presence of small amounts of olefins. In the absence of unsaturated compounds, the reaction did not take place at a practical rate under the conditions used.

This addition product, on decomposing with water, gave a 25% yield of hexahydrobenzaldehyde. No other oxidation product was identified.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, NAVAL RADIOLOGICAL DEFENSE LABORATORY]

The Association of Cerous Ion with Iodide, Bromide and Fluoride Ions[1]

BY STANLEY W. MAYER AND S. DAVID SCHWARTZ

The association constant for CeCl^{+2} has recently been measured by Connick and Mayer.[2] The ion exchange measurements of ion-pair formation between Ce^{+3} and the other important halides are reported in this paper.

Theoretical

It has been shown[2,3] that the equilibrium constant for the exchange between cerous and sodium ions may be written as

$$K_a = \frac{[Ce_R^{+3}][Na^+]^3}{[Ce^{+3}][Na_R^+]^3} = \frac{(Ce_R^{+3})(Na^+)^3\gamma_{Ce_R^{+3}}\gamma^6_{\pm NaX}}{(Ce^{+3})(Na_R^+)^3\gamma^4_{\pm CeX_3}\gamma^3_{Na^+_R}} \tag{1}$$

where brackets denote activities, parentheses denote concentrations in moles per 1000 g. of water or moles per 1000 g. of resin. The subscript R indicates that the ion is in the resin. X is a univalent anion.

The radiations from Ce^{141} and Ce^{144} nuclides were used to determine (Ce_R^{+3}) and (Ce^{+3}), allowing (Ce_R^{+3}) to be kept small relative to (Na_R^+). Consequently $\gamma_{Ce_R^{+3}}$ and $\gamma_{Na_R^+}$ were essentially constant throughout the measurements.

$$\frac{K_a\gamma^3 Na_R^+}{\gamma_{Ce_R^{+3}}} = A = \frac{(Ce_R^{+3})(Na^+)^3\gamma^6_{\pm NaX}}{(Na_R^+)^3(Ce^{+3})\gamma^4_{\pm CeX_3}} \tag{2}$$

Ion exchange measurements have established the empirical relationship[2] for the mixed electrolyte activity coefficients of trace concentrations of cerous perchlorate

$$\gamma^4_{\pm Ce(ClO_4)_3} \text{ in } Y \text{ molal NaClO}_4 = b\gamma^3_{\pm NaClO_4,Y}\gamma_{\pm CeCl_3,Y} \tag{3}$$

where b is a constant, Y is equal to the molality of sodium ion, and $\gamma_{\pm CeCl_3,Y}$ denotes the mean activity coefficient of CeCl$_3$ in Y molal CeCl$_3$ solution.

This relationship has been applied[2] to other univalent anions to calculate the mixed electrolyte activity coefficients of cerous salts. Then

$$Ab = B = \frac{(Ce_R^{+3})(Na^+)^3\gamma^3_{\pm NaX,Y}}{(Ce^{+3})(Na_R^+)^3\gamma_{\pm CeCl_3,Y}} = \frac{\text{Count}_{Ce_R^{+3}}(Na^+)^3\, g_{H_2O}\, \gamma^3_{\pm NaX,Y}}{\text{Count}_{Ce_{Aq}^{+3}}(Na_R^+)^3\, g_R\, \gamma_{\pm CeCl_3,Y}} \tag{4}$$

where Count denotes the count per second obtained from the tracer cerous ion in the indicated phase, and g_R denotes grams of resin.

All the factors of the right-hand member of (4) are experimentally measurable if the anion, X, does not form an ion-pair with Ce^{+3}. Then the value of B for the exchange between Ce^{+3} and Na$^+$ can be calculated.

