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UV-Vis spectrophotometric determination of rare earth elements (REE) speciation at near-neutral to alkaline pH. Part I: m-cresol purple properties from 25-75 °C and Er hydrolysis

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Determination of average number of OH^- ligand ($\vec{n}$) coordinated to Er^{3+}

In the Er-absent mCP-NaOH solutions, the total molar amount of OH^- in solutions (M_{OH^-}) depends on the dissociation/association of mCP (R1), NaOH, and H_2O (RS1-RS2),

$$\mathrm{NaOH} \rightleftharpoons \mathrm{Na^+} + \mathrm{OH^-} \tag{RS1}$$

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-} \tag{RS2}$$

Therefore, M_{OH^-} is calculated from the molar concentration of NaOH (M_{NaOH}) added in each experimental solution, the molar concentration of the I^{2-} form of mCP ($M_{I^{2-}}$), and the OH^- released from the dissociation of water ($M_{OH^-,w}$),

$$\mathrm{M_{OH^-}} = \mathrm{M_{NaOH}} - \mathrm{M_{I^{2-}}} + \mathrm{M_{OH^-,w}} \tag{S1}$$

In the presence of Er^{3+} ions in the mCP-NaOH solutions, the hydrolysis of Er^{3+} in the reaction R2 produces protons, decreases pH, and consumes OH^-. Hence, the Er hydrolysis drives reaction R1 for mCP to the left, resulting in stabilization of HI^-, i.e. the protonated form of mCP. Thus the amount of OH^- ligand bound to Er hydroxyl complexes ($\sum n[Er(OH)_n^{3-n}]$) permits reformulating Eq. S1 as follows,

$$\mathrm{M'_{OH^-}} = \mathrm{M_{NaOH}} - \mathrm{M'_{I^{2-}}} - \sum \mathrm{n[Er(OH)_n^{3-n}]} + \mathrm{M'_{OH^-,w}} \tag{S2}$$

where the prime signs indicates the concentrations in the Er-bearing mCP-NaOH solutions. Finally, the number of OH^- ligand bound to Er hydroxyl complexes ($\sum n[Er(OH)_n^{3-n}]$), can be found by the difference between Eqs. S1 and S2,

$$\sum \mathrm{n[Er(OH)_n^{3-n}]} = \mathrm{M_{OH^-}} - \mathrm{M'_{OH^-}} - \mathrm{M'_{I^{2-}}} + \mathrm{M_{I^{2-}}} + \mathrm{M'_{OH^-,w}} - \mathrm{M_{OH^-,w}} \tag{S3}$$

The number of OH^- ligand bound to the Er hydroxyl complexes ($\sum n[Er(OH)_n^{3-n}]$) in the experimental solution is averaged by the total Er concentration [Er] in solution according to,

$$\vec{n} = \frac{\sum n[\mathrm{Er(OH)_n^{3-n}}]}{[Er]} \tag{S4}$$

The total Er concentration [Er] is the sum of the concentrations of Er in the Er hydroxyl complexes and Er aqua ion,

$$[\mathrm{Er}] = [\mathrm{Er}^{3+}] + [\mathrm{Er(OH)}^{2+}] + [\mathrm{Er(OH)}_2^{+}] + [\mathrm{Er(OH)}_3^{0}] \qquad \text{(S5)}$$

With an assumption of the mass balance for the Er concentration in mCP-NaOH solutions, the total Er concentration [Er] is the same with the molar concentration of $ErCl_3$ added. Therefore, the average number of OH^- ligand ($\vec{n}$) coordinated to Er^{3+} for each of Er-bearing mCP-NaOH solutions can be determined by reformatting the Eqs. S4 with S3 as shown.

$$\vec{n} = \frac{\mathrm{M_{OH^-}} - \mathrm{M'_{OH^-}} - \mathrm{M'_{I^{2-}}} + \mathrm{M_{I^{2-}}} + \mathrm{M'_{OH^-,w}} - \mathrm{M_{OH^-,w}}}{[\mathrm{Er}]} \qquad \text{(S6)}$$

The amount of OH^- in each of Er-absent (M_{OH^-}) and Er-bearing (M'_{OH^-}) mCP-NaOH solutions were determined by pH determination using the UV-Vis/mCP method from Eq. 4.

