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Thermodynamic Properties of Rare Earth Complexes

X. Complex Formation in Aqueous Solution of Eu(III) and Iminodiacetic Acid

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The stability constants for the formation of the complexes EuA_r^{3-2r} ($r = 1-3$), $EuHA^{2+}$, and EuH_2A^{3+} (H_2A denotes iminodiacetic acid) have been determined at 25.0°C in an aqueous sodium perchlorate medium with ionic strength 1.00 M. A potentiometric standard method was used, *viz.* emf-measurements of the hydrogen ion concentration.

Lanthanoid (III) iminodiacetate complexes in aqueous solution have been described earlier.[1–4] The investigators have usually interpreted their experimental data by assuming that the complexes MA^+ and MA_2^- are formed (M is one of the lanthanoids). In one study,[2] the possible existence of the complex MA_3^{3-} is mentioned. It is difficult to estimate how well the previous authors can describe their experimental findings, as no primary data are given in the publications.

The existence of complexes $M_pH_qA_r^{3p+q-2r}$ with $q > 0$ can be regarded as rather probable, because of the strong basicity of the ion A^{2-}. H_2A exists in water mainly in the dipolar form $HOOC{\cdot}CH_2{\cdot}NH_2^+{\cdot}CH_2{\cdot}COO^-$ (*cf.* Ref. 5), and both H_2A and HA^- consequently should be able to coordinate to the central ion. Complexes with both HA^- and A^{2-} as ligands have been found in the solid state, *e.g.* $M_2(HA)_2ACl_2{\cdot}7H_2O$ and $[MA(H_2O)_3]Cl$.[6,7]

The present study of the europium(III) iminodiacetate system was performed to find out if metal complexes other than EuA^+ and EuA_2^- might be formed, and to make a comparison with other dicarboxylate ligands (*vide* Part IX in this series [8]).

The experimental method used in this investigation is the same as in the earlier studies,[1–4] *i.e.* a potentiometric determination of the hydrogen ion concentration by means of a glass electrode. All measurements were performed in a medium with ionic strength 1.00 M, using sodium perchlorate as the neutral salt. The temperature was (25.0 ± 0.1)°C.

The symbols used in the following have been defined previously.[8]

EXPERIMENTAL

Chemicals. Stock solutions of europium(III) perchlorate and sodium perchlorate were prepared and analysed as described previously.[8] Iminodiacetic acid (The British Drug Houses Ltd.) was used without further purification. The purity was checked by potentiometric titrations with sodium hydroxide. The experimental formula weight was 133.2. The theoretical value is 133.1.

Potentiometric determination of stability constants. The galvanic cells used and the titration technique have been described earlier.[8] The various S- and T-solutions, whose compositions are given in Table 1, were prepared from stock solutions of europium perchlorate, iminodiacetic acid, sodium perchlorate and perchloric acid or sodium hydroxide.

Table 1. Composition of the various S- and T-solutions. The related values of V_0 and the ranges of $\bar{n}_H$ are also given. (Series 1–9 refer to the proton system, series 10–23 to the Eu system.)

