

Thermodynamic Data of Rare Earth Bromates and Chlorates in Aqueous Solutions at 25.0 °C

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Mean molal activity coefficients, osmotic coefficients, and water activities of the rare earth bromates in aqueous solutions at (25.0 ± 0.1) °C have been determined from dilute to saturated solutions for aqueous lanthanide bromates and chlorates, and conductance data in dilute solutions are also presented. The isopiestic method was employed to obtain the osmotic coefficients, with subsequent computations of the mean molal activity coefficients and water activities. From the conductance data, the rare earth bromate solutions are shown to contain predominantly inner-sphere complexes, and the bromates may exist as the dibromate complexes in dilute solution. The $3\beta(0)/2$ values of Pitzer's equation of rare earth nitrates are comparatively lower than those of the chlorides, perchlorates, and bromides, and the values for the rare earth bromates are even lower. From the thermodynamic data, the trend would indicate that the bromates would have a more attractive interaction than the nitrates. The trend implied that the rare earth nitrates and bromates have predominantly inner-sphere complexes. A change of the hydration number as a function of the radius of the rare earth ion can explain the observations.

Introduction

The rare earth elements exist as trivalent ions in solution and behave very similarly except for the regular decrease in ionic size due to the lanthanide contraction. They form an ideal group of ions for the study of thermodynamic properties of aqueous solutions as a function of ionic size. Thermodynamic data such as mean molal activity coefficients and water activities are required to characterize the properties of aqueous solutions. As for the osmotic coefficients, mean molal activity coefficients, and water activities, those of the rare earth chlorides,^{1–3} perchlorates,⁴ and nitrates^{5,6} had already been published, and those on bromides^{7,8} were reported. Also, the data on the bromates of the lighter rare earths were presented earlier.⁹ For completing the data of the rare earth bromates, in the present paper is reported the thermodynamic results on the rare earth bromates including heavier rare earths obtained by the isopiestic and the conductance measurements. The discussion on the formation of complexes was given in this work. The lanthanide bromides, chlorides, and perchlorates are reportedly outer-sphere complexes, whereas the nitrates form an outer sphere in dilute solutions and predominantly an inner sphere at high concentration. Thus, in dilute solution, the ion-size parameters of those halides include those of cation, anion, and water molecules. When an inner-sphere complex is formed, the metal ion is surrounded by anions and is not simply a hydrated ion. In the present paper, by examining various thermodynamic data, the trends of the aqueous rare earth bromates series are discussed in view of the formation of either outer- or inner-sphere complexes. Conductance data are also presented for the aqueous lanthanide bromates and chlorates in dilute solution.

Experimental Section

Chemicals. The rare earth oxides were obtained from Shin-Etsu Chem. Ind., as 99.9% or higher purity. Potassium bromate and barium chloride dihydrate used for the preparation of rare earth bromates were from Wako Pure Chem. Ind. and were of reagent grade. Potassium chlorate, ammonium sulfate, and barium hydroxide for preparing rare earth chlorates were also from Wako Pure Chem. Ind., as reagent grade. Potassium chloride and calcium chloride for the isopiestic measurements were supplied from High Purity Chemetal Laboratory, of better than 99.9% or higher purity. The other chemicals were of analytical reagent grade or better quality.

All the solutions were prepared with conductivity water, which was obtained by distilling from deionized water. The conductivity water had a specific conductance of less than 6.64×10^{-7} S·cm⁻¹.

Preparations of Rare Earth Bromates and Chlorates. The preparations of rare earth bromate solutions were described in the previous papers.^{9–11} The preparation method of each rare earth bromate solution, except cerium, employed double decomposition between barium bromate and the lanthanum sulfate followed by filtration to remove the precipitated barium sulfate. The rare earth sulfates were made by the following procedures. The respective lanthanide oxide was weighed, and a sufficient sulfuric acid for converting the oxide to sulfate was diluted with an appropriate amount of water. Then the oxide was soaked in water, and the sulfuric acid solution was added slowly. The mixture was warmed on a hot plate and finally heated to 500 °C to convert it to the anhydrous rare earth sulfate.

The barium bromate was obtained by mixing the boiling solutions of barium chloride and potassium bromate, and was purified by recrystallization.

The rare earth sulfate was dissolved in ice-cold water, and the resulting solution was poured on a slight excess of barium bromate. The solution was warmed on a hot plate

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overnight and then evaporated using a rotary evaporator. The solution was concentrated to obtain crystals of the lanthanide bromate. The crystals were filtered with a glass funnel, air-dried at room temperature, and then recrystallized. The lanthanide bromate solution was prepared by dissolving the respective bromate in conductivity water. These lanthanide bromate solutions were prepared under careful temperature control, since bromate compounds are inclined to decompose partially to yield bromide.

The lanthanide chlorate solutions were prepared from barium chlorate and rare earth sulfates. Barium chlorate was prepared by a mixture of potassium chlorate and ammonium sulfate in hot water and was evaporated with constant stirring until a thin slurry formed. After the mixture was cooled to room temperature, a 4-fold quantity of 80% ethyl alcohol was added, and the precipitate, potassium sulfate, was separated from the ammonium chlorate solution using a fritted glass filter. Then the solution was heated overnight and reacted in an evaporating dish on a hot plate with a sufficient quantity of hot concentrated barium hydroxide solution so that the ammonia odor disappeared completely and the solution finally gave a definite alkaline reaction. It was then evaporated to dryness. The residue was dissolved in a 5-fold excess of water, and carbon dioxide was bubbled through the solution to complete the precipitation of the barium. The precipitate was filtered off, and the solution was evaporated to crystallization. The crystal was dried at 120 °C for 5 h in order to convert the barium chlorate hydrate into the anhydrous compound. The subsequent preparation was the same as that of the lanthanide bromate.

All the stock solutions of lanthanide bromates and chlorate were analyzed by both EDTA and gravimetric analysis methods with an accuracy of $\pm 0.1\%$ or better.