Table S1. UV-Vis spectrophotometric experiments of 0.03 mM mCP in HCl, NaOH, and Tris solutions at temperatures from 25 to 75 °C.

Exp	T (°C)	Acidic pH			Alkaline pH			pH of known buffer solution			
		HCl[a] (mM)	Absorbance of HI^-	Absorbance of I^{2-}	NaOH[a] (M)	Absorbance of HI^-	Absorbance of I^{2-}	Tris[a] (M)	pH by potentiometric measurement	Absorbance of HI^-	Absorbance of I^{2-}
1	25	0.10	0.4789	0.0022	0.01	0.0683	1.2590	0.02	8.07	0.4099	0.2437
2	25	0.10	0.4956	0.0022	0.01	0.0626	1.1737	0.02	8.08	0.4023	0.2569
3	25	0.10	0.4978	0.0019	0.01	0.0641	1.1514	0.02	8.08	0.3639	0.2286
4	25	0.10	0.5109	0.0039	0.01	0.0638	1.1526	0.02	8.06	0.4330	0.2372
5	25	0.10	0.5077	0.0035	0.01	0.0638	1.1545	0.02	8.05	0.4223	0.2408
6	25	0.10	0.5048	0.0023	0.01	0.0594	1.1150	0.02	8.05	0.4247	0.2434
7	25	0.10	0.4941	0.0018	0.01	0.0594	1.1223	0.02	8.02	0.4207	0.2310
8	25	0.10	0.4937	0.0011	0.01	0.0592	1.1193	0.02	8.06	0.4101	0.2432
9	25	0.10	0.4956	0.0009	0.01	0.0638	1.1164	0.02	8.05	0.4205	0.2091
10	25	0.10	0.4995	0.0019	0.01	0.0642	1.1197	0.02	8.08	0.4094	0.2378
11	25	0.10	0.4978	0.0025	0.01	0.0641	1.1237	0.02	8.13	0.3973	0.2733
12	25	0.10	0.4996	0.0022	0.01	0.0660	1.1579	0.02	8.12	0.3967	0.2543
13	25	0.10	0.5054	0.0011	0.01	0.0656	1.1533	0.02	8.08	0.4262	0.2249
14	25	0.10	0.5036	0.0008	0.01	0.0652	1.1484	0.02	8.08	0.4287	0.2180
15	25	0.10	0.5057	0.0006	0.01	0.0649	1.1190	0.02	8.07	0.4265	0.2177
16	25	0.10	0.4990	0.0031	0.01	0.0637	1.1174	0.02	8.07	0.3960	0.2925
17	25	0.10	0.5004	0.0033	0.01	0.0628	1.1166	0.02	8.09	0.3956	0.3084
18	35	0.10	0.4946	0.0067	0.01	0.0674	1.1004	0.02	7.82	0.4207	0.2040
19	35	0.10	0.4901	0.0025	0.01	0.0655	1.0961	0.02	7.86	0.4249	0.2179
20	35	0.10	0.4928	0.0028	0.01	0.0643	1.0962	0.02	7.84	0.4287	0.2103
21	35	0.10	0.4882	0.0008	0.01	0.0633	1.1077	0.02	7.87	0.4087	0.2095
22	35	0.10	0.4901	0.0003	0.01	0.0634	1.1079	0.02	7.80	0.4152	0.1850
23	35	0.10	0.4905	0.0002	0.01	0.0631	1.1021	0.02	7.86	0.4099	0.2063
24	35	0.10	0.4919	0.0036	0.01	0.0657	1.1022	0.02	7.89	0.4029	0.2312