Ser.	$C_{H(S)}$/mM	$C_{M(S)}$/mM	$C_{A(S)}$/mM	$C_{H(T)}$/mM	$C_{M(T)}$/mM	$C_{A(T)}$/mM	V_0/ml	$\bar{n}_H$-range
1	20.30	0	10.15	− 24.50	0	0	20.00	1.70–1.11
2	20.30	0	10.15	− 24.50	0	0	15.00	1.70–1.14
3	20.30	0	10.15	− 24.50	0	0	15.00	1.70–1.08
4	20.30	0	10.15	53.9	0	0	15.00	1.70–2.40
5	239.6	0	119.8	590	0	0	15.00	1.96–2.42
6	71.0	0	35.50	173.7	0	0	20.00	1.87–2.45
7	239.6	0	119.8	−198.1	0	0	15.00	1.96–0.35
8	71.0	0	35.50	−198.1	0	0	25.00	1.87–0.44
9	239.6	0	119.8	−996	0	0	25.00	1.96–0.38
10	25.00	14.18	25.00	143.1	14.18	25.00	15.00	0.99–2.31
11	25.00	44.7	25.00	139.5	44.7	25.00	15.00	0.99–2.21
12	15.72	29.82	15.72	145.3	29.82	15.72	20.00	0.98–2.31
13	25.00	29.82	25.00	139.0	29.82	25.00	15.00	0.99–2.27
14	14.19	7.09	25.00	145.7	7.09	25.00	20.00	0.64–1.27
15	29.16	29.82	50.0	107.8	29.82	50.0	20.00	0.58–1.25
16	28.63	14.91	50.0	107.2	14.91	50.0	15.00	0.57–1.23
17	32.06	7.09	40.0	273.3	7.09	40.0	20.00	0.80–1.32
18	23.29	20.87	50.0	107.4	20.87	50.0	15.00	0.47–1.25
19	52.8	7.09	50.0	− 98.5	0	0	20.00	1.05–0.43
20	164.5	41.3	156.3	−198.1	0	0	20.00	1.05–0.18
21	103.1	7.09	100.0	− 98.5	0	0	15.00	1.03–0.60
22	101.9	29.82	100.0	− 98.5	0	0	15.00	1.02–0.08
23	26.41	3.54	25.00	− 98.5	0	0	25.00	1.05–0.39

The glass electrodes used in acid and alkaline solutions were of type Beckman 40498 and Beckman 40495, respectively. Ag, AgCl electrodes were prepared according to Brown.[9]

Contamination of the solutions with carbon dioxide was prevented by passing a stream of nitrogen through the solution in the titration vessel.

The measured emf-values were corrected for the liquid junction potential as described before.[8]

All titrations were repeated at least twice. The reproducibility of the emf was usually within 0.1 mV. In the most alkaline solutions the emf-values sometimes could be reproduced only within (0.3–0.4) mV.

CALCULATION AND RESULTS

The proton iminodiacetate system. The protonation constants β_{0q1} ($q = 1-3$) were determined by the graphical standard methods of Leden and Fronæus.[10] The values were then refined by the least squares program LETAGROP VRID.[11] The titration series used in the final calculation are given in Tables 1 and 2 (series 1 – 9). The following results were obtained:

$$\beta_{011} = (2.064 \pm 0.035) \times 10^{9} \ \mathrm{M}^{-1}$$
$$\beta_{021} = (7.77 \pm 0.17) \times 10^{11} \ \mathrm{M}^{-2}$$
$$\beta_{031} = (5.91 \pm 0.13) \times 10^{13} \ \mathrm{M}^{-3}$$

The standard deviation in the error-carrying variable C_H/C_A (denoted *sig y* in the following) is equal to 6.28×10^{-3}. The errors in the above and the following constants are always given as three standard deviations.

The europium iminodiacetate system. The method of calculating stability constants was the same as described before.[8] The titration series used are given in Tables 1 and 2 (series 10 – 23). The experimental data could be described rather well by assuming the formation of the metal complexes EuA_r^{3-2r} ($r = 1-3$), $EuHA^{2+}$ and EuH_2A^{3+}. The following final constants were obtained in the least squares refinement (*sig* $y = 5.28 \times 10^{-3}$):

$$\beta_{101} = (3.08 \pm 0.10) \times 10^{6} \ \mathrm{M}^{-1}$$
$$\beta_{102} = (4.43 \pm 0.19) \times 10^{11} \ \mathrm{M}^{-2}$$
$$\beta_{103} = (5.01 \pm 0.29) \times 10^{15} \ \mathrm{M}^{-3}$$
$$\beta_{111} = (6.23 \pm 0.21) \times 10^{10} \ \mathrm{M}^{-2}$$
$$\beta_{121} = (7.26 \pm 0.80) \times 10^{12} \ \mathrm{M}^{-3}$$

Some other combinations of metal complexes were also tried with the LETAGROP VRID program. A trial of $EuHA_2$ lies near at hand. Complexes of corresponding composition have been found in the malonate [8] and thiodiacetate [12] systems. A refinement with this complex included gave a value of $\beta_{112} = (1 \pm 1) \times 10^{16} \ \mathrm{M}^{-3}$, while the value of *sig y* remained practically unchanged. Hence, the complex $EuHA_2$ is present in very small amounts, if at all, in the solutions studied. A trial of the complex $EuH_2A_2^{+}$ and some binuclear species gave similar results.

