Mean molal activity coefficients of aqueous rare earth bromide solutions at 25 °C

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Abstract

Mean molal activity coefficients and water activities of aqueous solutions of 15 rare earth elements were determined at 25.0 °C from dilute to saturated concentrations. Conductance and isopiestic measurements were carried out to obtain osmotic coefficients, from which mean molal activity coefficients and water activities were computed by fitting the values to the semi-empirical least-squares equations. The mean molal activity coefficients and water activities of the bromides were in between those of chlorides and perchlorates, showing the outer-sphere coordination of bromide to trivalent rare earth ions. The trends in the coefficients and activities are discussed in terms of ionic interactions, ionic radii and the numbers of coordination and hydration.

1. Introduction

Although a variety of thermodynamic data on electrolytic solutions has been published for the rare earth compounds, no thorough results on the rare earth bromides have been given. Spedding et al. [1] reported the activity coefficients of six rare earth bromides, and the authors recently published the activity data of eight rare earth bromides from dilute to saturated concentrations [2]. The present work includes the revised and complete data on the 15 rare earth bromides.

2. Experimental details

The experimental details, including isopiestic and conductance measurements, were the same as reported in the authors' previous papers [2,3]. The isopiestic equilibrium was attained when the molalities of duplicate samples agreed to within ±0.1%, however, in most cases the equilibrations were obtained with an accuracy of ±0.05%. The isopiestic equilibration period required 2–3 days for concentrated solutions and 2–3 weeks for dilute samples. The solubility measurements of the rare earth bromides have been made in separate experiments, and the results will be published later.

The rare earth bromide solutions were prepared from respective rare earth oxides of 99.9% or higher purity

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(from Shin-etsu Chem, Ind. Co., Ltd.). The stock solutions were adjusted to the equivalence pH values and analysed gravimetrically through the precipitation of oxalates. Solutions of potassium and calcium chlorides were prepared from the salts of repeated recrystallization, and used as isopiestic standards, as well as sulphuric acid. All the solutions were prepared with conductivity water, and all the measurements were made in a thermostatted bath of 25.0±0.1 °C.

3. Results and discussion

The molal osmotic coefficient, ϕ, of an electrolyte solution is given by

$$\phi = \nu^* \phi^* m^* / \nu m \tag{1}$$

where ν is the total number of ions formed at complete dissociation of one molecule of the solute, and m is the molality of the solute; the asterisk refers to the standard solution. The osmotic coefficients of potassium chloride are taken from the work of Hamer and Wu [4], while those of calcium chloride and sulphuric acid were from the works of Rard et al. [5–7].

The resulting osmotic coefficients of the rare earth bromide solutions were fitted to

$$\phi = 1 - (A/3)m^{1/2} + \sum A_i m^{r_i} \tag{2}$$

where $A = 8.6430$ is the Debye–Hückel limiting slope for 3:1 electrolytes. The mean molal activity coefficient, $\gamma_\pm$, can be obtained by combining eqn. (2) with the

TABLE 1. Parameters for eqns. (2) and (3)