The potassium chloride solution used as the standard solution of the isopiestic method was prepared by dissolving the recrystallized anhydrous potassium chloride in conductivity water. The standard calcium chloride solution was prepared by dissolving the salt in the conductivity water and was analyzed gravimetrically as calcium oxide. In this analysis, since the hydroscopic degree of calcium oxide was very high, magnesium perchlorate was used as desiccant. The average deviation for the analysis was within 0.06%.

Measurements. A conductance meter and a pH meter of Denki Kagaku Keiki, models AOL-40 and PHL-40, were used, respectively. During the measurement, the conductance cell was immersed in a water bath thermostated at (25.0 ± 0.1) °C. The test solutions were bubbled with nitrogen gas for 20 min, in order to remove carbon dioxide, and then left to stand to allow thermal equilibrium. Measurements were made three times or more for each test solution, and the average resistances were reliable to $\pm 0.3\%$. During the pH measurement, the test solutions were bubbled with nitrogen gas for 15 min. The densities were measured using Kyoto Denshi model DA-110; these data were used for computing the corresponding molality.

The conductance measurement was used for calculating ion-size parameters. The ion-size parameter is a mean distance of closest approach between the cation and the anion of the electrolyte in solution, and it was obtained by Onsager's equation including electrophoretic and relaxation effects.^{12–15} A value of the osmotic coefficient was calculated from the ion-size parameter. The electromotive force measurement with an electrochemical cell would give the most precise results among the conventional methods. However, in the present work, the electrode system was found not to be satisfactory for higher molalities of lithium

bromate and chlorate.

The isopiestic apparatus used for measuring the osmotic coefficients was the same one employed in the authors' previous paper.⁹ The osmotic coefficient values of potassium chloride solutions were taken from Hamer and Wu,¹⁶ and those of the calcium chloride solutions were quoted from Rard et al.¹⁷ The equilibrium molalities obtained were the average of two determinations in each case.¹⁸ All the measurements were performed at (25.00 ± 0.1) °C.

The isopiestic equilibrations for rare earth bromate solution concentrations required 2–7 days for the solutions above 0.6 mol kg⁻¹ and 2–4 weeks for the dilute samples, in contrast to the emf method, which takes only 1 h or so. The molalities after equilibrium agreed within the error of 0.17% for each couple, and the values were adopted within an error of 0.1%. The solubilities of the rare earth bromates were also obtained through the measurements of the osmotic coefficients, but with only two digits. The solubilities of bromates obtained were apparently higher than those values given by the previous work.⁹

Calculation. The specific conductances were given by the following equation

$$\kappa = \frac{J}{R} - \kappa_{\text{H}_2\text{O}} - \kappa_{\text{H}^+} \quad (1)$$

where κ is the specific conductance due only to the solute, J is the cell constant, R is the measured resistance, $\kappa_{\text{H}_2\text{O}}$ is the specific conductance of pure water used in preparation of the sample solution, and κ_{H^+} is the specific conductance of hydrogen ion in the solution minus that of hydrogen in water.

When the concentration is expressed by molality, molar conductivity, Λ_- , is implied

$$\Lambda_- = \frac{1000\kappa}{C} \quad (2)$$

where C is the molality of the electrolyte salt. The equivalent conductance is used for calculating the ion-size parameter. The equivalent conductance, λ , is also represented

$$\Lambda_- = 3\lambda \quad (3)$$

The osmotic coefficients, ϕ , at low concentration are given by the following equation

$$\phi = 1 - \left(\frac{A}{(B\alpha)3m} \right) \left[(1 + B\alpha\sqrt{m}) - \frac{1}{1 + B\alpha\sqrt{m}} - 2 \ln(1 + B\alpha\sqrt{m}) \right] \quad (4)$$

where α is the ion-size parameter calculated from the conductances, and A and B were the Debye–Hückel constants for the 3–1 electrolyte at 25 °C ($A = 8.6430$ for 3–1 electrolytes; $B = 0.8052$).

Osmotic coefficients of an electrolyte solution were calculated using the equation for isopiestic equilibrium

$$\phi = \frac{v^* \phi^* m^*}{vm} \quad (5)$$

where m is the molality of the solution of interest, v is the number of ions formed by the dissociation of one molecule of solute, and the corresponding quantities for the KCl or CaCl₂ reference standards are denoted with asterisks.

Experimental osmotic coefficients and other available activity data were represented by the least-squares equa-

tions of the type

$$\phi = 1 - \left(\frac{A}{3}\right)\sqrt{m} + \sum A_i m^{r_i} \quad (6)$$

Mean molal activity coefficients, γ_{\pm} , can be calculated from these least-squares parameters by using

$$\ln \gamma_{\pm} = \sqrt{Am} + \sum A_i \left(\frac{(r_i + 1)m^{r_i}}{r_i}\right) \quad (7)$$

Water activities, a_w , are given by the following equation

$$\ln a_w = -\frac{vm\phi M_1}{1000} \quad (8)$$

where M_1 was the molecular weight of the solvent, water in this work.

These osmotic coefficients were also represented by Pitzer's equations;^{18–20} these equations may be

$$\phi - 1 = |z_M z_X| f^{\phi} + m \left(\frac{2v_M v_X}{v}\right) B_{MX}^{\phi} + m^2 \left[\frac{2(v_M v_X)^{3/2}}{v}\right] C_{MX}^{\phi} \quad (9)$$

$$\ln \gamma_{\pm} = |z_M z_X| f^{\phi} + m \left(\frac{2v_M v_X}{v}\right) B_{MX}^{\phi} + m^2 \left[\frac{2(v_M v_X)^{3/2}}{v}\right] C_{MX}^{\phi} \quad (10)$$

where v_M and v_X are the numbers of M and X ions in the formula, z_M and z_X are the respective charges, $v = v_M + v_X$, and m is the molality of the solute.