Finally, a calculation of the protonation constants was made in solutions where $C_M \neq 0$. The final europium constants, β_{1qr}, were kept constant, while the protonation constants, β_{0q1}, were varied. The new β_{0q1}-values differ very little (0.5 – 0.6 %) from those obtained when $C_M = 0$.

Fig. 1 shows the distribution of the various europium complexes as a function of $\log(a/\mathrm{M})$ at three different values of h, *viz.* 10^{-2} M, 10^{-4} M and 10^{-6} M. The values of a at these hydrogen ion concentrations cannot exceed 6×10^{-9} C_A, 5×10^{-6} C_A, and 5×10^{-4} C_A, respectively.

The differences $(C_{H(calc)}/C_A) - (C_{H(exp)}/C_A)$ are also given in Table 2. From these values it is obvious that systematic errors are present in some of the titration series. The errors are very small and may be caused for instance by small analytical errors in the S- and T-solutions.

Table 2. Corresponding values of v/ml, $-\log(h/\mathrm{M})$ and Δy for the proton iminodiacetate system (series 1 – 9) and the europium iminodiacetate system (series 10 – 23). Δy is equal to $(C_{\mathrm{H(calc)}} - C_{\mathrm{H(exp)}}) C_{\mathrm{A}}^{-1} \times 10^3$.

v/ml	-lg(h/M)	Δy
Series 1		
0.00	2.512	2.87
0.50	2.551	5.90
1.00	2.595	3.14
1.50	2.641	0.77
2.00	2.684	3.90
2.50	2.733	3.51
3.00	2.784	4.57
3.50	2.843	-0.09
4.00	2.901	2.49
4.50	2.968	0.53
5.00	3.041	0.87
5.50	3.127	-1.36
6.00	3.224	-0.65
6.50	3.344	-1.51
7.00	3.496	-0.47
Series 2		
0.00	2.509	8.61
1.00	2.622	6.26
2.00	2.750	3.23
3.00	2.904	-0.94
4.00	3.102	-4.12
5.00	3.405	-6.57
Series 3		
0.00	2.509	8.61
1.00	2.622	6.26
1.50	2.683	6.24
2.00	2.750	3.23
2.50	2.823	1.44
3.00	2.905	0.77
3.50	2.994	-1.14
4.00	3.100	-2.89
4.50	3.230	-4.55
5.00	3.400	-5.18
5.50	3.658	-6.49
Series 4		
0.00	2.510	5.73
0.50	2.419	5.85
1.00	2.340	6.10
1.50	2.270	4.90
2.20	2.166	4.06
3.00	2.105	1.13
3.90	2.030	-10.06
5.00	1.954	-19.65
6.30	1.883	-39.30
Series 5		
0.00	2.265	5.18
0.40	2.155	8.01
0.80	2.049	9.23
1.20	1.942	11.47
1.70	1.816	7.15
Series 6		
0.00	2.343	3.58
0.40	2.275	3.37
0.90	2.196	2.65
1.50	2.106	2.35
2.20	2.010	1.21
2.93	1.920	-4.63
3.50	1.856	-9.44
4.00	1.804	-13.59
Series 7		
0.00	2.264	7.20
1.00	2.363	2.79
2.00	2.466	-1.24
3.00	2.575	-3.86
4.00	2.695	-8.04
5.00	2.826	-8.32
6.00	2.985	-9.07
6.50	3.082	-9.72
7.00	3.192	-8.38
7.50	3.330	-7.85
8.00	3.516	-5.74
8.50	3.819	-5.70
10.00	8.381	-2.02
10.50	8.593	-1.91
10.80	8.692	-2.07
11.10	8.780	-2.44
11.50	8.882	-1.79
12.00	8.997	-1.83
12.50	9.102	-1.69
13.00	9.200	-0.99
13.50	9.296	-0.95
14.00	9.391	-0.22
14.50	9.489	-0.33
15.00	9.590	0.19