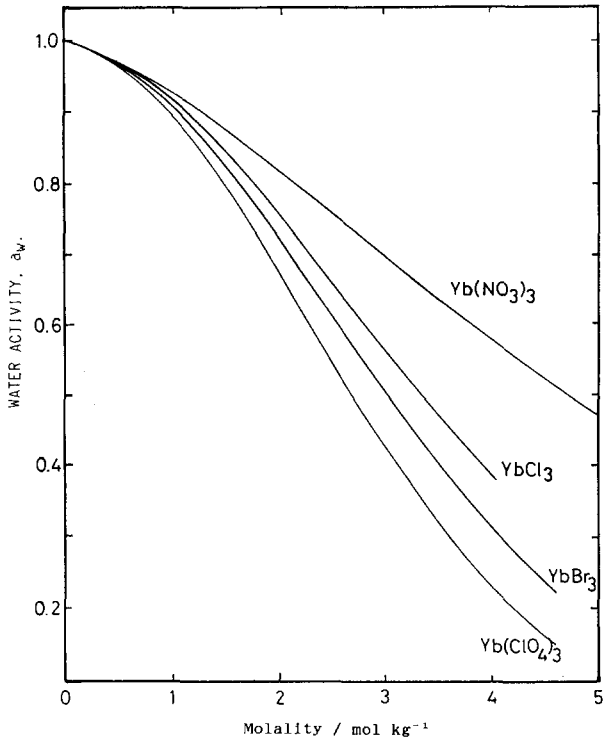| i	r_i	A_i	i	r_i	A_i
LaBr$_3$			CeBr$_3$		
1	0.75	-6.92422	1	0.75	3.56212
2	0.875	4.62168×10	2	0.875	8.26590
3	1.00	-6.06831×10	3	1.00	-1.55400×10
4	1.125	2.46058×10	4	1.125	6.85851
5	2.50	-3.55795×10^{-2}	5	7.00	1.24390×10^{-4}
6	3.00	-1.13100×10^{-2}	6	9.00	-1.18117×10^{-5}
7	12.00	2.34399×10^{-9}	7	12.00	6.50692×10^{-8}
	SD 5.1680×10^{-2}			SD 2.4034×10^{-1}	
PrBr$_3$			NdBr$_3$		
1	0.75	-8.89084	1	0.75	-2.15740
2	0.875	5.19359×10	2	0.875	2.78228×10
3	1.00	-6.60484×10	3	1.00	-3.75259×10
4	1.125	2.61932×10	4	1.125	1.50466×10
5	3.00	-2.50449×10^{-2}	5	8.00	-3.89736×10^{-5}
6	7.00	5.22062×10^{-6}	6	10.00	3.12024×10^{-6}
7	12.00	1.69795×10^{-9}	7	12.00	-6.74326×10^{-8}
	SD 4.7091×10^{-2}			SD 5.967×10^{-2}	
SmBr$_3$			EuBr$_3$		
1	0.75	-1.29530×10	1	0.75	-3.54736
2	0.875	6.76695×10	2	0.875	3.23571×10
3	1.00	-8.56814×10	3	1.00	-4.23959×10
4	1.125	3.41835×10	4	1.125	1.67877×10
5	3.00	-4.42684×10^{-2}	5	7.00	-1.79168×10^{-4}
6	6.00	1.13316×10^{-4}	6	9.00	1.19936×10^{-5}
7	10.00	-9.24688×10^{-9}	7	12.00	-4.51272×10^{-8}
	SD 3.29×10^{-2}			SD 4.2376×10^{-2}	
GdBr$_3$			TbBr$_3$		
1	0.75	-8.39599	1	0.75	-5.33963
2	0.875	5.08259×10	2	0.875	3.88407×10
3	1.00	-6.54809×10	3	1.00	-5.00484×10
4	1.125	2.62875×10	4	1.125	1.97946×10
5	3.00	-3.22270×10^{-2}	5	7.00	-2.59464×10^{-4}
6	8.00	5.03728×10^{-6}	6	9.00	1.69540×10^{-5}
7	12.00	-3.81631×10^{-9}	7	12.00	-6.31734×10^{-8}
	SD 9.4458×10^{-2}			SD 5.8294×10^{-2}	
DyBr$_3$			HoBr$_3$		
1	0.75	-1.11005×10	1	0.75	-3.68189×10^{-1}
2	0.875	6.20769×10	2	0.875	2.28595×10
3	1.00	-8.03726×10	3	1.00	-3.31083×10
4	1.125	3.27180×10	4	1.125	1.38660×10
5	2.25	6.31163×10^{-2}	5	5.00	-1.09362×10^{-3}
6	2.50	-1.34977×10^{-1}	6	7.00	3.66880×10^{-5}
7	15.00	9.13499×10^{-11}	7	12.00	-3.36165×10^{-9}
	SD 3.6391×10^{-2}			SD 8.2478×10^{-2}	
ErBr$_3$			TmBr$_3$		
1	0.75	-4.72659	1	0.75	-9.17687
2	0.875	2.21456×10	2	0.875	5.53377×10
3	1.00	-3.13482×10	3	1.00	-7.24884×10
4	1.125	1.29275×10	4	1.125	2.96236×10
5	8.00	-3.29975×10^{-5}	5	3.00	-4.27506×10^{-2}
6	10.00	2.59181×10^{-6}	6	7.00	3.83570×10^{-5}
7	12.00	-5.80431×10^{-8}	7	12.00	-9.52081×10^{-9}
	SD 1.2879×10^{-1}			SD 6.1636×10^{-2}	
YbBr$_3$			LuBr$_3$		
1	0.75	3.10909	1	0.75	-9.24158
2	0.875	1.21880×10	2	0.875	4.94582×10
3	1.00	-2.22797×10	3	1.00	-5.95383×10
4	1.125	1.02257×10	4	1.125	2.25492×10
5	7.00	-1.33013×10^{-4}	5	6.00	-2.48547×10^{-4}
6	9.00	8.06360×10^{-6}	6	9.00	2.08922×10^{-6}
7	12.00	-2.77240×10^{-8}	7	12.00	-6.24829×10^{-9}
	SD 1.1658×10^{-1}			SD 1.3201×10^{-1}	
YBr$_3$					
1	0.75	-1.13284×10			
2	0.875	5.84125×10			
3	1.00	-7.13719×10			
4	1.125	2.75185×10			
5	6.00	-1.26523×10^{-3}			
6	9.00	1.75743×10^{-5}			
7	12.00	7.07772×10^{-7}			
	SD 2.4458×10^{-2}				