The other quantities are defined by the following equations

$$f^{\phi} = -\frac{A_{\phi} I^{1/2}}{1 + bI^{1/2}} \quad (11)$$

$$f^{\phi} = -A_{\phi} \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \quad (12)$$

$$B_{MX}^{\phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2}) \quad (13)$$

$$B_{MX}^{\phi} = 2\beta_{MX}^{(0)} \left(\frac{2\beta_{MX}^{(1)}}{\alpha^2 I} \right) \left[1 - \left(1 + \alpha I^{1/2} - \frac{1}{2} \alpha^2 I \right) \exp(-\alpha I^{1/2}) \right] \quad (14)$$

$$C_{MX}^{\phi} = \frac{3}{2} C_{MX}^{\phi} \quad (15)$$

where A_{ϕ} is the Debye–Hückel constant, 0.3910 for water at 25 °C. It was found that good fits could be obtained with the parameters b and α fixed at their customary values of $b = 1.2$ and $\alpha = 2.0$.¹⁸

Results and Discussion

Preparations of the Reagents Employed. Since the preparations of the bromate and chlorate solutions were rather difficult, some sophisticated processes were required for obtaining the salts of the lanthanides. Because bromate compounds are inclined to decompose partially to yield bromide, the bromate solutions had to be prepared at temperatures lower than 110 °C. The solutions containing bromide were reddish, whereas pure bromate ion should be colorless. In the present work, the bromate solutions were not reddish, showing no bromide had been formed.

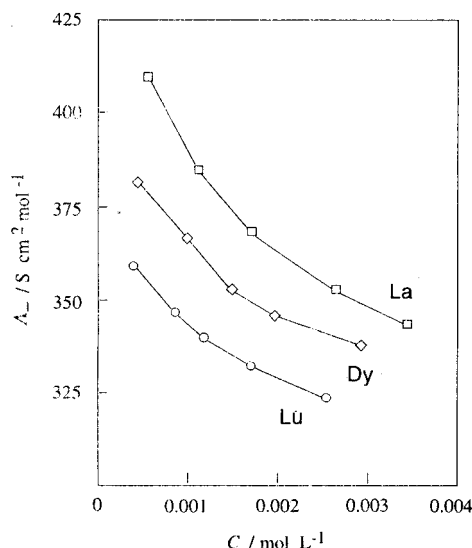


Figure 1. Molar conductances of lanthanum, dysprosium, and lutetium bromate solutions at 25.0 °C.

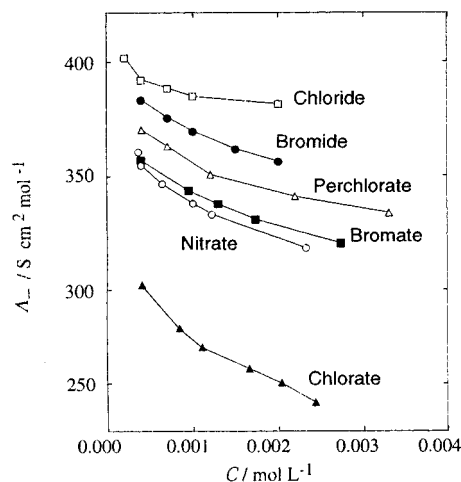


Figure 2. Molar conductances of ytterbium chlorate, bromate perchlorate, nitrate, chloride, and bromide solutions at 25.0 °C.

Chlorate might be reduced to chloride, by reducing agents, if it had been prepared or kept in a vessel, since chlorate is a strong oxidant. We obtained a commercially available high purity barium chlorate, although it still had a small amount of chloride. As the chlorates were not stable, chloride ions were removed from the chlorate solutions by an anion exchange purification process.

Conductances. The electrical conductances of lanthanide bromates and some lanthanide chlorates in dilute solutions are given in Table 1. The relative errors were less than 0.3% in any case. The pH values of each solution were from 5.11 to 5.92 for the bromates and from 5.66 to 6.54 for the chlorates. It is reported that the heavier lanthanide ions tend to hydrolyze and form $\text{Ln}_2(\text{OH})_2^{4+}$ and $\text{Ln}_3(\text{OH})_5^{4+}$ in solution.²¹ As the sample solution was slightly hydrolyzed, the conductance might be affected by hydrolysis.

The electrical conductances of lanthanum, dysprosium, and lutetium bromates are plotted against molar concentration in Figure 1. Those values of bromates decreased with increasing molality, and the changes are smooth with increasing atomic number of the lanthanide elements. With decreasing ionic radius, the surface charge density of the ion increases, and the ion tends to hydrate more strongly. Since an ion is surrounded with the hydrating water molecules, its movement would not be free, and the

Table 1. Equivalent Conductances of Rare Earth Bromates and Chlorates in Aqueous Solutions at 25 °C

