

conium. Other ions which are known to react in this manner are UO_2^{++} and Be^{++} . It seems likely that such a behavior is more common than is generally assumed and that more cations when carefully studied will be found to act similarly.

Summary

The polymerization of zirconium(IV) in 1 M and 2 M perchloric acid solutions has been investigated by measurement of the extraction of the zirconium chelate of thenoyltrifluoroacetone into benzene as a function of the zirconium concentration. Polymer formation is quantitatively reflected as a decrease in the extraction coefficient of the zirconium, and equations expressing this relationship have been developed and applied to the data.

In 2 M perchloric acid polymers begin to form

at zirconium concentrations of approximately $2 \times 10^{-3} M$ while in 1 M perchloric acid they appear at concentrations as low as $2 \times 10^{-4} M$. The dimer was shown to exist; it contains between 3 and 5 hydroxide groups. Higher polymers were formed and it is believed that a continuous series of polymers, starting with the dimer, exists.

Assuming relatively simple relationships between the successive equilibrium quotients for polymer formation, it was shown that theoretical curves could be deduced which fitted the data within the accuracy of the measurements.

The limits of the extraction coefficient at low zirconium concentrations indicated that the zirconium(IV) monomer in 1 to 2 M perchloric acid solutions is mainly present as unhydrolyzed Zr^{+4} .

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Ion Exchange Measurements of Activity Coefficients and Association Constants of Cerous Salts in Mixed Electrolytes¹

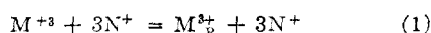
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Introduction.—In the study of equilibria involving polyvalent ions it is often important to know the activity coefficients of such ions in mixed electrolytes. In many cases the deviations of activity coefficients from normal behavior are caused by complex-ion formation and a knowledge of the dissociation constants of such species is equally desirable. These data are not available except for a few cases, particularly insoluble salts.²

It has been pointed out by several investigators^{3a,b,4} that measurements of ion exchange equilibria provide a convenient method of obtaining such information and it was adopted in the present work for the study of cerous salts.

Theory.—It has been shown by Bauman and Eichhorn⁵ that a cation exchange resin of the Dowex type may be thought of as a highly concentrated salt phase in which the negative ions are fixed in position but the positive ions move more or less freely, as in a normal aqueous phase. In order to neutralize the negative charges of the resin an equal number of positive charges must always be present within the resin and, therefore, the normality of positive ions is fixed by the "capacity" of the resin.

The exchange equilibrium of +3 and +1 positive ions between a resin and an aqueous phase may be represented by



(1) Presented at the Atlantic City Meeting of the American Chemical Society, September, 1949.

(2) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, Chapt. 14.

(3) (a) C. E. Boyd, J. Schubert and A. W. Adamson, *THIS JOURNAL*, **69**, 2818 (1947); (b) E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).

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

(5) W. C. Bauman and J. Eichhorn, *THIS JOURNAL*, **69**, 2830 (1947).

where the subscript R represents the resin phase. The equilibrium constant for this reaction is

$$K = \frac{[M_{\text{R}}^{+3}][N^{+}]^3}{[M^{+3}][N_{\text{R}}^{+}]^3} = \frac{(M_{\text{R}}^{+3})(N^{+})^3 \gamma_{M_{\text{R}}^{+3}} \gamma_{N^{+}}^3}{(M^{+3})(N_{\text{R}}^{+})^3 \gamma_{M^{+3}} \gamma_{N_{\text{R}}^{+}}^3} \quad (2)$$

where brackets indicate activities, parentheses represent concentrations and γ is the activity coefficient of the species indicated.

