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

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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	Soln. comp. in moles/l. 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.

[2] Present address: Argonne National Laboratory, P. O. Box 5207, Chicago 80, Illinois.

[3] Present address: Merck and Company, Rahway, New Jersey.

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

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[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.

From the experimental data in Table I the dissociation constants of BaCit$^-$ were calculated in the usual manner.[5] The values of the exchange constants and the dissociation constants of the salts of Ba^{++} and Sr^{++} are summarized in Table II. It should be noted that the concentrations of the carrier-free tracer cations in these experiments were less than 10^{-10} molar.

The exchange constants, $K_{ex.}$, were calculated from the relation[5,8]

$$[K_{ex.}]_{pH} = \lambda_0 \times (NH_4)^2/NH_4R \qquad (1)$$

where λ_0 is the ratio of the fraction of M^{++} in the resin and liquid phases, respectively.[4] The concentrations of NH_4^+ and NH_4R are expressed in moles per liter.

The data in Table II show that in ammonium citrate solution Ba^{++} is much less strongly bound by the citrate ion than is Sr^{++} while its affinity for the exchanger is slightly greater. The combination of these two factors enhances the difference in adsorbability between these elements just as is the case for the rare earths,[6f,9] except that the relation of atomic number to the adsorption and complex affinity of the latter are in reverse order as compared to the alkaline earths.

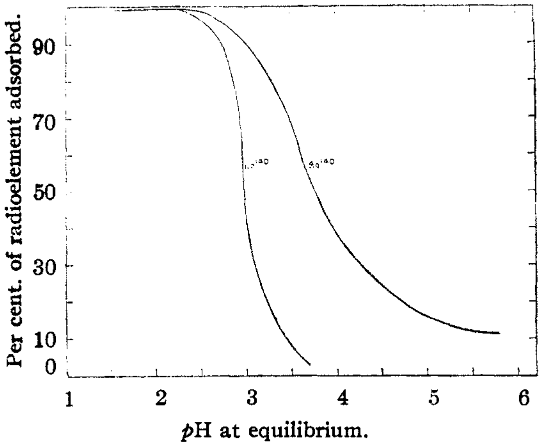

Fig. 1.—Adsorption of Ba^{140} and La^{140}, by the hydrogen form of the cation exchanger, Amberlite IR-1, from 5% (0.24 *M*) citric acid as a function of *p*H. The weight of resin was 0.50 g. air-dried and the volume of solution was 25 ml. The solution *p*H was adjusted by adding ammonium hydroxide. The molarity of the NH_4^+ at the different *p*H's was as follows:

*p*H	Molarity of NH_4^+	*p*H	Molarity of NH_4^+
1.79	0.0	4.34	0.45
2.32	.075	4.73	.53
2.83	.15	5.09	.60
3.21	.23	5.56	.73
3.70	.30	5.82	.80
3.92	.38		

At a *p*H ≤ 2 citric acid exists principally in the undissociated form[10] and therefore contributes very little to the effective cation concentration of a solution. The complexing action of citric acid becomes less pronounced as the *p*H is decreased.[6a,9] It was found that concentrations of citric acid (or of acetic) as high as 0.8 *M* had no effect on the adsorption of Ba^{++} from salt solutions at a *p*H of 2. As the *p*H of a solution is increased the citric acid dissociates further and produces a greater concentration of the ions possessing the stronger complexing action. In Fig. 1 is shown the effect of *p*H on the adsorption of Ba^{140} and La^{140} from citric acid solutions. It is seen that at a *p*H of about 3 the adsorption of La^{+3} decreases very rapidly principally because of complex ion formation while the adsorption of Ba^{++} is nearly unchanged. This marked difference is responsible for the simple and effective manner in which the divalent fission product cations are separated from the trivalent rare earths.[6a]

Barium becomes appreciably complexed at a *p*H ~ 4 (after discounting the effect of NH_4^+) as is indicated in Fig. 1 and it seems likely that a weak complex ion, Ba(HCit) exists. The formation of a complex Ca(HCit) in the *p*H region 3.6–5.2 is known.[11]

More exact measurements of the dissociation constants of complex ions by the ion exchange method than reported here can be made. The following factors should be considered: (a) a resin such as Dowex 50[12] whose capacity is independent of *p*H over a very wide range should be used and (b) the values for λ_0 should be kept between the approximate limits of 1–2 whenever possible because of the sensitivity of K_c to small errors in λ_0. For example, in Table I in the case in which λ_0 = 10.0, a 1% error in this value of λ_0 gives a 10% error in K_c.

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[9] E. R. Tompkins and S. W. Mayer, *ibid.*, 69, 2859 (1947).

[10] N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab. Selskab. Mat-fys. Medd.*, IX, 1 (1929).

[11] J. Muus and H. Lebel, *Kgl. Dansk Veidenskab. Selskab Mat.-fys Medd.*, 13, No. 19 (1936).

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Note Concerning the Constitution of Chlorogenin

BY MILLARD SEELEY AND C. R. NOLLER

On the basis of molecular weight determinations in benzene, it was concluded[1] that the amorphous reaction product of hydrazine with the diketone obtained by the oxidation of chlorogenin (chlorogenone) and that with 3,6-cholestanedione were polymeric, and hence that the products were not dihydropyridazines and that their formation did not necessarily prove the 1,4 relation of the carbonyl groups postulated by Marker and Rohrmann.[2] Later Bursian[3] reported that there was

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[1] Noller, THIS JOURNAL, 61, 2976 (1939).

[2] Marker and Rohrmann, *ibid.*, 61, 946 (1939).

[3] Bursian, *Ber.*, 73, 922 (1940).