v/ml	-lg(h/M)	Δy
Series 8		
0.00	2.343	3.58
0.50	2.429	2.93
1.00	2.520	3.01
1.50	2.622	0.49
2.00	2.733	-0.53
2.50	2.862	-1.29
3.00	3.019	-2.49
3.30	3.138	-3.82
3.60	3.283	-3.66
3.82	3.422	-3.44
4.00	3.572	-3.18
4.10	3.682	-3.14
4.90	8.322	1.39
5.00	8.427	1.40
5.10	8.517	1.05
5.30	8.660	1.61
5.50	8.779	2.24
5.70	8.882	2.76
5.90	8.975	3.24
6.25	9.123	3.40
6.60	9.260	4.41
7.00	9.414	5.43
Series 9		
0.00	2.264	7.20
0.30	2.351	4.01
0.60	2.443	0.70
0.90	2.539	-2.61
1.20	2.644	-6.13
1.50	2.755	-6.72
1.80	2.886	-8.21
2.00	2.985	-8.16
2.20	3.104	-8.53
2.40	3.246	-6.70
2.61	3.452	-5.45
2.75	3.658	-4.57
3.20	8.157	-0.79
3.31	8.370	-1.14
3.37	8.457	-1.26
3.45	8.554	-0.47
3.60	8.709	-1.58
3.75	8.834	-1.56
3.94	8.971	-1.77
4.15	9.105	-1.42
4.35	9.225	-1.88
4.58	9.358	-2.07
4.88	9.533	0.01
Series 10		
0.00	3.807	-4.76
0.10	3.684	-5.08
0.20	3.567	-4.43
0.30	3.465	-4.44
0.45	3.337	-4.79
0.60	3.227	-3.55
0.80	3.110	-3.60
1.10	2.970	-2.37
1.50	2.828	-2.36
2.10	2.666	-1.30
2.60	2.559	-0.64
3.30	2.458	-0.33
4.10	2.324	-0.50
5.00	2.218	1.19
6.20	2.101	3.87
7.70	1.985	7.07
9.70	1.865	10.15
Series 11		
0.00	3.557	-3.18
0.10	3.467	-2.47
0.20	3.381	-1.30
0.30	3.301	-0.35
0.40	3.230	-0.16
0.55	3.132	1.60
0.70	3.050	2.09
0.90	2.953	3.57
1.10	2.872	4.22
1.30	2.801	5.15
1.60	2.710	6.24
1.90	2.632	7.08
2.30	2.544	7.21
2.80	2.451	7.58
3.40	2.358	6.92
4.00	2.279	6.85
4.70	2.199	6.46
5.60	2.111	8.13
6.70	2.022	10.03
7.90	1.942	8.44
9.40	1.861	5.54

v/ml	-lg(h/M)	Δy
Series 12		
0.00	3.640	-6.95
0.10	3.521	-7.45
0.20	3.408	-6.75
0.30	3.307	-6.15
0.40	3.219	-6.40
0.50	3.139	-5.74
0.65	3.038	-5.59
0.80	2.952	-5.56
1.00	2.855	-6.64
1.20	2.771	-5.49
1.40	2.700	-6.98
1.70	2.605	-6.09
2.00	2.524	-5.37
2.40	2.433	-7.28
2.90	2.336	-10.87
3.50	2.235	-8.03
4.10	2.150	-9.15
4.70	2.076	-7.83
5.50	1.993	-12.65
6.40	1.910	-6.91
7.50	1.831	-16.20
Series 13		
0.00	3.641	-4.56
0.10	3.543	-3.57
0.20	3.452	-2.97
0.30	3.367	-2.23
0.40	3.291	-1.78
0.50	3.224	-1.85
0.65	3.132	-1.18
0.80	3.053	-0.38
1.00	2.963	-0.33
1.20	2.886	0.26
1.45	2.803	0.22
1.70	2.730	1.01
2.00	2.654	1.97
2.40	2.568	2.01
2.90	2.477	1.71
3.50	2.384	1.89
4.20	2.294	-1.04
5.00	2.204	0.58
5.90	2.120	0.77
7.00	2.032	2.92
8.30	1.946	5.36
10.00	1.856	4.31
Series 14		
0.30	5.638	6.15
0.40	5.528	4.60
0.51	5.411	2.31
0.60	5.313	1.28
0.70	5.207	-0.05
0.80	5.105	-2.14
0.90	5.002	-3.55
1.00	4.901	-5.13
1.10	4.794	-5.54
1.20	4.688	-6.12
1.32	4.556	-6.52
1.43	4.431	-6.87
1.60	4.223	-6.57
1.73	4.057	-6.19
1.86	3.898	-6.31
2.03	3.709	-5.64
2.22	3.542	-5.92
2.46	3.378	-5.89
2.80	3.205	-5.49
3.25	3.039	-5.11
Series 15		
0.00	4.857	3.52
0.50	4.767	2.78
1.00	4.681	2.40
1.50	4.598	1.94
2.00	4.519	1.00
2.50	4.439	0.65
3.10	4.343	0.91
3.70	4.248	0.48
4.30	4.152	0.32
5.00	4.039	-0.15
5.80	3.907	-0.44
6.60	3.773	0.07
7.20	3.678	0.02
7.90	3.574	0.53
8.70	3.467	0.98
9.60	3.364	1.55
10.80	3.251	2.35
12.20	3.144	3.92
13.70	3.055	4.95
15.70	2.960	6.51