Multiplying numerator and denominator of equation (2) by γ_{X}^3 gives

$$K = \frac{(M_{\text{R}}^{+3})(N^{+})^3 \gamma_{M_{\text{R}}^{+3}} \gamma_{\text{NX}}}{(M^{+3})(N_{\text{R}}^{+})^3 \gamma_{\text{MX}}^3 \gamma_{\text{NR}}^3} = \frac{Q \gamma_{M_{\text{R}}^{+3}} \gamma_{\text{NX}}}{\gamma_{\text{MX}}^3 \gamma_{\text{NR}}^3} \quad (3)$$

The quantity Q is experimentally measurable. If in a series of experiments the concentration of M^{+3} is kept small relative to that of N^{+} in both phases, γ_{NR}^3 and $\gamma_{M_{\text{R}}^{+3}}$ should remain constant and γ_{NX} should be equal to that for solutions containing only NX. Then

$$\gamma_{\text{MX}}^3 = k_{N^{+}} [Q \gamma_{\text{NX}}^3]^{1/4} \quad (4)$$

where $k_{N^{+}}$ is a constant for a given temperature if the resin is nearly all in the N^{+} form. Similar equations are readily derived for other types of electrolytes.

Experimental.—The experimental method was the same as that described by Tompkins and Mayer³ except that the temperature was maintained within $\pm 0.5^\circ$ at 25° in all experiments.

Materials.—A single, large batch of Dowex 50 resin, 100–200 mesh, was the source of resin for all experiments. It was thoroughly washed with 6 molar hydrochloric acid and water and dried in air at 99% relative humidity in the acid form. The capacity of this resin was 2.700 equivalents per 1000 g. For equilibrations involving sodium salts, a portion of this resin was neutralized with sodium hydroxide, washed and air-dried. The

capacity of the sodium form was 3.05 equivalents per 1000 g. All reagents were of reagent grade.

The Ce¹⁴¹-Ce¹⁴⁴ fission product mixture, obtained from Oak Ridge National Laboratory, consisted of greater than 99% cerium activity.

Results.—Measurements were made of cerous salts in perchloric acid, sodium perchlorate, hydrochloric acid, nitric acid and sodium sulfate solutions. The data are presented in Tables I to VI. All concentrations are expressed as moles per 1000 g. of water in the aqueous phase, designated by *m*, and moles per 1000 g. of resin (dried as previously indicated) in the resin phase. The radioactive analyses are given as total counts per second (designated as ct.) of cerium in the phase indicated.

TABLE I

EFFECT ON *Q* OF VARYING THE EQUIVALENT FRACTION OF CERIUM IN THE RESIN
0.495 *m* HClO₄; 30.6 g. of water; initial cerium 0.98 × 10⁻⁴ *m*

Resin, g.	Ct. aq.	Ct. resin	Equiv. fracn. cerium in resin	<i>Q</i>
0.0300	39.2	194.7	0.092	41.8
.0299	39.3	194.6	.093	41.8
.0303	38.7	195.2	.092	41.9
.0302	39.6	194.3	.092	40.9
.1007	10.8	222.5	.0316	42.5
.1001	10.9	222.4	.0318	42.3
.1004	10.6	222.7	.0317	43.5
.1001	10.9	222.4	.0318	42.4

TABLE II

CEROUS PERCHLORATE IN PERCHLORIC ACID SOLUTIONS

HClO ₄ , <i>m</i>	Water, g.	Resin, g.	Ct. aq.	Ct. resin	<i>Q</i> ^a	γ_{\pm}^b HClO ₄	$\log \gamma_{\pm}^c$ -log $k_{H^+}^d$	$\log \gamma_{\pm}^e$ k_{H^+}/α
0.433	10.2	0.0152	16.7	202.1	42.5	0.767	0.234	0.358
.495	10.2	.0176	20.0	198.8	43.4	.769	.238	.357
.594	10.2	.0185	30.3	188.5	43.8	.775	.244	.358
.928	10.4	.1087	13.9	171.8	49.6	.811	.287	.351
2.236	11.0	.653	38.8	146.9	36.4	1.130	.470	^c
2.657	11.2	1.365	17.4	168.3	75.7	1.299	.640	
4.235	12.0	6.19	9.9	175.8	132.8	2.283	1.069	

^a Initial cerium molarity = 10⁻³/g. water. ^b Reference (6). ^c Reference (8). ^d γ_{\pm} signifies $\gamma_{\pm} \text{Ce}(\text{ClO}_4)_3$.