25	35	0.10	0.4906	0.0013	0.01	0.0652	1.0998	0.02	7.77	0.4182	0.1863
26	35	0.10	0.4913	0.0015	0.01	0.0662	1.1040	0.02	7.83	0.4141	0.2109
27	35	0.10	0.4885	0.0026	0.01	0.0564	1.0945	0.02	7.80	0.4175	0.1858
28	35	0.10	0.4897	0.0024	0.01	0.0564	1.0932	0.02	7.87	0.4105	0.2154
29	35	0.10	0.4898	0.0026	0.01	0.0559	1.0923	0.02	7.90	0.4028	0.2289
30	35	0.10	0.5065	0.0019	0.01	0.0660	1.1044	0.02	7.90	0.3956	0.2263
31	35	0.10	0.4899	0.0009	0.01	0.0658	1.1094	0.02	7.91	0.3945	0.2365
32	35	0.10	0.4902	0.0012	0.01	0.0659	1.1062	-	-	-	-
33	45	0.10	0.4799	0.0025	0.01	0.0650	1.0717	0.02	7.53	0.4320	0.1296
34	45	0.10	0.4812	0.0025	0.01	0.0655	1.0725	0.02	7.59	0.3994	0.1402
35	45	0.10	0.4816	0.0025	0.01	0.0664	1.0796	0.02	7.48	0.4376	0.1185
36	45	0.10	0.4800	0.0025	0.01	0.0670	1.0905	-	-	-	-
37	50	0.10	0.4796	0.0041	0.01	0.0696	1.0517	0.02	7.54	0.4369	0.1022
38	50	0.10	0.4752	0.0035	0.01	0.0663	1.0499	0.02	7.32	0.4384	0.0829
39	50	0.10	0.4793	0.0036	0.01	0.0661	1.0446	0.02	7.32	0.4408	0.0899
40	50	0.10	0.4805	0.0035	0.01	0.0671	1.0524	0.02	7.24	0.4435	0.0695
41	50	0.10	0.4871	0.0137	0.01	0.0669	1.0490	0.02	7.32	0.4490	0.0834
42	50	0.10	0.4855	0.0135	0.01	0.0654	1.0475	0.02	7.36	0.4498	0.0889
43	50	0.10	0.4881	0.0136	0.01	0.0659	1.0515	0.02	7.34	0.4532	0.0884
44	75	0.10	0.4600	0.0053	0.01	0.0721	0.9872	0.02	7.43	0.4522	0.1139
45	75	0.10	0.4655	0.0050	0.01	0.0693	0.9873	0.02	7.37	0.4233	0.0839
46	75	0.10	0.4602	0.0044	0.01	0.0694	0.9595	0.02	7.71	0.4158	0.1638
47	75	0.10	0.4647	0.0191	0.01	0.0633	0.9969	0.02	7.56	0.4193	0.1373
48	75	0.10	0.4699	0.0201	0.01	0.0769	0.9916	0.02	7.54	0.4109	0.1432
49	75	0.10	0.4630	0.0035	0.01	0.0729	0.9948	0.02	7.54	0.4182	0.1863
50	75	0.10	0.4616	0.0016	-	-	-	0.02	7.59	0.4141	0.2109
51	75	0.10	0.4627	0.0067	-	-	-	0.02	7.52	0.4175	0.1858
52	75	-	-	-	-	-	-	0.02	7.46	0.4102	0.1031

[a]Concentration at room temperature.

Table S2. UV-Vis spectrophotometric experiments of solutions containing mCP and NaOH with addition of varying Er concentrations from 0.0 to ~0.057 mM at 25 °C ($Er^{3+} + nH_2O = Er(OH)_n^{3-n} + nH^+$, with n=1 to 3).