v/ml	-lg(h/M)	Δy
Series 16		
0.00	5.629	2.93
0.20	5.541	3.26
0.40	5.459	3.18
0.60	5.377	3.44
0.80	5.301	3.14
1.10	5.190	3.28
1.40	5.085	3.04
1.70	4.985	2.69
2.00	4.889	2.49
2.30	4.796	2.27
2.60	4.706	1.84
2.90	4.618	1.47
3.20	4.530	1.39
3.50	4.444	1.06
3.80	4.358	0.75
4.10	4.272	0.41
4.40	4.186	0.02
4.70	4.098	0.01
5.00	4.013	-0.53
5.40	3.900	-0.46
5.80	3.797	-1.13
6.20	3.699	-0.97
6.60	3.613	-1.18
7.00	3.535	-1.01
7.50	3.450	-0.78
8.10	3.366	-0.97
8.90	3.271	-0.51
10.00	3.168	0.09
11.30	3.073	0.70
Series 17		
0.00	5.271	0.01
0.10	5.087	-0.68
0.20	4.904	-1.18
0.30	4.725	-1.99
0.40	4.542	-2.45
0.50	4.355	-2.68
0.60	4.164	-2.81
0.70	3.981	-3.35
0.80	3.815	-3.77
0.90	3.675	-4.37
1.10	3.455	-4.46
1.30	3.296	-4.64
1.60	3.122	-5.52
2.00	2.952	-5.90
Series 18		
0.00	5.540	6.48
0.30	5.428	6.91
0.60	5.325	6.84
0.90	5.229	6.53
1.20	5.137	6.29
1.50	5.051	5.92
1.80	4.970	5.22
2.10	4.891	5.12
2.50	4.791	4.43
3.00	4.672	3.30
3.50	4.556	2.96
4.00	4.443	2.24
4.50	4.329	1.69
5.00	4.214	1.40
5.50	4.099	0.80
6.00	3.981	0.90
6.50	3.866	0.58
7.00	3.756	0.25
7.60	3.633	0.55
8.20	3.525	0.86
8.90	3.418	1.04
9.70	3.317	1.59
10.80	3.207	1.73
12.10	3.104	2.92
13.70	3.006	4.31