TABLE III

CEROUS PERCHLORATE IN SODIUM PERCHLORATE SOLUTIONS

NaClO ₄ , <i>m</i>	Resin, g.	Ct. aq.	Ct. resin	<i>Q</i> ^a	γ_{\pm}^b NaClO ₄	$\log \gamma_{\pm}^c$ -log $k_{\text{Na}^+}^d$	$\log \gamma_{\pm}^e$ k_{Na^+}/β
0.453	0.0186	23.4	80.7	16.14	0.673	0.044	0.50
.505	.0209	23.9	80.2	18.72	.666	.053	.49
.533	.0162	35.8	68.2	16.54	.663	.038	.51
.575	.0249	33.8	70.2	13.41	.658	.009	.54
.896	.0249	54.7	45.1	18.95	.634	.023	.53
.997	.0209	61.2	38.6	23.85	.629	.042	.52
1.092	.0217	68.3	31.5	21.49	.625	.027	.54
1.094	.0162	76.4	23.4	19.21	.625	.015	.56
1.491	.1018	39.4	51.5	31.12	.614	.056	.54
1.556	.1015	42.9	48.0	30.30	.613	.052	.56
1.711	.1034	42.0	48.9	41.14	.611	.083	.54
1.712	.1004	46.7	44.2	34.42	.611	.063	.56
1.857	.1039	48.3	42.6	39.51	.610	.077	.56
1.959	.1023	47.2	43.7	49.47	.608	.099	.55

^a Initial cerium concentration 1.00 × 10⁻⁴ *m*; 20.0 g. of water used in each equilibration. ^b J. H. Jones, *J. Phys. Chem.*, 51, 516 (1947). ^c γ_{\pm} signifies $\gamma_{\pm} \text{Ce}(\text{ClO}_4)_3$.

The values of $\log \gamma_{\pm} \text{CeX}_3 - \log k_{\text{N}^+}$ are plotted in Figs. 1 and 2 as a function of the concentration

TABLE IV

CEROUS CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS

HCl, <i>m</i>	Water, g.	Resin, g.	Ct. aq.	Ct. resin	<i>Q</i> ^{a,b}	γ_{\pm}^c HCl	$\log \gamma_{\pm}^d$ -log k_{H^+}
0.414	10.6	0.0172	15.6	198	34.2	0.754	0.199
.514	10.7	.0144	38.0	176	28.6	.758	.184
.594	10.8	.0101	73.3	141	26.9	.762	.180
.702	11.0	.0101	65.8	73.3	24.5	.772	.179
.849	11.3	.0111	86.4	52.7	19.8	.789	.170
1.002	11.6	.0104	104.5	34.6	18.0	.809	.176
1.56	12.5	.3958	41.4	158	20.5	.908	.265

^a Initial cerium molality = 10⁻³/g. water. ^b The values of *Q* have been corrected for the presence of CeCl⁺⁺ in the resin (see text). ^c Reference (2), based on data from H. S. Harned and R. W. Ehlers, *THIS JOURNAL*, 55, 2179 (1933). ^d γ_{\pm} signifies $\gamma_{\pm} \text{CeCl}_2$.