$C/\text{mol L}^{-1}$	$\Lambda_{\infty}/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$C/\text{mol L}^{-1}$	$\Lambda_{\infty}/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$C/\text{mol L}^{-1}$	$\Lambda_{\infty}/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$C/\text{mol L}^{-1}$	$\Lambda_{\infty}/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
La(BrO ₃) ₃		Gd(BrO ₃) ₃		Tm(BrO ₃) ₃		Sm(ClO ₃) ₃	
0.000 550 1	409.2	0.000 470 6	366.7	0.000 436 0	373.8	0.000 361 4	373.0
0.001 120	384.5	0.000 953 0	352.7	0.000 953 0	359.4	0.000 745 8	348.8
0.001 727	367.4	0.001 487	342.5	0.001 376	337.2	0.001 110	336.6
0.002 635	352.6	0.001 954	334.0	0.001 902	326.4	0.001 518	322.1
0.003 438	343.0	0.002 961	325.7	0.002 775	317.0	0.002 374	301.6
Pr(BrO ₃) ₃		Tb(BrO ₃) ₃		Yb(BrO ₃) ₃		Gd(ClO ₃) ₃	
0.000 507 0	394.0	0.000 477 5	375.3	0.000 396 2	370.6	0.000 342 6	351.1
0.000 989 3	372.8	0.000 982 5	359.7	0.000 944 0	354.3	0.000 823 2	322.0
0.001 508	360.3	0.001 480	350.8	0.001 297	346.9	0.001 305	305.8
0.002 005	350.8	0.002 002	345.5	0.001 734	339.0	0.001 714	295.4
0.003 046	339.1	0.002 969	331.8	0.002 741	326.2	0.002 210	286.9
						0.002 584	276.9
Nd(BrO ₃) ₃		Dy(BrO ₃) ₃		Lu(BrO ₃) ₃		Dy(ClO ₃) ₃	
0.000 490 3	392.5	0.000 448 9	382.1	0.000 390 9	359.1	0.000 465 2	318.8
0.000 979 1	372.6	0.000 990 3	366.0	0.000 858 5	346.0	0.000 857 1	300.0
0.001 473	359.7	0.001 477	352.6	0.001 178	339.2	0.001 240	285.4
0.001 973	352.2	0.001 957	345.8	0.001 692	331.9	0.001 659	277.5
0.002 953	337.7	0.002 913	337.5	0.002 544	323.4	0.001 986	270.1
						0.002 400	262.0
Sm(BrO ₃) ₃		Ho(BrO ₃) ₃		Y(BrO ₃) ₃		Er(ClO ₃) ₃	
0.000 508 7	380.9	0.000 466 9	370.1	0.000 413 7	378.2	0.000 438 2	318.4
0.000 996 9	366.2	0.000 982 5	353.0	0.001 032	361.0	0.001 262	285.5
0.001 495	353.1	0.001 480	350.8	0.001 462	352.4	0.001 648	276.7
0.002 028	340.1	0.002 002	345.5	0.001 929	344.3	0.001 934	266.2
0.002 957	330.8	0.002 969	331.8	0.002 931	331.7	0.002 331	260.6
				0.002 584	276.9		
Eu(BrO ₃) ₃		Er(BrO ₃) ₃		Pr(ClO ₃) ₃		Yb(ClO ₃) ₃	
0.000 492 2	392.5	0.000 487 0	400.5	0.000 438 2	378.3	0.000 401 2	305.8
0.001 029	362.9	0.000 990 3	383.7	0.000 685 0	365.7	0.000 837 7	280.3
0.001 489	351.9	0.001 483	368.8	0.001 131	345.9	0.001 106	269.9
0.002 009	341.6	0.001 970	359.7	0.001 394	333.1	0.002 035	250.7
0.002 957	335.5	0.003 076	343.6	0.001 884	323.1	0.002 432	240.2
				0.002 305	314.0		

Table 2. Ion-Size Parameters of Lanthanide Bromates and Chlorates

salt	$a/10^{-10}$ m	salt	$a/10^{-10}$ m
La(BrO ₃) ₃	4.7	Yb(BrO ₃) ₃	4.1
Pr(BrO ₃) ₃	4.3	Lu(BrO ₃) ₃	4.7
Nd(BrO ₃) ₃	4.5	Y(BrO ₃) ₃	4.2
Sm(BrO ₃) ₃	3.5		
Eu(BrO ₃) ₃	3.5	Nd(ClO ₃) ₃	2.8
Gd(BrO ₃) ₃	4.0	Sm(ClO ₃) ₃	2.8
Tb(BrO ₃) ₃	4.8	Gd(ClO ₃) ₃	2.6
Dy(BrO ₃) ₃	4.0	Dy(ClO ₃) ₃	2.8
Ho(BrO ₃) ₃	3.3	Er(ClO ₃) ₃	2.9
Er(BrO ₃) ₃	4.2	Yb(ClO ₃) ₃	2.7
Tm(BrO ₃) ₃	4.4		

equivalent conductance decreases. As the ionic radius of the lanthanide ion decreases due to the lanthanide contraction, the equivalent conductance of bromates would be affected by an increasing interionic interaction and decrease with an increase in atomic number.

A comparison of the equivalent conductances of ytterbium bromate and chlorate with those of other ytterbium salts is shown in Figure 2. Those of chlorate are lower than those of other halides, and the curve of the bromates is similar to that of the nitrates. In dilute solution, where the slope of the curve for the nitrates is large, the equivalent conductances of bromates are larger than those of nitrates. The equivalent conductances of chlorates were the lowest among all the other compounds, and the slope of the curves was the largest. The ion-size parameters that were calculated from the equivalent conductances are listed in Table 2. Those parameters of lanthanide bromates are smaller than those of halides, and those of the chlorates were the lowest among them. The ion-size parameter may be taken as a measure of the sum of the crystallographic

radii of the cation and anion of the electrolytes. The bromides, chlorides, and perchlorates are reportedly outer-sphere complexes, whereas the nitrates form outer-sphere complexes in dilute solution. Thus, the ion-size parameters of the rare earth halides include cation, anion, and water molecules. However, in dilute solutions, the rare earth bromates form inner-sphere complexes, as indicated from the values of ion-size parameter, and those parameters of the bromates may be the sum of the radii of bromate ion and the rare earth ion, not including those of the water molecule like other halides. The shapes of nitrate and bromate ions are not spherical;²² however, the nitrates only have a planar structure. Therefore, the bromate ion would approach the metal ion closer than nitrate; as a result, bromates predominantly formed the inner-sphere complexes. It was reported that the monoligand complexes of lanthanide bromate exist predominantly as an outer-sphere species, and the dibromate complexes have inner-sphere coordination in dilute solutions.^{23,24} For this work, as the bromate solutions are thought to contain inner-sphere complexes, the bromates may exist in dibromate complexes in dilute solution. As the chlorates are not also spherically shaped, and the radius of chlorate ion is larger than that of bromate ion, the chlorates may likewise be the inner-sphere complexes.

