exchanger.[6a–g] Most of these separations were effected by elution with citric acid adjusted to a given *p*H with ammonium hydroxide, and hence it was of interest to obtain some quantitative measurements in such media. This report gives data on the following: (a) dissociation constants of barium (and strontium) citrate; (b) the effect of *p*H on the adsorption of Ba^{140} and La^{140} in citric acid solution; and (c) the cation exchange constants for the reactions where Ba^{140} and Sr^{89} in ammonium chloride solutions are adsorbed by the ammonium form of a cation exchanger.

The materials and procedures employed were the same as described previously.[5] Radiochemical assays for Ba^{140} were made by precipitating the tracer with added barium chloride carrier and counting the radioactivity of the mounted precipitate with a mica window bell-type G. M. counter tube. The radiations from La^{140} were counted directly after evaporation of a given aliquot. All radioactive measurements were made on a relative basis, thus minimizing corrections for self-absorption, decay, etc.[7]

TABLE I

THE DISSOCIATION CONSTANTS OF THE BARIUM CITRATE COMPLEX ION, ($BaCit^-$), CALCULATED FROM ION EXCHANGE DATA AT 25° ± 1°

NH_4R[a], g.	Soln., ml.	Soln. comp. in moles/l. NH_4	citric acid	Equil. *p*H of soln.	Ba^{++} ads., %	λ_0	Dissoc. constant $K_c \times 10^{+3}$
0.50	50.0	0.165	0	7.2	90.9 ± 0.7	10.0	..
0.50	50.0	0.165	.020	7.2	66.6 ± 0.3	10.0	5.0
2.00	50.0	1.05	0	7.5	51.3 ± 2	1.05	..
2.00	50.0	1.05	.050	7.3	19.8 ± 0.2	0.99[b]	17
4.00	50.0	1.05	0	7.0	66 ± 1	1.9_4	..
4.00	50.0	1.05	.020	6.8	45.5 ± 0.8	1.8_0[b]	17

[a] Each gram of the air-dried NH_4R contained 1.92 millimoles of exchangeable NH_4^+. [b] Corrected for the *p*H change by assuming that the effect of *p*H on λ_0 was the same as was observed with strontium.[5]

TABLE II[a]

SUMMARY OF THE DISSOCIATION CONSTANTS FOR ($BaCit^-$) AND ($SrCit^-$) IN AMMONIUM CHLORIDE, AND THE EXCHANGE CONSTANTS, $K_{ex.}$, FOR THE REACTION $M^{++} + 2NH_4R \rightleftharpoons MR_2 + 2NH_4^+$ AT *p*H 7.2 WITH THE CATION EXCHANGER AMBERLITE-IR-1

Concn. of NH_4^+	Temp., °C.	Dissoc. constants $K_c \times 10^3$		Exchange constants K_{ex}	
		Ba^{140}	Sr^{89}	Ba^{140}	Sr^{89}
0.165	25	5.0	1.5	14	13
0.165	37	≅8	≅2	..	..
1.05	25	17	6.6	13	12

[a] The data for Sr^{89}, except at 37°, were derived from ref. 5.

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(1) The experiments reported here were begun in 1944 and reported by the authors in Manhattan Project Documents CH-2563 and CN-2575 in February and May, 1945, respectively, under Contract No. W-7405-eng-39.

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(3) Present address: Merck and Company, Rahway, New Jersey.

(4) J. Schubert, *J. Phys. Coll. Chem.*, **52**, 340 (1948).

(5) J. Schubert and J. W. Richter, *ibid.*, **52**, 350 (1948).

(6) (a) E. R. Tompkins, J. X. Khym and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947); (b) F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, *ibid.*, **69**, 2777 (1947); (c) J. A. Marinsky. L. E. Glendenin and C. D. Coryell, *ibid.*, **69**, 2781 (1947); (d) F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, *ibid.*, **69**, 2786 (1947); (e) D. H. Harris and E. R. Tompkins, *ibid.*, **69**, 2792 (1947); (f) B. H. Ketelle and G. E. Boyd, *ibid.*, **69**, 2800 (1947); (g) F. H. Spedding, E. I. Fulmer, T. A. Butler, E. M. Gladrow, M. Gobush, P. E. Porter, J. E. Powell and J. M. Wright, *ibid.*, **69**, 2812 (1947).

(7) We wish to thank W. M. Byerly and the Clinton Laboratories Analytical Group for making many of these analyses.