TABLE V

CEROUS NITRATE IN NITRIC ACID

HNO ₃ , <i>m</i>	Water, g.	Resin, g.	Ct. aq.	Ct. resin	<i>Q</i> ^{a,b}	γ_{\pm}^c HNO ₃	$\log \gamma_{\pm}^d$ -log k_{H^+}
0.368	10.2	0.0109	13.4	116	27.3	0.723	0.148
.475	10.3	.0150	20.3	108	23.3	.716	.124
.568	10.4	.0192	24.8	103	22.9	.714	.121
.892	10.6	.0938	23.7	174	28.8	.718	.149
1.729	11.2	.879	29.2	165	13.1	.760	.100
3.19	12.6	8.37	20.4	173	11.1	.896	.190

^a Initial cerium molality = 10⁻³/g. water. ^b The values of *Q* have been corrected for the presence of CeNO₃⁺⁺ in the resin (see text). ^c W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, based on data from F. Hartmann and P. Rosenfeld, *Z. physik. Chem.*, A164, 377 (1933). ^d γ_{\pm} signifies $\gamma_{\pm} \text{Ce}(\text{NO}_3)_3$.

TABLE VI

CEROUS SULFATE IN SODIUM SULFATE SOLUTIONS

Na ₂ SO ₄ , <i>m</i>	resin, g.	Ct. aq.	Ct. resin	<i>Q</i> ^a	γ_{\pm}^b Na ₂ SO ₄	$\log \gamma_{\pm}^c$ -log k_{Na^+}
0.1915	0.644	13.2	90.7	0.428	0.370	-0.924
.2150	.603	17.9	86.0	.452	.357	-.944
.2285	.612	22.4	81.5	.404	.346	-.978
.2385	.599	23.5	80.4	.442	.346	-.972
.492	.644	78.5	21.2	.282	.269	-1.246
.492	.599	76.1	23.6	.349	.269	-1.210
.516	.603	80.0	19.7	.317	.265	-1.238
.581	.612	85.7	14.0	.296	.250	-1.295

^a Initial cerium 1.00 × 10⁻⁴ *m*; 20.0 g. of water used in each equilibration. ^b Reference (1), based on data from H. S. Harned and J. C. Hecker, *THIS JOURNAL*, 56, 650 (1934). ^c γ_{\pm} signifies $\gamma_{\pm} \text{Ce}_2(\text{SO}_4)_3$.

of the major electrolyte. The activity coefficient curves for pure perchloric acid,⁶ sodium perchlorate⁷ and cerous chloride⁸ are given for comparison. No other data are available for cerous salts at these concentrations.

In the derivation of equation (4) it was specified that the concentration of Ce⁺³ in the resin remain small in order that the activity coefficients of H⁺ (or Na⁺) and Ce⁺³ in the resin would be nearly constant. In the worst case the equivalent fraction of Ce⁺³ in the resin phase reached 0.094. The experiments in Table I were performed to determine the error thus introduced. When the equivalent fraction changed from 0.032 to 0.092

(6) R. A. Robinson and O. J. Baker, *Trans. Roy. Soc., New Zealand*, 76, Part 2, 250 (1946).

(7) J. H. Jones, *J. Phys. Chem.*, 51, 516 (1947).

(8) C. M. Mason, *THIS JOURNAL*, 60, 1638 (1938); 63, 220 (1941); recalculated by H. S. Harned and B. B. Owen, ref. (2), p. 573. The activity coefficients of CeCl₂ are available only up to 2 *m* CeCl₂.