Osmotic Coefficients, Water Activities, and Mean Molal Activity Coefficients. Isopiestic molalities and coefficients of standard and rare earth bromate solutions are given in Table 3. The parameters and the powers of eqs 6 and 7 for the lanthanide bromates are listed in Table 4, along with the standard deviation of each fit. It was found that good fits could be obtained for the lanthanide bromates by using seven terms in the series with the first

Table 3 (Continued)

<i>m</i> , standard	<i>m</i> , Ln(BrO ₃) ₃	ϕ Ln(BrO ₃) ₃	<i>m</i> , standard	<i>m</i> , Ln(BrO ₃) ₃	ϕ Ln(BrO ₃) ₃	<i>m</i> , standard	<i>m</i> , Ln(BrO ₃) ₃	ϕ Ln(BrO ₃) ₃	<i>m</i> , standard	<i>m</i> , Ln(BrO ₃) ₃	ϕ , Ln(BrO ₃) ₃
Ho(BrO ₃) ₃ vs CaCl ₂											
1.175	0.9821	0.9821	1.586	1.287	1.135	1.887	1.514	1.247	2.243	1.761	1.401
1.176	0.9839	0.9909	1.685	1.364	1.169	1.918	1.528	1.267	2.259	1.776	1.405
1.501	1.225	1.102	1.852	1.488	1.234	2.142	1.688	1.360	2.426	1.858	1.486
Er(BrO ₃) ₃ vs KCl											
0.2513	0.1477	0.7735	0.7960	0.4304	0.8301	1.653	0.7720	0.9700	2.707	1.112	1.130
0.3340	0.2058	0.7851	0.8656	0.4590	0.8463	1.849	0.8509	0.9881	2.836	1.152	1.147
0.5584	0.3073	0.8067	1.229	0.6102	0.9061	2.005	0.8952	1.022	2.983	1.187	1.175
0.6011	0.3358	0.7986	1.409	0.6814	0.9329	2.168	0.9627	1.031	3.027	1.199	1.182
Er(BrO ₃) ₃ vs CaCl ₂											
1.359	1.069	1.099	1.852	1.411	1.301	1.983	1.502	1.356	2.189	1.647	1.442
1.501	1.169	1.155	1.887	1.434	1.317	2.066	1.553	1.397	2.382	1.758	1.545
1.617	1.252	1.200	1.915	1.453	1.328	2.141	1.604	1.430	2.406	1.771	1.559
1.671	1.290	1.222	1.923	1.467	1.325	2.179	1.626	1.450	3.104	2.184	1.930
1.732	1.336	1.248									
Tm(BrO ₃) ₃ vs KCl											
0.5378	0.2022	0.7902	0.8561	0.4344	0.8561	1.045	0.5233	0.9074	1.337	0.6414	0.9396
0.5570	0.3127	0.8093	1.041	0.5189	0.9010	1.229	0.6304	0.9359	1.912	0.8487	1.026
0.6653	0.3646	0.8193									
Tm(BrO ₃) ₃ vs CaCl ₂											
1.176	0.9055	1.066	1.586	1.185	1.233	2.142	1.539	1.492	2.717	1.905	1.768
1.300	0.9909	1.115	1.685	1.259	1.266	2.259	1.617	1.543	2.956	2.050	1.893
1.420	1.070	1.167	1.918	1.406	1.377	2.406	1.728	1.598			
Yb(BrO ₃) ₃ vs KCl											
0.2322	0.1641	0.7666	0.7156	0.3853	0.8541	1.045	0.5226	0.9086	1.719	0.7705	1.012
0.5570	0.3099	0.8079	0.8561	0.4730	0.8701	1.229	0.6123	0.9031	1.912	0.8287	1.050
0.6653	0.3498	0.8338	1.041	0.5186	0.9015						
Yb(BrO ₃) ₃ vs CaCl ₂											
1.176	0.9071	1.067	1.685	1.250	1.276	2.259	1.605	1.555	2.938	2.025	1.896
1.300	0.9887	1.117	1.918	1.396	1.387	2.406	1.728	1.598	2.956	2.033	1.908
1.586	1.181	1.237	2.142	1.528	1.503	2.717	1.896	1.777	3.104	2.119	1.989
Lu(BrO ₃) ₃ vs KCl											
0.5378	0.2923	0.8073	1.229	0.6094	0.9075	1.653	0.7818	0.9578	2.983	1.203	1.160
0.6817	0.3670	0.8340	1.409	0.6905	0.9205	2.005	0.9068	1.009	3.027	1.214	1.168
0.9855	0.5093	0.8688									
Lu(BrO ₃) ₃ vs CaCl ₂											
1.131	1.026	1.092	2.066	1.561	1.390	2.717	1.938	1.738	2.956	2.079	1.866
1.732	1.338	1.241	2.382	1.763	1.541	2.938	2.069	1.856	3.104	2.160	1.951
1.915	1.460	1.322									
Yb(BrO ₃) ₃ vs KCl											
0.5584	0.3050	0.8230	1.267	0.6415	0.8890	1.930	0.9011	0.9754	2.127	0.9715	1.002
0.8656	0.4590	0.8463	1.408	0.7003	0.9071	2.015	0.9313	0.9869	2.667	1.147	1.078
1.005	0.5253	0.8589	1.846	0.8710	0.9633	2.083	0.9542	0.9972			
Y(BrO ₃) ₃ vs CaCl ₂											
1.073	0.8792	0.9736	1.501	1.201	1.125	1.852	1.456	1.261	2.141	1.662	1.380
1.259	1.023	1.034	1.503	1.208	1.120	1.983	1.584	1.286	2.406	1.836	1.504

four terms fixed at $r_1 = 0.75$, $r_2 = 0.875$, $r_3 = 1$, and $r_4 = 1.125$ while the other terms were allowed to vary from 1.175 to 20.

The osmotic coefficients of lanthanum, gadolinium, and thulium bromate solutions are shown as a function of molality with calculated values in Figure 3. Those same trends appear for each of the rare earth bromates, and the slope rises more sharply in going to heavier lanthanides. These approximate data from electrical conductance were in fair agreement with isopiestic data for the rare earth bromates. The differences between the calculated and observed values were smaller in the cases of lighter lanthanides.

Figure 4 shows the mean molal activity coefficients of praseodymium, dysprosium, and lutetium bromates versus molality. In dilute solution, as the ionic interaction defined by Debye–Hückel theory is strong, the mean molal activity coefficient decreases. After going through a plateau, the activity coefficients began to increase. The heavier lanthanides have steeper curve shapes than the lighter

lanthanides. The decreases of osmotic and activity coefficients at lower molalities are explained in terms of increasing electrostatic interactions.