v/ml	-lg(h/M)	Δy
Series 19		
0.00	3.694	-1.18
0.40	3.920	-0.94
0.70	4.125	-0.64
1.00	4.343	-0.16
1.20	4.490	0.12
1.40	4.635	0.48
1.60	4.781	0.72
1.80	4.926	0.96
2.00	5.071	1.33
2.30	5.293	1.81
2.50	5.443	2.07
2.70	5.597	2.22
2.90	5.751	2.78
3.10	5.910	3.22
3.30	6.070	4.00
3.50	6.233	5.09
3.70	6.402	5.82
3.90	6.571	6.99
4.10	6.753	7.29
4.30	6.948	7.45
4.50	7.171	6.76
4.65	7.365	5.81
4.75	7.512	4.89
4.85	7.666	4.11
4.95	7.824	3.13
5.05	7.967	2.42
5.15	8.092	1.91
5.30	8.250	1.20
5.50	8.410	1.00
5.70	8.542	0.51
6.00	8.697	0.15
6.40	8.868	-0.80
Series 20		
0.00	3.545	2.64
1.00	3.807	3.50
1.70	4.006	3.44
2.40	4.196	3.86
3.10	4.383	1.31
3.80	4.559	-0.91
4.50	4.738	-5.29
5.70	5.056	-13.43
6.30	5.225	-17.18
6.90	5.398	-19.09
7.50	5.582	-20.98
8.10	5.766	-20.27
8.70	5.959	-19.13
9.30	6.155	-16.87
10.00	6.390	-15.44
10.40	6.527	-10.94
10.70	6.633	-9.10
11.00	6.748	-7.95
11.30	6.860	-5.45
11.60	6.985	-3.88
11.85	7.100	-3.00
12.10	7.225	-2.16
12.30	7.337	-1.70
12.50	7.463	-1.60
12.70	7.607	-1.54
12.85	7.729	-1.52
13.00	7.864	-1.48
13.10	7.974	-2.22
13.20	8.084	-2.60
13.30	8.194	-2.86
13.45	8.356	-3.33
13.61	8.517	-4.03
13.80	8.676	-4.29
Series 21		
0.00	3.898	-2.53
1.00	4.497	-0.93
1.80	5.126	-3.06
2.10	5.386	-3.18
2.30	5.567	-2.67
2.50	5.756	-1.87
2.70	5.950	-0.68
2.90	6.152	0.63
3.05	6.311	1.50
3.20	6.480	2.26
3.35	6.671	2.63
3.50	6.892	2.76
3.60	7.066	2.59
3.70	7.256	2.57
3.80	7.445	2.09
3.90	7.611	1.90
4.00	7.751	1.57
4.15	7.913	1.26
4.30	8.040	0.84
4.50	8.170	0.56
4.80	8.321	0.08
5.20	8.474	-0.85
5.80	8.647	-1.54
6.60	8.824	-2.28

v/ml	-lg(h/M)	Δy
Series 22		
0.00	3.687	1.38
0.60	3.861	1.53
1.20	4.037	2.24
1.80	4.208	2.64
2.40	4.370	2.74
3.00	4.527	2.05
3.60	4.679	1.44
4.20	4.853	0.00
4.80	4.987	-0.97
5.40	5.146	-2.25
6.00	5.311	-3.85
6.60	5.482	-5.03
7.20	5.658	-5.66
7.80	5.839	-5.67
8.40	6.028	-5.77
8.90	6.187	-4.79
9.40	6.351	-3.77
9.80	6.486	-3.01
10.20	6.622	-1.56
10.60	6.764	-0.62
11.00	6.907	0.95
11.40	7.065	1.65
11.80	7.228	2.31
12.20	7.409	2.82
12.50	7.561	2.76
12.80	7.732	2.46
13.00	7.862	1.83
13.20	8.003	1.50
13.40	8.165	0.60
13.60	8.346	-0.34
13.80	8.540	-1.13
13.95	8.689	-1.57
14.10	8.856	-1.90
14.25	8.976	-1.93
Series 23		
0.00	3.751	-2.52
0.20	3.946	-2.46
0.30	4.061	-2.41
0.40	4.186	-2.36
0.50	4.319	-2.58
0.60	4.453	-2.54
0.70	4.585	-2.37
0.80	4.711	-1.74
0.90	4.838	-1.24
1.00	4.960	-0.14
1.10	5.085	0.80
1.20	5.207	1.83
1.30	5.328	3.13
1.40	5.450	4.44
1.50	5.575	5.32
1.60	5.697	6.53
1.70	5.820	7.49
1.80	5.945	8.25
1.90	6.070	9.08
2.00	6.196	10.06
2.10	6.329	10.22
2.20	6.459	10.97
2.30	6.595	11.33
2.40	6.728	12.04
2.50	6.867	12.37
2.60	7.012	12.27
2.70	7.164	11.97
2.77	7.277	11.53
2.85	7.416	10.73
2.92	7.545	9.97
3.00	7.703	8.63
3.06	7.822	7.86
3.12	7.938	7.04
3.20	8.082	6.11
3.30	8.256	5.36
3.40	8.364	4.84
3.50	8.474	4.29
3.60	8.569	3.86
3.70	8.652	3.63
3.85	8.760	3.63
4.00	8.858	3.05
4.20	8.973	2.93