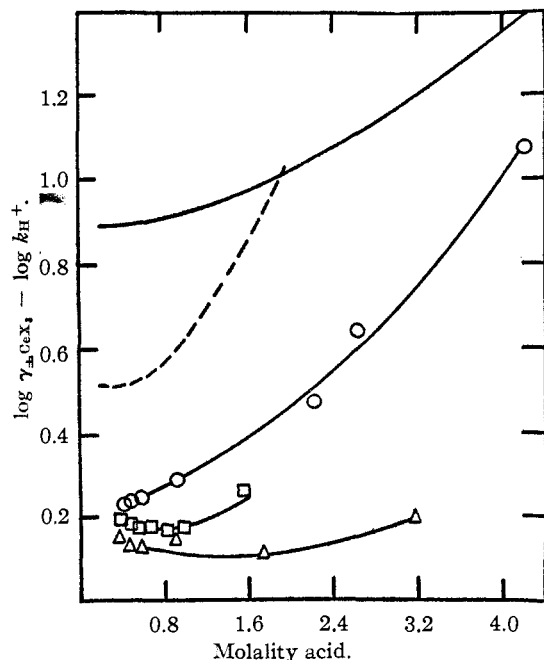


Fig. 1.—The relative activity coefficients of *ca.* 10^{-4} molal cerous salts in acid solutions: O, $\text{Ce}(\text{ClO}_4)_3$ in HClO_4 ; □, CeCl_3 in HCl ; Δ, $\text{Ce}(\text{NO}_3)_3$ in HNO_3 ; —, HClO_4 ; - - - -, CeCl_3 .

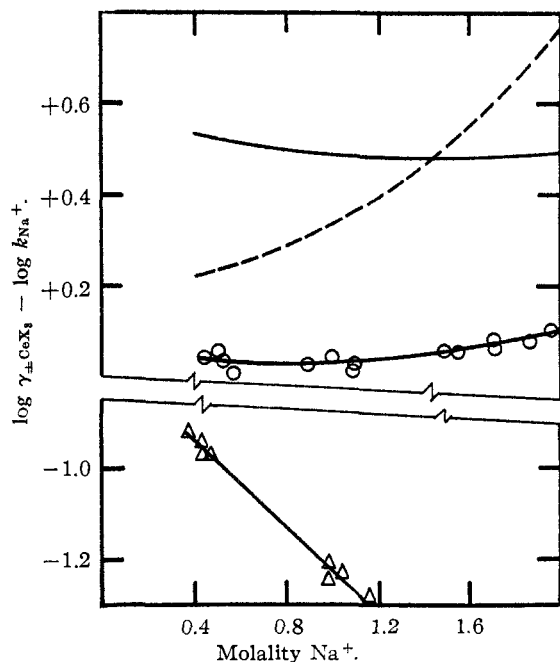


Fig. 2.—The relative activity coefficients of *ca.* 10^{-4} molal cerous salts in sodium salt solutions at pH 3.10: O, $\text{Ce}(\text{ClO}_4)_3$ in NaClO_4 ; Δ, $\text{Ce}_2(\text{SO}_4)_3$ in Na_2SO_4 ; —, NaClO_4 ; - - - -, CeCl_3 .

the value of Q varied only 2.1%. The small correction thus indicated was made on Q where significant, assuming a linear dependence on the equivalent fraction. The same correction was applied to the sodium form of the resin.

Discussion.—It is not possible on the basis of the present information to evaluate k_{H^+} and k_{Na^+} and thus calculate activity coefficients based

on the usual standard state. The experiments could not be carried to lower ionic strengths because nearly all of the cerium is then taken up by the resin. The data do furnish relative values of activity coefficients in the regions covered and this is all that is usually desired.

It is generally found that the activity coefficient of the minor constituent of a mixed electrolyte exhibits a behavior intermediate between that of the pure major and minor components.¹ Qualitatively this is shown by the perchloric acid and sodium perchlorate curves as far as their general shape is concerned, if it is assumed that cerous chloride may be substituted for cerous perchlorate. In fact, the data may be represented nearly within the accuracy of the measurements by the empirical expressions

$$\gamma_{\pm \text{Ce}(\text{ClO}_4)_3} \text{ in } x m \text{ HClO}_4 = \alpha (\gamma_{\pm x m \text{ HClO}_4}^3 \times \gamma_{\pm x m \text{ CeCl}_3})^{1/4} \quad (5)$$

$$\gamma_{\pm \text{Ce}(\text{ClO}_4)_3} \text{ in } x m \text{ NaClO}_4 = \beta (\gamma_{\pm x m \text{ NaClO}_4}^3 \times \gamma_{\pm x m \text{ CeCl}_3})^{1/4} \quad (6)$$

where α and β are undetermined constants. This is shown by the constancy of k_{H^+}/α and k_{Na^+}/β in the last columns of Tables II and III, calculated from equations (4), (5) and (6). It is to be noted that the activity coefficients of the pure electrolytes in equations (5) and (6) are taken at the same molality and not the same ionic strength. Very possibly, the use of activity coefficient data of pure cerous perchlorate rather than cerous chloride would necessitate a change in the functional form of equations (5) and (6).