The osmotic coefficients, water activities, and mean molal activity coefficients at constant molalities, as functions of the ionic radii,²⁵ of 8-coordination are shown in Figures 5–7. The osmotic coefficients increase with decreasing ionic radius, from lanthanum to ytterbium. Since the ionic radii decrease with increasing surface charge densities of ion with the same valence number, the water molecules tend to hydrate more strongly, and the coordination power between the rare earth ion and bromate ion becomes weak. The curve shape of bromate of high concentration is larger than that of low concentration. Since the primary hydration number of the rare earth ions varies from 9 to 8 between europium and dysprosium in the absence of inner-sphere complexes, the curve shapes of lighter rare earths are different from those of the heavier ones. The osmotic coefficient of lutetium bromate is smaller than those of thulium and ytterbium. Since the lutetium

Table 4. Parameters for Eqs 6 and 7

i	r_i	A_i	i	r_i	A_i	i	r_i	A_i	i	r_i	A_i
La(BrO ₃) ₃			Pr(BrO ₃) ₃			Ho(BrO ₃) ₃			Er(BrO ₃) ₃		
1	0.750	24.303 724	1	0.750	33.112 955	1	0.750	75.625 465	1	0.750	17.745 31
2	0.875	-188.990 89	2	0.875	-227.852 66	2	0.875	-517.384 29	2	0.875	-125.583 67
3	1.000	563.301 14	3	1.000	582.342 59	3	1.000	1370.1956	3	1.000	334.598 66
4	1.125	-654.619 74	4	1.125	-545.459 13	4	1.125	-1919.0879	4	1.125	-304.855 63
5	1.300	313.748 94	5	1.375	212.851 52	5	1.200	1002.4074	5	1.400	100.204 14
6	1.625	-68.013 65	6	1.675	-58.292 907	6	1.825	-8.890 792	6	1.825	-22.821 131
7	1.900	12.881 126	7	2.100	5.829 677 8	7	20.00	2.485 941 × 10 ⁻⁷	7	2.250	3.661 227 5
SD = 2.1 × 10 ⁻²			SD = 1.6 × 10 ⁻²			SD = 3.7 × 10 ⁻²			SD = 5.8 × 10 ⁻²		
Nd(BrO ₃) ₃			Sm(BrO ₃) ₃			Tm(BrO ₃) ₃			Yb(BrO ₃) ₃		
1	0.750	-10.652 714	1	0.750	63.151 508	1	0.750	43.690 104	1	0.750	40.827 76
2	0.875	50.618 503	2	0.875	-421.633 71	2	0.875	-341.899 9	2	0.875	-828.683 03
3	1.000	-49.780 766	3	1.000	1100.048 2	3	1.000	1103.579 6	3	1.000	1727.282 1
4	1.125	-31.079 805	4	1.125	-1513.806 9	4	1.125	-2071.391	4	1.125	-1330.709 1
5	1.150	43.523 088	5	1.200	783.472 35	5	1.200	1453.550 6	5	1.300	322.103 56
6	4.750	3.085 621 3 × 10 ⁻³	6	1.900	-5.557 156 59	6	1.350	-184.522 74	6	3.250	-28.024 056
7	11.50	-1.062 367 9 × 10 ⁻⁴	7	10.25	1.600 431 9 × 10 ⁻⁴	7	9.50	7.498 883 4 × 10 ⁻⁵	7	12.00	7.018 748 1 × 10 ⁻³
SD = 2.7 × 10 ⁻²			SD = 2.8 × 10 ⁻²			SD = 6.5 × 10 ⁻²			SD = 6.7 × 10 ⁻²		
Eu(BrO ₃) ₃			Gd(BrO ₃) ₃			Lu(BrO ₃) ₃			Y(BrO ₃) ₃		
1	0.750	57.105 694	1	0.750	56.671 753	1	0.750	44.659 32	1	0.750	22.174 31
2	0.875	-345.913 69	2	0.875	-357.034 28	2	0.875	-322.550 63	2	0.875	-141.332 85
3	1.000	738.404 98	3	1.000	808.655 13	3	1.000	874.683 5	3	1.000	341.903 00
4	1.125	-547.285 75	4	1.125	-657.626 94	4	1.125	-914.506 54	4	1.125	-305.903 00
5	1.525	156.733 24	5	1.425	197.154 14	5	1.350	479.813 46	5	1.400	86.504 45
6	1.950	-443.937 19	6	1.875	-106.003 75	6	1.600	-236.935 79	6	1.825	-0.470 909 6
7	1.975	387.567 12	7	1.980	60.899 372	7	1.75	77.799 702	7	2.250	2.383 89 × 10 ⁻²
SD = 2.2 × 10 ⁻²			SD = 3.5 × 10 ⁻²			SD = 4.3 × 10 ⁻²			SD = 4.7 × 10 ⁻²		
Tb(BrO ₃) ₃			Dy(BrO ₃) ₃								
1	0.750	-369.516 2	1	0.750	140.827 76						
2	0.875	2588.884 6	2	0.875	-828.583 03						
3	1.000	-8987.184 6	3	1.000	1 727.282 1						
4	1.125	68 801.296	4	1.125	-1 330.709 1						
5	1.150	-99 415.439	5	1.375	322.103 56						
6	1.175	37 384.729	6	1.850	-28.024 056						
7	20.00	3.586 787 5 × 10 ⁻⁸	7	7.00	7.018 748 1 × 10 ⁻³						
SD = 3.5 × 10 ⁻²			SD = 4.5 × 10 ⁻²								