In order to determine the constant for ion-pair formation with the anion, Z, the exchange is then carried out in the presence of a known concentration of Z.[4] Equation (4) and the measured value of B are then utilized to calculate (Ce^{+3}), making the correction for the (CeZ^{+2}) in the resin.[2]

$$\sum_{n=0}(CeZ_n) = (Ce^{+3}) + \sum_{n=1}(CeZ_n) \tag{5}$$

For the case in which the only ion-pair formed is CeZ^{+2}

$$K_a = \frac{(CeZ^{+2})\gamma_{CeZ^{+2}}}{(Ce^{+3})(Z^-)\gamma_{Ce^{+3}}\gamma_{Z^-}} = K_m K_\gamma \tag{6}$$

where K_m is the concentration quotient and K_γ is the activity coefficient quotient.

For those cases in which other ions than CeZ^{+2} are formed, the method of Leden[5] or the graphical method of Connick and McVey[6] can be employed to calculate the reaction constants.

Experimental

Materials.—Dowex 50[7] resin, 100–200 mesh, was used as the cation exchanger throughout these measurements. The resin was thoroughly washed with acid and water. It was then neutralized with sodium hydroxide solution, washed, and finally dried in air. The capacity of the resin was 3.11 equivalents per 1000 g.

The purified mixture of Ce^{141}–Ce^{144} fission product, secured from the Oak Ridge National Laboratory, contained less than 1% of radiochemical impurities.

All the sodium salts were of reagent grade, and were dried to a moisture content of not more than one-tenth of one per cent.

Procedure.—The method was similar to that heretofore employed.[2,8] For the measurements involving bromide and iodide ions the concentration of cerous ion was 10^{-4} molal. For the equilibrations with fluoride ion (Ce^{+3}) was decreased to 10^{-5} molal because of the low solubility of cerous fluoride.

Results

In a series of eight replicate ion exchange equilibrations between 0.501 molal sodium perchlorate and 1.0 × 10^{-4} molal cerous perchlorate, B was found to have the mean value 13.9, with a standard deviation of 0.4. In a series of four replicate ion exchange equilibrations between 0.501 molal sodium iodide and 1.0 × 10^{-4} molal cerous perchlorate, B was again found to have the mean value of 13.9, with a standard deviation of 0.4. The

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Atlantic City Meeting, September, 1949.

[2] R. E. Connick and S. W. Mayer, THIS JOURNAL, to be published.

[3] G. E. Boyd, J. Schubert and A. W. Adamson, *ibid.*, **69**, 2818 (1947).

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

[5] I. Leden, *Z. physik. Chem.*, **188**, 160 (1941).

[6] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[7] W. C. Bauman and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

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

pH of both solutions was 3.1. The mean activity coefficient of 0.501 molal sodium iodide is 0.726,[9a] and the mean activity coefficient of cerous chloride at that concentration is 0.324.[9b]

Data and calculations for the equilibrations in the presence of bromide and fluoride ions are summarized in Tables I and II. The distribution of cerium is tabulated in terms of the counts per second obtained for the aqueous and resin phases. C_m is a molality quotient, for the formation of $CeBr^{+2}$, calculated from equations (4), (5) and (6), but neglecting the activity coefficient factors. f_m is the factor introduced to correct for the absorption of $CeBr^{+2}$ or CeF^{+2} by the resin.[2] In Table II, K_m is the concentration quotient for the net reaction

$$Ce^{+3} + HF = CeF^{+2} + H^+ \qquad (7)$$

TABLE I

CEROUS BROMIDE IN SODIUM BROMIDE SOLUTIONS[a]