From the curve for cerous sulfate in sodium sulfate solutions in Fig. 2 it is clear that sulfate ion readily complexes Ce^{+3} .

In Fig. 1 the curve for hydrochloric acid solutions lies appreciably below that for perchloric acid in contrast to the pure acids themselves. Therefore it seems likely that some complexing of Ce^{+3} by chloride ion is taking place. The data for nitric acid lie even lower and will be treated later. Shifts of bands in rare earth absorption spectra at high nitrate^{8a} and chloride⁹ ion concentrations may be qualitatively interpreted as arising from complex ion formation.

TABLE VII

ASSOCIATION CONSTANTS FOR CEROUS AND CHLORIDE IONS

HCl, <i>m</i>	<i>f</i>	<i>C</i>	<i>f_a</i>	<i>C_a</i>
0.414	0.99	0.67	0.98	0.82
.514	.97	1.06	.97	1.20
.594	.96	1.10	.96	1.25
.702	.94	1.20	.94	1.32
.849	.89	1.62	.90	1.71
1.002	.85	1.67	.87	1.73
1.56	.80	1.04	.86	1.09

Chloride and Nitrate Complexing.—An attempt was made to estimate the amount of chloride complexing by assuming that the activity coefficients of Ce^{+3} and H^+ were the same in hydrochloric acid as in perchloric acid of equal concentration and that there was no complexing in the perchlorate

(8a) L. L. Quill, P. W. Selwood and B. S. Hopkins, *THIS JOURNAL*, **50**, 2929 (1928).

(9) S. Datta and M. Dee, *Ind. J. Physics*, **10**, 163 (1936).

system. The concentration of Ce^{+3} was calculated for each hydrochloric acid solution using equation (2) and the perchloric acid system data. Assuming $CeCl^{++}$ is the only important complex

$$\begin{aligned} \Sigma(Ce^{+3}) &= (Ce^{+3}) + (CeCl^{++}) \\ C &= (CeCl^{++}) / ((Ce^{+3})(Cl^-)) \end{aligned} \quad (7)$$

Values of C are given in Table VII.

In using equation (2) it was necessary to make a correction for the amount of $CeCl^{++}$ in the resin. The assumption was made that $CeCl^{++}$ behaved, with respect to the resin, like Sr^{++} which was found to give

$$(Sr_R^{++})(H^+)^2 / (Sr^{++})(H_R^+)^2 = 13.0$$

in 0.2 M perchloric acid at 25° ($10^{-4} m$ Sr^{++}). The factor by which the ct. resin had to be multiplied to give only the counts of Ce^{+3} is designated as f in Table VII.

The chloride complexing was also calculated using activity coefficient corrections for cerous perchlorate and chloride and for hydrochloric and perchloric acids. Values for cerous perchlorate were taken from equation (5) and those for cerous chloride were calculated from equation (5) after replacing γ_{HClO_4} by γ_{HCl} , still using the same value of α . Correction was made as before for the amount of $CeCl^{++}$ in the resin but this time activity coefficient corrections were estimated for $CeCl^{++}$ in the aqueous phase using data for $BaCl_2$. The values of the equilibrium quotient thus calculated, designated as C_a , are given in column 5 of Table VII and are seen to be of the same order of magnitude as those calculated previously.

The data for nitric acid solutions of cerous nitrate, when treated in the same manner, also gave evidence of complex formation. Values for the first complexing constant are listed in Table VIII. The values of C_a are to be preferred since in the calculation of C the highly questionable assumption is made that the activity coefficients of species in perchloric acid are the same as in nitric acid at equal concentrations.