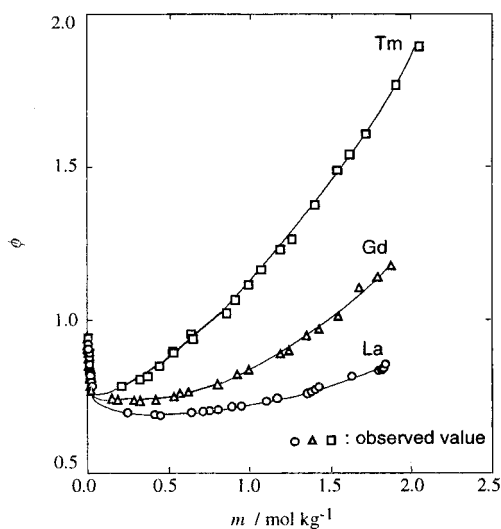


Figure 3. Osmotic coefficients, ϕ , of lanthanum, gadolinium, and thulium bromate solutions at 25.0 °C.

has a closed shell structure, the electrons of lutetium in the compound would be slightly more attracted to the atomic nucleus than in the case of thulium and ytterbium compounds, resulting in the formation of stable lutetium compounds. The osmotic coefficients of lutetium bromate fall between those of dysprosium and holmium. The trend is reasonable for their ionic radii.

The changes of the mean molal activity coefficients were the same as those of the osmotic coefficients but are more irregular. The coefficient values of lighter lanthanides of various concentrations are similar for each element; how-

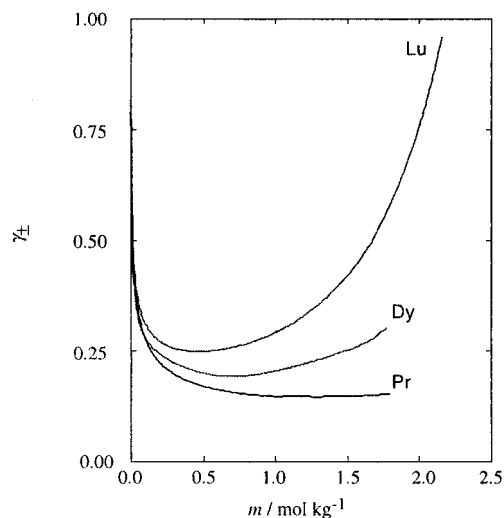


Figure 4. Mean molal activity coefficients, γ_{\pm} , of praseodymium, dysprosium, and lutetium bromate solutions at 25.0 °C.

ever, the heavier lanthanide bromates behave much differently. The mean molal activities of gadolinium bromate are different than those of other lanthanides. The reason is not clear.

The mean molal activity coefficients of neodymium bromate, together with nitrate, bromide, chloride, and perchlorate salts are shown in Figure 8. The mean molal activities of the bromates have the smallest values among them. As the molarity for the minimum value, the value of bromate was larger than that of nitrate. The nitrates form appreciable amounts of inner-sphere complexes es-

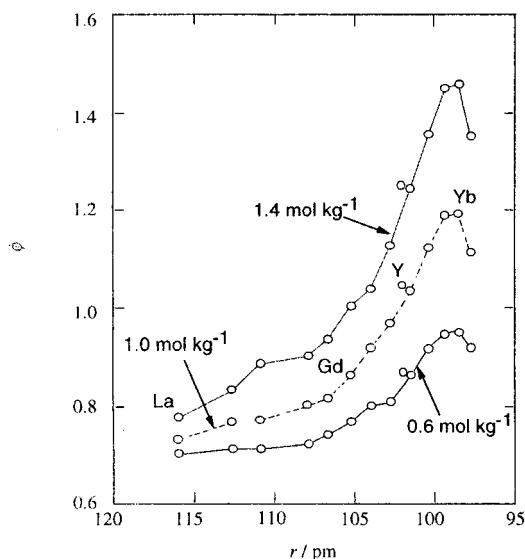


Figure 5. Osmotic coefficients, ϕ , of some lanthanide bromates at constant molalities as a function of ionic radius, r .

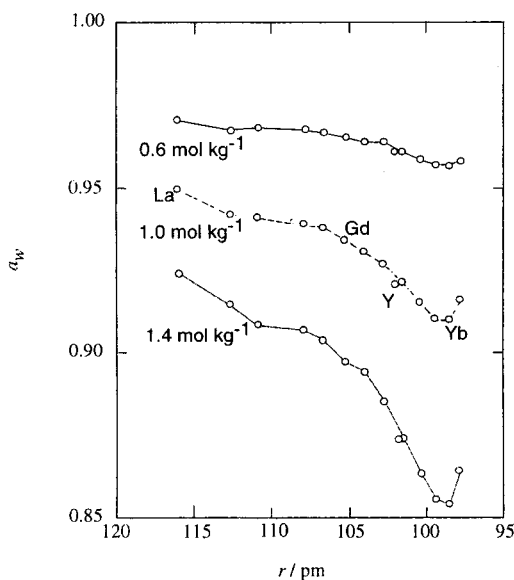


Figure 6. Water activities, a_w , of some lanthanide bromates at constant molalities as a function of ionic radius, r .

pecially at high concentration.³ The formation of inner-sphere complexes will result in the displacement of a water molecule from the rare earth ion's inner-sphere and will reduce the charge on the rare earth ion. Consequently, inner-sphere complex formation is probably much more important than bromate ion-water molecule interactions in determining the thermodynamic properties of rare earth bromate solutions.

Pitzer Parameters. Pitzer's equation contains a short-range interaction parameter, $3\beta(0)/2$, which contains information about complex formation at high concentration. The values of the three parameters of Pitzer's equation, $3\beta(0)/2$, $3\beta(1)/2$, and $3^{3/2}C^\phi$, are listed in Table 5, and the values of $3\beta(0)/2$ are plotted in Figure 9 as a function of the ionic radius.²⁵ The values of $3\beta(0)/2$ form S-shaped curves as a function of the cationic radius for the rare earth chlorides and perchlorates, and the behavior can be attributed to the hydration trends of cations. For the rare earth bromates, $3\beta(0)/2$ varied slightly from La to Sm, and then increased for the remaining rare earths. The shape of the bromate curve looks similar to those of the curves of nitrates.