Exp	NaOH (mM)	Er (mM)	mCP (mM)	Abs_{435nm}	Abs_{578nm}	R	pH by potentiometric measurement	pH by UV-Vis	Average number of OH^- ligand ($\vec{n}$)
Er-a-0	0.125	0.000	0.029	0.1109	1.0605	9.56	9.64	9.60	-
Er-a-1	0.125	0.011	0.029	0.1392	0.9355	6.72	9.42	9.32	3.11
Er-a-2	0.125	0.017	0.029	0.1975	0.7811	3.95	9.07	8.99	2.93
Er-a-3	0.126	0.023	0.029	0.2769	0.5773	2.08	8.77	8.66	2.67
Er-a-4	0.125	0.029	0.029	0.3876	0.2850	0.74	8.24	8.17	2.49
Er-a-5	0.126	0.034	0.029	0.4534	0.1144	0.25	7.39	7.69	2.24
Er-a-6	0.126	0.040	0.029	0.4738	0.0701	0.15	7.18	7.45	1.96
Er-a-7	0.125	0.046	0.029	0.4755	0.0523	0.11	7.07	7.31	1.72
Er-a-8	0.126	0.051	0.029	0.4816	0.0444	0.09	7.03	7.23	1.54
Er-a-9	0.125	0.057	0.029	0.4848	0.0351	0.07	6.96	7.12	1.38
Er-b-0	0.125	0.000	0.029	0.1084	1.0200	9.41	9.65	9.56	-
Er-b-1	0.126	0.006	0.029	0.1323	0.9636	7.28	9.31	9.38	2.79
Er-b-2	0.125	0.012	0.029	0.1696	0.8649	5.10	9.16	9.14	2.48
Er-b-3	0.125	0.017	0.029	0.2331	0.7067	3.03	8.81	8.85	2.27
Er-b-4	0.125	0.023	0.029	0.3408	0.4199	1.23	8.38	8.41	2.21
Er-b-5	0.125	0.029	0.029	0.4386	0.1644	0.37	7.29	7.86	2.06
Er-b-6	0.125	0.035	0.029	0.4662	0.0898	0.19	6.96	7.57	1.79
Er-b-7	0.126	0.040	0.029	0.4789	0.0591	0.12	6.91	7.36	1.57
Er-b-8	0.125	0.046	0.029	0.4796	0.0474	0.10	6.86	7.26	1.37
Er-b-9	0.125	0.052	0.029	0.4843	0.0416	0.09	6.71	7.20	1.23
Er-b-10	0.125	0.058	0.029	0.4831	0.0362	0.07	6.70	7.14	1.10
Er-c-0	0.128	0.000	0.029	0.1079	1.0361	9.60	9.68	9.61	-
Er-c-1	0.128	0.011	0.029	0.1789	0.8630	4.83	9.16	9.11	2.79
Er-c-2	0.128	0.017	0.029	0.2497	0.6789	2.72	8.72	8.79	2.52
Er-c-3	0.128	0.023	0.029	0.3396	0.4472	1.32	8.23	8.44	2.30

Er-c-4	0.129	0.029	0.029	0.4375	0.2020	0.46	7.50	7.96	2.13
Er-c-5	0.129	0.034	0.029	0.4758	0.0908	0.19	6.84	7.56	1.87
Er-c-6	0.130	0.040	0.029	0.4876	0.0685	0.14	6.52	7.42	1.63
Er-c-7	0.129	0.046	0.029	0.4882	0.0541	0.11	6.39	7.32	1.42
Er-c-8	0.129	0.052	0.029	0.4921	0.0472	0.10	6.41	7.25	1.27
Er-c-9	0.130	0.057	0.029	0.4989	0.0427	0.09	6.38	7.20	1.15
Er-d-0	0.129	0.000	0.029	0.1030	1.0388	10.09	9.78	9.65	-
Er-d-1	0.130	0.006	0.029	0.1198	1.0160	8.48	9.61	9.50	2.23
Er-d-2	0.129	0.013	0.029	0.1406	0.9465	6.73	9.42	9.32	2.04
Er-d-3	0.129	0.019	0.029	0.1974	0.7907	4.00	8.98	9.00	2.14
Er-d-4	0.129	0.026	0.029	0.2750	0.6024	2.19	8.57	8.68	2.00
Er-d-5	0.129	0.032	0.029	0.3927	0.2987	0.76	8.04	8.18	1.96
Er-d-6	0.129	0.038	0.029	0.4690	0.1010	0.22	6.91	7.62	1.79
Er-d-7	0.129	0.045	0.029	0.4801	0.0687	0.14	6.74	7.43	1.55
Er-d-8	0.129	0.051	0.029	0.4840	0.0552	0.11	6.61	7.33	1.36
Er-d-9	0.130	0.057	0.029	0.4903	0.0485	0.10	6.55	7.26	1.22
Er-e-0	0.131	0.000	0.030	0.1075	1.0159	9.45	9.43	9.57	-
Er-e-1	0.131	0.007	0.030	0.1303	0.95408	7.32	9.29	9.37	2.51
Er-e-2	0.131	0.019	0.030	0.2240	0.72083	3.22	8.91	8.88	2.03
Er-e-3	0.132	0.025	0.030	0.3006	0.53570	1.78	8.55	8.58	1.87
Er-e-4	0.131	0.032	0.030	0.4152	0.23311	0.56	7.94	8.05	1.81
Er-e-5	0.131	0.038	0.030	0.4564	0.11953	0.26	7.30	7.70	1.61
Er-e-6	0.132	0.044	0.030	0.4740	0.07395	0.16	6.67	7.47	1.41
Er-e-7	0.131	0.051	0.030	0.4790	0.05645	0.12	6.60	7.34	1.24
Er-e-8	0.130	0.057	0.030	0.4770	0.04868	0.10	6.54	7.28	1.11