(NaBr)	Resin, g.	$Count_R/Count_{Aq}$	C_m	$\gamma_{\pm NaBr}$ [b]	$\gamma_{\pm CeCl_3}$ [c]	f_m	K_m
0.493	0.0222	2.08	1.39	0.696	0.324	1.13	1.03
.493	.0198	1.75	1.52	.696	.324	1.12	1.22
.493	.0216	2.19	1.12	.696	.324	1.14	0.81
.493	.0209	2.07	1.21	.696	.324	1.13	0.87
.895	.0216	0.378	0.57	.686	.395	1.34	1.12
.902	.0198	.290	.88	.686	.396	1.31	1.31
.906	.0209	.303	.87	.686	.396	1.30	1.29
.927	.0222	.322	.71	.686	.400	1.31	1.19
.895	.1016	1.99	.33	.686	.395	1.83	1.01
.902	.1054	1.78	.58	.686	.396	1.96	1.53
.906	.1087	1.94	.47	.686	.396	1.87	1.01
.927	.1121	2.02	.30	.686	.400	1.78	1.19
1.601	.1016	0.431	.02	.709	.696	1.77	1.24
1.659	.1054	.393	.05	.712	.742	1.77	1.47
1.689	.1087	.379	.02	.713	.768	1.76	1.39
1.697	.1121	.389	.03	.714	.776	1.78	1.47

[a] 19.7 grams of water was used in each equilibration (pH 3.1). [b] Ref. (9) based on data from H. S. Harned and C. C. Crawford, THIS JOURNAL, **59**, 1903 (1947). [c] Ref. (9b).

TABLE II

CEROUS FLUORIDE IN SOLUTIONS OF SODIUM PERCHLORATE AND SODIUM FLUORIDE[a]

Resin, g.	$Count_R/Count_{Aq}$	(HF)[b]	f_m	K_m [c]
0.0104	2.52	0.00486	1.21	6.0
.0103	2.57	.00486	1.23	5.4
.0100	2.43	.00486	1.21	6.0

[a] 10.3 grams of water was used in each equilibration (pH 1.41). [b] In 0.475 molal $NaClO_4$. [c] $\gamma_{\pm NaClO_4} = 0.669$, J. H. Jones, *J. Phys. Chem.*, **51**, 516(1947); $\gamma_{\pm CeCl_3} = 0.323$, ref. (9b).

Discussion

Iodide Solutions.—The measured values of K_m for cerous and halide ions are listed in the second column of Table III. Calculation of K_γ involves assumptions relative to the mixed electrolyte activity coefficients of very dilute electrolytes such as CeX_3, $(CeI)X_2$ and HX in moderately concentrated uni-univalent electrolytes. Connick and Mayer[2] have utilized Equation (3) on an empirical basis for the calculation of $\gamma_{\pm CeX_3}$. An examination of data[9] on the mixed electrolyte activity coefficients of dilute acids in moderately concentrated uni-univalent solutions shows that $\gamma_{\pm HX}$ can be calculated (generally with an error of less than 10%) by the relationship

$$\gamma^2_{\pm HX} \text{ in } Y \text{ molal NaX} = \gamma_{\pm NaX,Y}\ \gamma_{\pm HX,Y} \qquad (8)$$

TABLE III

CONSTANTS FOR ION-PAIR FORMATION BETWEEN CEROUS ION AND HALIDES

Solution,[a] m	K_m	K_γ [c]	K_a
0.6 HCl[b]	1.25 ± .08[b]	2.41[d]	3.01
.5 NaBr	0.98 ± .16	2.32	2.27
.9 NaBr	1.23 ± .08	2.02	2.48
.9 NaBr	1.19 ± .21	2.02	2.40
1.7 NaBr	1.39 ± .09	1.80	2.49
0.5 NaI	0.00 ± .02	2.22	0.00[e]
.005 NaF + .475 $NaClO_4$	5.8 ± .3	1.26	1.0×10^4 [f]

[a] Containing Ce^{+3} in concentrations less than 10^{-4} molal. [b] Ref. (2). [c] $\gamma_{\pm BaI_2}$, R. A. Robinson, *Trans. Faraday Soc.*, **38**, 445 (1942). [d] $\gamma_{\pm HCl}$, Ref. (9), based on data from H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933). [e] Standard deviation = 0.04. [f] $H^+ + F^- = HF$ (Aq), $K_a = 1.39 \times 10^3$, W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

In the absence of data on the activity coefficients of 2-1 electrolytes in 1-1 electrolytes, the equation of the same form as Equations (3) and (8) was utilized.

$$\gamma^3_{\pm (CeI)X_2} \text{ in } Y \text{ molal NaX} = \gamma^2_{\pm NaX,Y}\ \gamma_{\pm (CeI)X_2,Y} \qquad (9)$$

The activity coefficient of CeI^{+2} was considered to be equal to that of Ba^{+2}, the divalent ion in the same row of the periodic table as cerium.