TABLE VIII

ASSOCIATION CONSTANTS FOR CEROUS AND NITRATE IONS

HNO_3, m	f	C	f_a	C_a
0.368	0.97	1.58	0.97	2.42
.475	.95	1.82	.94	2.79
.568	.94	1.59	.93	2.56
.892	.95	0.65	.93	1.44
1.729	.67	1.86	.69	4.5
3.19	.33	3.7	.53	12.6

In Tables IV and V the Q values and cerium activity coefficients have been corrected for the presence of $CeCl^{++}$ and $CeNO_3^{++}$ in the resin phase using the activity coefficient corrections described above.

Sulfate Complexing.—In order to avoid large activity coefficient corrections in measuring sulfate complexing a series of experiments was run at nearly constant ionic strength with varying concentrations of sodium sulfate and sodium perchlorate. The data are given in Table IX. Values of the complexing constant

$$C_1 = (CeSO_4^+) / ((Ce^{+3})(\Sigma SO_4^-))$$

were calculated from the equation

$$C_1 = \left(\frac{Q_{NaClO_4}}{Q} - 1 \right) \frac{1}{(\Sigma SO_4^-)}$$

and are listed in column 5. The term Q_{NaClO_4} is the value of Q in 0.50 m $NaClO_4$ and was taken to be 16.3. The total sulfate which appears in the equations is the sum of the SO_4^- and HSO_4^- concentrations. The solutions were maintained at a pH of 3.10 where the principal species is SO_4^- .

TABLE IX

CEROUS SULFATE IN SODIUM SULFATE AND SODIUM PERCHLORATE SOLUTIONS

Na_2SO_4, m^a	Resin, g.	Ct. ^b aq.	Ct. resin	C_1
0.0099	0.0212	58.2	92.2	80.1
.0102	.0196	60.0	90.4	70.9
.0338	.0212	79.6	63.4	56.1
.0338	.1064	26.9	113.3	59.7
.0360	.0196	82.3	60.7	50.5
.0360	.1086	26.9	113.3	56.0
.0431	.0195	91.1	51.9	56.7
.0431	.1038	34.3	105.9	61.7
.0442	.0202	93.1	49.9	63.1
.0442	.0974	37.8	102.4	64.7
.0544	.1086	39.8	97.0	61.5
.0654	.1064	49.7	87.1	66.4
.0672	.0974	56.0	80.8	72.1
.0764	.1038	58.7	78.1	68.2
.0981	.1086	65.7	69.0	59.5
.1033	.0974	79.9	54.8	77.6
.1299	.1064	87.0	47.7	69.0
.1390	.1038	91.5	43.2	68.6

^a The concentration of $NaClO_4$ was 0.501 molal. ^b Initial cerium molality $1.00 \times 10^{-4} m$; 20.0 g. of water were used in each equilibration.

The values of C_1 at the two lowest concentrations of sodium sulfate, where the complexing is least, are subject to the greatest experimental uncertainty. The fact that they appear high may mean that Q_{NaClO_4} was chosen somewhat too high. The C_1 values were calculated assuming all activity coefficients to be constant. When corrections were estimated for the activity coefficient changes arising from the relatively small change in ionic strength, the values of C_1 at the higher concentrations of sodium sulfate were raised. This may indicate the formation of a small amount of the second sulfate complex at these higher concentrations.

Summary

Ion exchange equilibria of Dowex 50 resin and aqueous solution containing a small concentration of cerous ion and a relatively large concentration of perchloric acid, sodium perchlorate, hydrochloric acid, nitric acid or sodium sulfate have been measured. Relative values of activity coefficients of the cerous salts were calculated from the data.

Deviations of the activity coefficients of cerous chloride and nitrate from that of cerous perchlorate have been interpreted in terms of complex ion formation.

Sulfate ion was shown to complex cerous ion fairly strongly in 0.5 m sodium perchlorate; the first complexing constant is approximately 60.

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