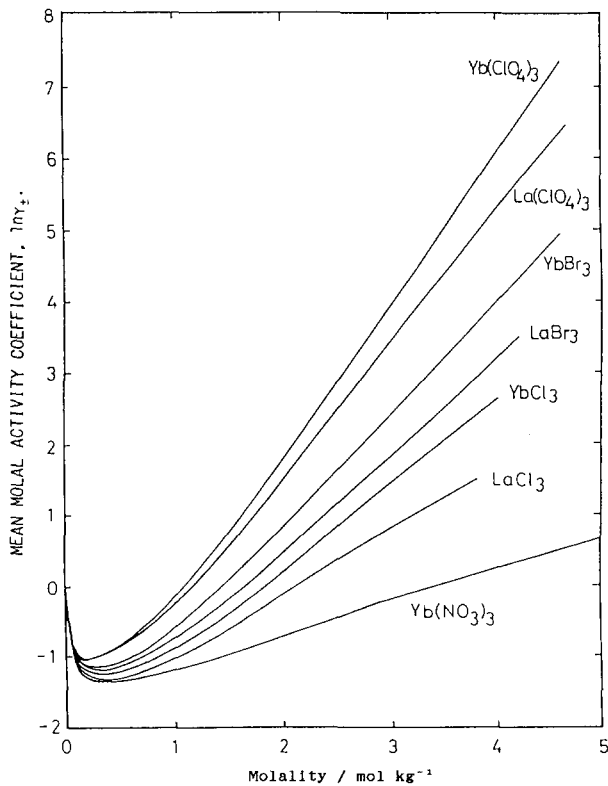Fig. 1. Water activity of aqueous $Yb(NO_3)_3$, $YbCl_3$, $YbBr_3$ and $Yb(ClO_4)_3$ solutions at 25.0 °C.

Fig. 2. Mean molal activity coefficient of aqueous $LaCl_3$, $YbCl_3$, $LaBr_3$, $YbBr_3$, $La(ClO_4)_3$, $Yb(ClO_4)_3$ and $Yb(NO_3)_3$ solutions at 25.0 °C.
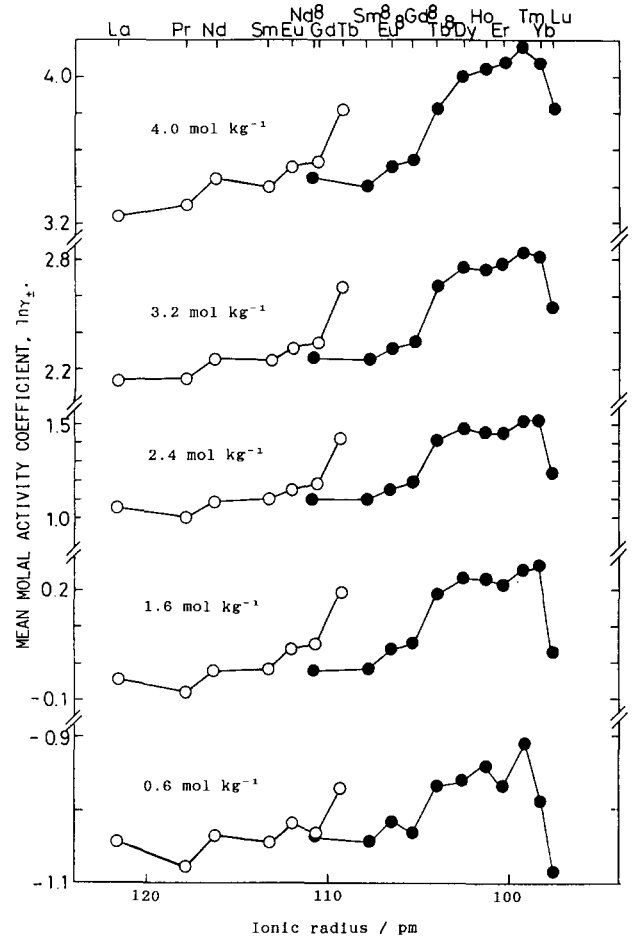