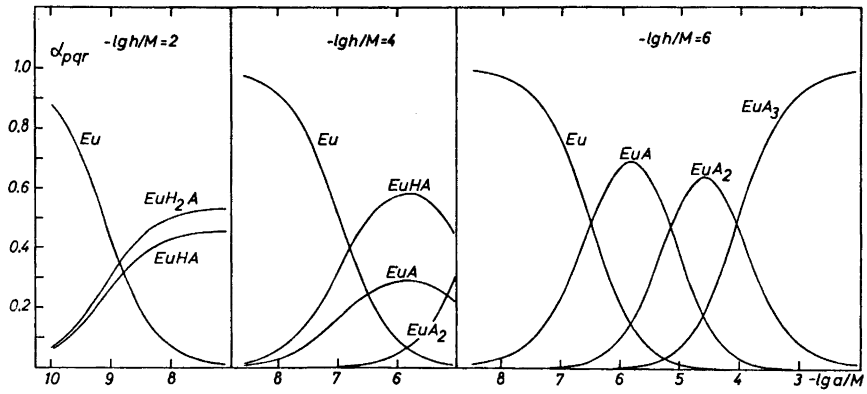

Fig. 1. Distribution curves at various hydrogen ion concentrations. α_{pqr} is plotted *versus* $-\log(a/\mathrm{M})$.

DISCUSSION

Several investigations of the proton iminodiacetate system have been carried out previously.[2–4,13] Table 3 shows the constants obtained. The values of β_{011} and β_{021} found in the present study agree well with the previous results obtained under similar experimental conditions. The species H_3A^+ has not been detected in any of these studies. Its existence has been indicated, however, in an IR investigation [5] of a solution where $\log(h/\mathrm{M}) = -0.4$. Our study has shown that H_3A^+ is present in fairly large amounts also in solutions of pure iminodiacetic acid. $[H_3A^+]/C_A$ has (in 1 M $NaClO_4$) values between 0.11 and 0.22, if C_A is in the range 0.01 M to 0.12 M.

A comparison of the values of β_{101} and β_{102} for the europium iminodiacetate systems investigated is given in Table 3 (Ref. 1 – 3, and this study). The

Table 3. Stability constants β_{pqr} obtained in different studies. All investigations were performed at 25°C. (I = ionic strength.)

I/M and inert salt	$\log(\beta_{011}\mathrm{M})$	$\log(\beta_{021}\mathrm{M}^2)$	$\log(\beta_{101}\mathrm{M})$	$\log(\beta_{102}\mathrm{M}^2)$	Ref.
0.1 (KCl)	–	–	7.26	–	1
0.1 (KNO_3)	9.33	11.91	6.73	12.11	2
0.3 (KCl)	9.60	12.61	6.22	10.94	3
0.1 (KNO_3)	9.34	11.94	–	–	4
0.1 (KNO_3)	9.40	11.90	–	–	13
1 (KNO_3)	9.38	11.93	–	–	13
1 ($NaClO_4$)	9.32	11.89	6.49	11.65	This study

differences can be explained by the fact that previous investigators have not taken into account the species H_3A^+, MHA^{2+}, MH_2A^{3+}, and MA_3^{3-} (in one study,[1] only MA^+ was considered).

The possible existence of the complex MA_3^{3-} is mentioned by Thompson.[2] Prutkova and Martynenko [4] have investigated the Nd and Yb iminodiacetate systems. Some of their $\bar{n}$-curves show that a third complex is formed. Nevertheless, these authors used only two constants to describe their experimental data.