Since some assumptions involved in the calculation of K_γ have not been tested in previous studies, the errors in the calculated values of K_a are of unknown magnitude. The relative values of K_a, particularly those for NaBr solutions, should be comparatively reliable, inasmuch as the assumptions have been identical throughout the calculations of K_a.

The data for NaI solutions, in Table III, show that cerous ion does not associate more strongly with iodide ion than with perchlorate. This result is in agreement with observations on the relative sizes[10] of the iodide and perchlorate ions, and the activity coefficients of MgI_2[11] and $Mg(ClO_4)_2$.[12]

Bromide Solutions.—The K_a values of Table III show that the association of cerous with bromide ion is weaker than with chloride ion. It is to be expected that Br^- will associate less strongly because the ionic radius of Br^- is greater than that of Cl^-.[10]

Relative decreases in the activity coefficients of alkaline earth salts at higher concentrations have been attributed[13] to ion-pair formation. Inasmuch as the activity coefficient of concentrated alkaline earth chlorides are lower than those of the bromides, the measured K_a's agree with this hypothesis. Furthermore, as the K_a values indicate, the difference between the activity coefficients of

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(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, based on data from: (a) R. A. Robinson, THIS JOURNAL, **57**, 1161 (1935); (b) C. M. Mason, *ibid.*, **60**, 1638 (1938); **63**, 220 (1941).

(10) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

(11) R. A. Robinson and R. H. Stokes, *ibid.*, **36**, 733 (1940).

(12) R. H. Stokes and B. J. Levien, THIS JOURNAL, **68**, 333 (1946).

(13) R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948).

the alkaline earth iodides and bromides is greater than the difference between the activity coefficients of the bromides and chlorides.

In Table I it can be seen that C_m decreases sharply at higher concentrations of NaBr. When the activity coefficients are applied to calculate the concentration quotient, K_m increases slightly at higher (NaBr). $K\gamma$ decreases slightly as (NaBr) is increased. Consequently, when the activity coefficients are utilized, the calculated equilibrium constant, K_a, does remain constant (within experimental error) over a range of concentrations.

Fluoride Solutions.—Cerous fluoride is very sparingly soluble even in acid solution. However, preliminary tests showed that when the concentration of cerous ion was reduced to less than 10^{-5} molal, and when the hydrogen fluoride concentration was less than 7×10^{-3} molal in solutions at pH 1.41, the precipitation of cerium was negligible, and about one-fifth of the cerium was associated with fluoride ion. Because of the limitations on the concentration of HF which are imposed by the insolubility of CeF_3, no high degree of accuracy can be claimed for the measurement of the association constant.

In accordance with the observed behavior of cerous ion with other univalent anions when the fraction of complexed cerium is small, CeF^{+2} was considered to be the complex formed. Equation (7) was considered to represent the net reaction inasmuch as the charge of Ce^{+3} should make the momentarily-formed acid $HCeF^{+3}$ completely strong.[6] The product of the equilibrium constant for the reaction of Equation (7) and the equilibrium constant for the association of H^+ with F^- equals K_a for the ion-pair formation

$$Ce^{+3} + F^- = CeF^{+2} \qquad (10)$$

The value of 1.0×10^4 agrees qualitatively with the value for the association of ferric ion and fluoride.[14]

Summary

The distribution of cerous ion between cation exchange resin and solutions of sodium iodide, bromide, fluoride and perchlorate has been measured. The constants for ion-pair formation between Ce^{+3} and the halides have been calculated.