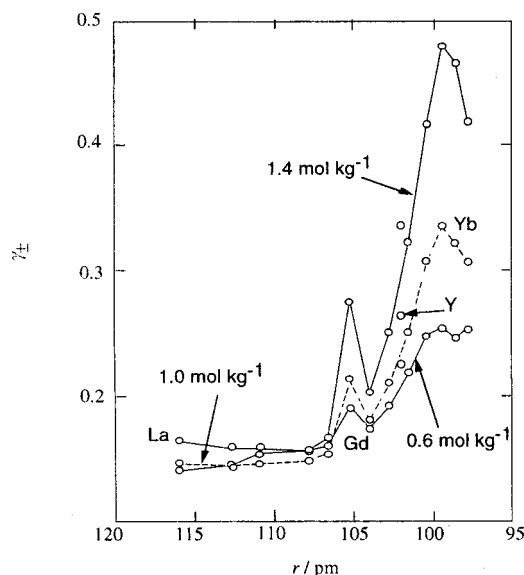


Figure 7. Mean molal activity coefficients, g_{\pm} , of some lanthanide bromates at constant molalities as a function of ionic radius, r .

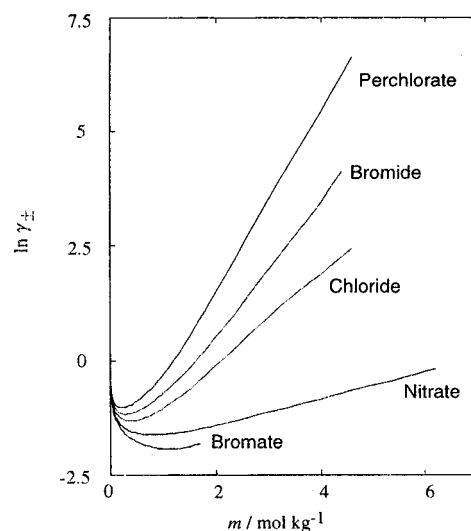


Figure 8. Mean molal activity coefficients, γ_{\pm} , of aqueous neodymium bromide, chloride, perchlorate, nitrate, and bromate solutions at 25.0 °C.

Table 5. Pitzer Parameters of Lanthanide Bromates

salt	$3/2\beta(0)$	$3/2\beta(1)$	$(3^{3/2})C^\phi$	SD
La(BrO ₃) ₃	0.4858	7.852	-0.087 36	4.5×10^{-2}
Pr(BrO ₃) ₃	0.5193	8.092	-0.085 54	4.5×10^{-2}
Nd(BrO ₃) ₃	0.4699	7.584	-0.039 75	4.8×10^{-2}
Sm(BrO ₃) ₃	0.5015	7.366	-0.047 55	8.6×10^{-2}
Eu(BrO ₃) ₃	0.4949	7.861	-0.028 09	9.2×10^{-2}
Gd(BrO ₃) ₃	0.5135	8.192	-0.012 64	8.6×10^{-2}
Tb(BrO ₃) ₃	0.6203	8.424	-0.062 99	1.6×10^{-1}
Dy(BrO ₃) ₃	0.6248	8.046	-0.029 32	1.1×10^{-1}
Ho(BrO ₃) ₃	0.6523	9.221	0.001 591	1.0×10^{-1}
Er(BrO ₃) ₃	0.6770	9.672	0.036 99	1.2×10^{-1}
Tm(BrO ₃) ₃	0.7780	8.802	0.011 62	8.4×10^{-2}
Yb(BrO ₃) ₃	0.7647	9.068	0.026 91	1.1×10^{-1}
Lu(BrO ₃) ₃	0.7825	11.847	0.087 73	1.5×10^{-1}
Y(BrO ₃) ₃	0.6773	10.412	-0.003 58	8.1×10^{-2}

The values of $3\beta(0)/2$ for the rare earth bromates suggest that the complex formation is rather encouraged for the lighter rare earths and relatively discouraged for the heavier rare earths. The nitrates have a similar trend, and the series behavior of the rare earth nitrates is consistent with stability constant values^{24,26} and electrical conduc-

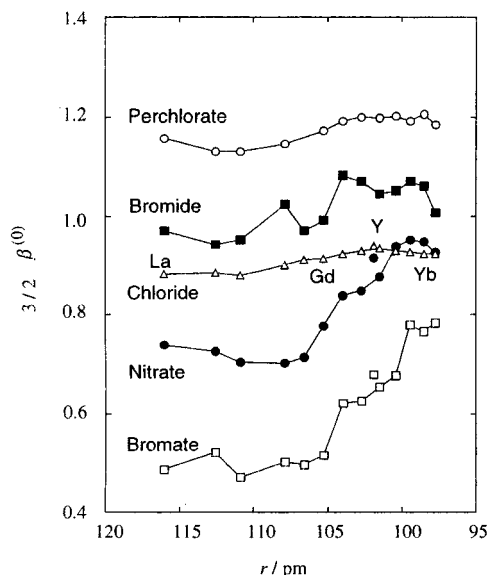


Figure 9. Pairwise short-range interaction parameter as a function of cationic radius.

tance data.^{27,28} The $3\beta(0)/2$ values of rare earth nitrates are comparatively lower than those of chlorides, perchlorates, and bromides. For those thermodynamic data, as has been discussed, the trend would indicate that the bromate has a more attractive interaction than the nitrates. The trend implied that the rare earth nitrates and bromates have an inner-sphere complex predominantly. A change of the hydration number was apparently observed as a function of the ionic radius of the rare earth ion, but it is somewhat modified from that observed for the more dissociated chloride, perchlorate, and bromide salts.

Acknowledgment

The author is indebted to Dr. Yasuo Suzuki, an emeritus professor of Meiji University, for many valuable insights into this problem. The authors thank Mr. Eiji Iwamoto, Hiroki Ishida, and Shin Saito, Department of Industrial Chemistry, Meiji University, for their assistance with the electrical conductance method.

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Received for review June 19, 2000. Accepted November 22, 2000.

JE000184X