Fig. 3. Mean molal activity coefficient of aqueous rare earth bromide solutions at constant molalities at 25.0 °C: O vs. nine-coordinate ionic radius, ● vs. eight-coordinate ionic radius.

Gibbs–Duhem equation

$$\ln \gamma_{\pm} = -Am^{1/2} + \sum A_i(r_i + 1)m^{r_i}/r_i \qquad (3)$$

The values of A_i and r_i, together with the revision to our previous results [2], are given in Table 1. Water activity, a_w, can be obtained from the equation

$$\ln a_w = -4\phi m M_1/1000 \qquad (4)$$

where M_1 is the molecular weight of water. The water activities of ytterbium bromide at various molalities are shown in Fig. 1, together with those of ytterbium nitrate, chloride and perchlorate [8–13]. The differences in the activities may be due to the varied strength of hydration of the anions.

The mean molal activities of lanthanum and ytterbium bromides, together with those of perchlorates, chlorides and nitrates are given in Fig. 2. The trends of the coefficients may be elucidated by the interaction between the cation and anion; the variation of the anions has a much larger effect than that of the rare earth ions.

The mean molal activity coefficients plotted versus nine- and eight-coordinate cationic radii [8] of the rare
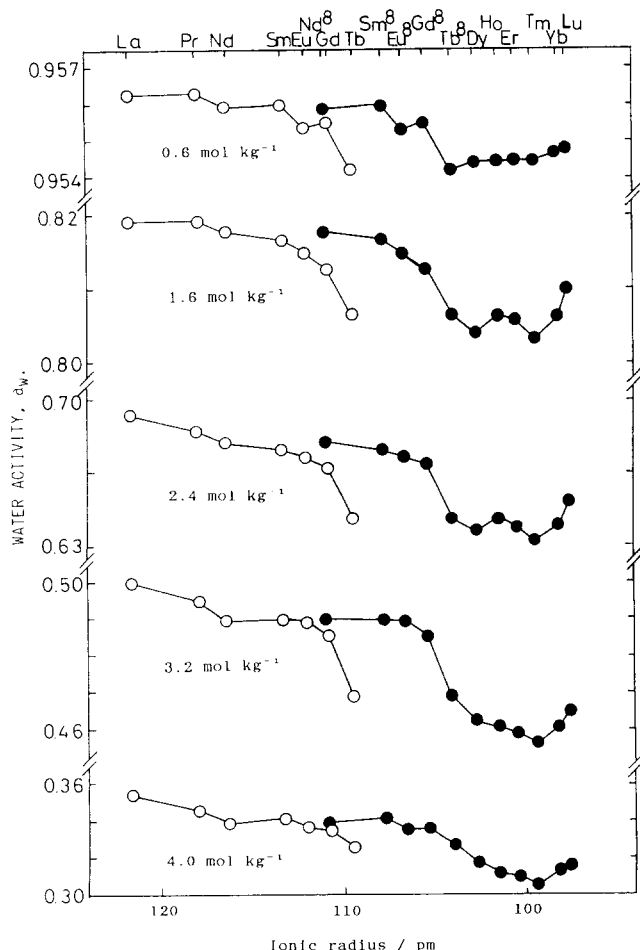
Fig. 4. Water activity of aqueous rare earth bromide solutions at constant molalities at 25.0 °C: O vs. nine-coordinate ionic radius; ● vs. eight-coordinate ionic radius.
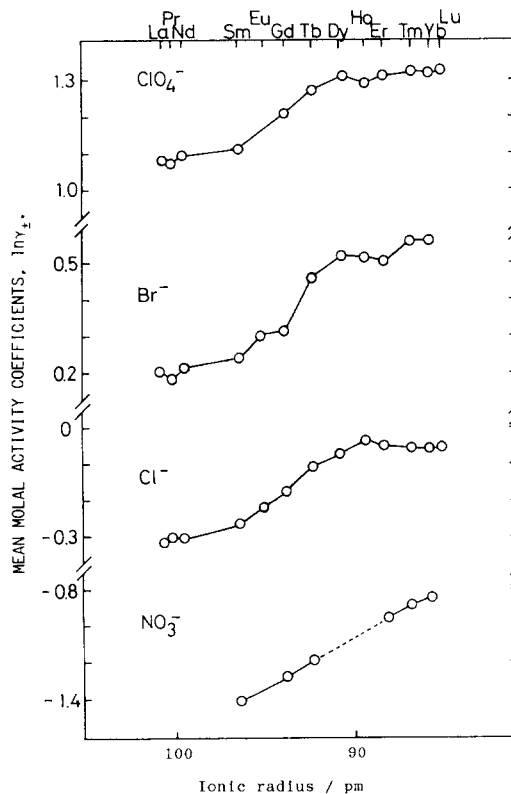