Er-f-0	0.126	0.000	0.029	0.1166	1.0015	8.59	9.41	9.51	-
Er-f-1	0.125	0.029	0.029	0.4175	0.1974	0.47	7.79	7.97	1.77
Er-f-2	0.126	0.035	0.029	0.4628	0.0805	0.17	7.00	7.52	1.59
Er-f-3	0.126	0.040	0.029	0.4690	0.0640	0.14	6.78	7.41	1.39
Er-f-4	0.126	0.046	0.029	0.4713	0.0496	0.11	6.74	7.29	1.21
Er-f-5	0.126	0.052	0.029	0.4763	0.0394	0.08	6.72	7.18	1.09
Er-f-6	0.126	0.058	0.029	0.4784	0.0343	0.07	6.67	7.12	0.98
Er-g-0	0.133	0.000	0.030	0.1033	1.0274	9.95	9.80	9.64	-
Er-g-1	0.133	0.038	0.030	0.4233	0.1957	0.46	7.91	7.96	1.67
Er-g-2	0.134	0.045	0.030	0.4577	0.1101	0.24	7.06	7.66	1.49
Er-g-3	0.134	0.051	0.030	0.4681	0.0788	0.17	6.87	7.50	1.32
Er-g-4	0.133	0.058	0.030	0.4745	0.0628	0.13	6.85	7.40	1.18
Er-h-0	0.130	0.000	0.030	0.1132	1.0111	8.93	9.38	9.54	-
Er-h-1	0.130	0.039	0.030	0.4520	0.1210	0.27	7.39	7.71	1.47
Er-h-2	0.130	0.045	0.030	0.4752	0.0685	0.14	7.07	7.43	1.31
Er-h-3	0.130	0.051	0.030	0.4811	0.0552	0.11	6.59	7.33	1.15
Er-h-4	0.131	0.057	0.030	0.4843	0.0479	0.10	6.54	7.26	1.04

Table S3. Sources of thermodynamic data from the Supcrt92 dataset considered in the Er aqueous speciation as function of pH calculated at 25 °C using GEMS code package and the aquifer groundwater of the Zudong heavy REE deposit described in the study by Li et al. [8].

Species		Refs.
Er-species	Er^{3+}	1, 2
	$Er(OH)^{2+}$, $Er(OH)_2^{+}$, $Er(OH)_3^{0}$, $Er(OH)_4^{-}$	3
	$Er(CO_3)^{+}$, $Er(HCO_3)^{2+}$	4
	ErF_2^{+}	4
	$ErCl^{2+}$	5
	$Er(SO_4)^{+}$	6
Other species	H^{+}, OH^{-}	1, 2

References: [1]Shock et al. (1997); [2]Shock and Helgeson (1988); [3]Haas et al. (1995); [4]Sverjensky et al. (1997); [5]Migdisov et al. (2009); [6]Migdisov et al. (2016).