(14) H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949).

SAN FRANCISCO 24, CALIF. RECEIVED APRIL 11, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE ROYAL INSTITUTE OF SCIENCE]

The Behavior of Solutions of Titanium Dioxide in Sulfuric Acid in the Presence of Metallic Sulfates

BY S. M. MEHTA AND S. R. PATEL

A systematic study of the behavior of solutions of titania in sulfuric acid in the presence of different amounts of alkali sulfate has not been made so far. This paper reports results of such a study.

When titanium dioxide (0.1 g.) is heated alone with sulfuric acid (40 cc., sp. gr. 1.8) to 230°, a clear solution results which on further heating to about 285° gives a white precipitate. This precipitate when washed free from sulfate with absolute alcohol and then dried at 350–400° (yield about 84%), corresponds to the formula $TiOSO_4$[1] as reported by the majority of previous investigators.[2]

When the heating is carried out as before but in the presence of ammonium, sodium or potassium sulfate, in weight ten times that of titanium dioxide, the yield of $TiOSO_4$ obtained is 39, 13 and 50%, respectively. When, however, the weight of the alkali sulfate is one hundred times that of the titanium dioxide, the solution remains clear even on boiling for 10–15 minutes. Sodium sulfate is thus better than the other sulfates in promoting the solution of titanium dioxide in sulfuric acid.

In trial experiments it was noticed that bivalent metallic sulfates showed a different behavior from that observed in the case of monovalent metallic sulfates. The effect of the sulfates of zinc, manganese, cobalt, copper and ferrous ammonium sulfate has been studied and the results obtained are described below. The experimental procedure followed in conducting these experiments was similar to that described for the monovalent metallic sulfates.

When $ZnSO_4 \cdot 7H_2O$ was used in place of the alkali sulfate, in weights varying from one-fourth to six times the weight of titanium dioxide, it was observed that with a weight of zinc sulfate greater than that of titanium dioxide, the precipitate when dried at 220° has the formula $ZnSO_4 \cdot Ti(SO_4)_2$. When, however, the weight of zinc sulfate so taken was equal or less than the weight of titanium dioxide, the precipitate obtained appeared to be a mixture of $ZnSO_4 \cdot Ti(SO_4)_2$ and $TiOSO_4$. The data obtained for these precipitates are given in Table I.

TABLE I

TiO_2, g.	$ZnSO_4 \cdot 7H_2O$, g.	H_2SO_4, cc.	Ti, %	Zn, %	SO_4, %	Formula
0.1134	0.0289	40	16.92	7.76	66.32	....
.1022	.0767	40	17.70	9.00	66.00	....
.1267	.1267	60	15.11	11.25	67.64	....
.1000	.2000	60	12.03	17.12	71.76	$ZnSO_4 \cdot Ti(SO_4)_2$
.1000	.2500	60	12.11	16.42	71.80	
.0980	.7840	125	12.14	16.44	72.01	

(1) Titanium was estimated according to the method of Hope, Moran and Ploetz, *Ind. Eng. Chem., Anal. Ed.*, **8**, 48 (1936).

(2) Merz in Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. **7**, p. 93 (1927); Blondel, *J. Chem. Soc.*, (ii)**76**, 556 (1899); Spence and Sons, Ltd., British Patent, 263,886 (1925), *C. A.*, **22**, 143 (1928); Rosenheim and Schütte, *Z. anorg. Chem.*, **26**, 250 (1901); Berzelius and Rose, Mellor, *op. cit.*, p. 94; Boguslavskaya, *C. A.*, **33**, 8135 (1939); Boguslavskaya and Ottamanovskaya, *ibid.*, **35**, 2432 (1941); Hixson and Frederickson, *ibid.*, **39**, 3720 (1945).