If too few titrations are made, it may sometimes be difficult to discover mixed complexes. In some cases, not even a relatively large variation of the ratio C_H/C_A does reveal the formation of such species. This point was discussed in some detail in the preceding communication.[8] It is possible to get a fairly good description of most of the experimental material, using only the species EuA_r^{3-2r}. From the titration series 14 – 18, the following values were obtained: $\beta_{101} = (1.37 \pm 0.12) \times 10^6$ M^{-1}, $\beta_{102} = (2.1 \pm 0.3) \times 10^{11}$ M^{-2}, $\beta_{103} = 5.0 \times 10^{15}$ M^{-3} (not varied). The value of $sig\ y = 14.8 \times 10^{-3}$ is considerably higher than in the final calculation with the mixed complexes included. The errors $(C_{H(calc)}/C_A) - (C_{H(exp)}/C_A)$ also tend to increase with increasing h. Hence, it is necessary to introduce the acid complexes in order to describe satisfactorily the entire experimental material.

The complexes EuA_r^{3-2r} are very stable, and at most three iminodiacetate ligands are coordinated. The shape of the $\bar{n}$-curves at the highest values obtained ($2.9 < \bar{n} < 3.0$) clearly shows that a fourth complex, if formed at all, must be very weak. From the above findings it seems reasonable to assume that iminodiacetate acts as a three-dentate ligand, and that europium is at least nine-coordinated in the complex EuA_3^{3-}.

The ligand HA^- ($^-OOC{\cdot}CH_2{\cdot}NH_2^+{\cdot}CH_2{\cdot}COO^-$) is a potential chelating agent. The magnitude of the equilibrium constant, K_{EuHA}, for the reaction

$$Eu^{3+} + HA^- \rightarrow EuHA^{2+}$$

should give an indication whether a chelate is formed or not. K_{EuHA} is equal to 30 M^{-1} and has the same magnitude as the corresponding constants in the malonate [8] and thiodiacetate [12] systems. The value does not differ much from the β_1-value in the europium acetate system,[14] *i.e.* HA^- seems to be coordinated as a unidentate ligand. A similar coordination can also be expected for the dipolar ligand H_2A, since the equilibrium constant for the reaction

$$Eu^{3+} + H_2A \rightarrow EuH_2A^{3+}$$

is as low as 9 M^{-1}. The difference in the relative stability between Eu^{3+} and the ligands HA^- and H_2A is negligible if the statistical factors for the two ligands are taken into account.

The coordinated ligands HA^- and H_2A are stronger acids than the corresponding free species. The increase in acid strength is much larger for $EuHA^{2+}$ compared to HA^- than for EuH_2A^{3+} compared to H_2A (a factor 10^5 as compared to 3). This large difference may be correlated with the large difference in distance between the dissociating proton and the coordinated metal ion in the two species.[15]

Note added in proof. Kupriyanova and Martynenko have in a recent communication (*Russ. J. Inorg. Chem.* **15** (1970) 1024) determined the stability constant for the tris-iminodiacetato complex of neodymium by a spectrophotometric method.

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REFERENCES

1. Harder, R. and Chaberek, S. *J. Inorg. Nucl. Chem.* **11** (1959) 197.
2. Thompson, L. C. *Inorg. Chem.* **1** (1962) 490.
3. Misumi, S. and Aihara, M. *Bull. Chem. Soc. Japan* **39** (1966) 2677.
4. Prutkova, N. M. and Martynenko, L. I. *Russ. J. Inorg. Chem.* **14** (1969) 801.
5. Nakamoto, K., Morimoto, Y. and Martell, A. E. *J. Am. Chem. Soc.* **84** (1962) 2081.
6. Albertsson, J. and Oskarsson, Å. *Acta Chem. Scand.* **22** (1968) 1700.
7. Oskarsson, Å. *Acta Chem. Scand.* **25** (1971) 1206.
8. Dellien, I. and Grenthe, I. *Acta Chem. Scand.* **25** (1971) 1387.
9. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
10. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York, Toronto, London 1961.
11. Ingri, N. and Sillén, L.-G. *Arkiv Kemi* **23** (1965) 97.
12. Dellien, I. and Grenthe, I. *To be published.*
13. Rajan, K. S. and Martell, A. E. *J. Inorg. Nucl. Chem.* **26** (1964) 789.
14. Grenthe, L. *Acta Chem. Scand.* **16** (1962) 1695.
15. Schwarzenbach, G. *Z. Physik. Chem.* (*Leipzig*) **A 176** (1936) 133.

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