Fig. 5. Mean molal activity coefficient of aqueous rare earth perchlorate, bromide, chloride and nitrate solutions at 1.8 mol kg^{-1} and at 25.0 °C.

coordinates to the rare earth ions to form outer-sphere complexes, as well as perchlorate and chloride.

earth elements at constant molalities are shown in Fig. 3. An abrupt increase and decrease in the activity coefficients in gadolinium to dysprosium and in ytterbium to luletium, respectively, and a moderate increase both in lighter and heavier rare earths, can be explained by the change of hydration or coordination number in the midst of the lanthanides, although no appropriate elucidation can yet be made on the decrease in the heavier rare earths.

Figure 4, with similar plots of the water activities, shows a reverse relationship to that of the activity coefficients, again with abrupt changes in the values in the identical rare earth elements. The water activities at high molalities indicate only a moderate decrease through the lanthanides, however, the activity coefficients showed a rather exaggerated increase at the heavier rare earths.

The mean molal activity coefficients of the rare earth perchlorate, bromide, chloride and nitrate solutions [9–14] at 1.8 mol kg^{-1} are plotted versus six-coordinate cationic radii [15] (Fig. 5). It indicates that bromide

Acknowledgment

References

1 F.H. Spedding and I.S. Yaffe, *J. Phys. Chem.*, *74* (1952) 4751.
2 K. Fukushi, A. Mutoh, K. Ishikawa and Y. Suzuki, *J. Alloys Comp.*, *192* (1993) 290.
3 Y. Suzuki, R. Yoshino, H. Saitoh, K. Fukushi and Y. Sonehara, *J. Alloys Comp.*, *180* (1992) 383.
4 W.J. Hamer and Y.-C. Wu, *J. Phys. Chem. Ref. Data*, *1* (1972) 1050.
5 J.A. Rard, A. Habenschuss and F.H. Spedding, *J. Chem. Eng. Data*, *21* (1976) 374.
6 J.A. Rard and F.H. Spedding, *J. Chem. Eng. Data*, *22* (1977) 56.
7 J.A. Rard, A. Habenschuss and F.H. Spedding, *J. Chem. Eng. Data*, *22* (1977) 180.
8 R.D. Shannon, *Acta Crystallogr.*, *Sect. A*, *32* (1976) 751.

9 F.H. Spedding, H.O. Weber, V.W. Saeger, H.H. Petheram, J.A. Rard and A. Habenschuss, *J. Chem. Eng. Data, 21* (1976) 341.

10 J.A. Rard, H.O. Weber and F.H. Spedding, *J. Chem. Eng. Data, 22* (1977) 187.

11 J.A. Rard, L.E. Shiers, D.J. Heiser and F.H. Spedding, *J. Chem. Eng. Data, 22* (1977) 337.

12 J.A. Rard and D.G. Miller, *J. Chem. Eng. Data, 24* (1979) 348.

13 J.A. Rard and F.H. Spedding, *J. Chem. Eng. Data, 26* (1981) 391.

14 J.A. Rard and F.H. Spedding, *J. Chem. Eng. Data, 27* (1982) 454.

15 D.H. Templeton and C.H. Dauben, *J. Am. Chem. Soc., 76* (1954) 5237.