Solubilisation–microstructure relationship of trivalent salts in hydrotropic ternary systems

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1- XRF calibration

Multiple samples with known concentrations of REEs in ternary solutions containing water/NaSal/EA were prepared from standard known concentration solutions of REEs by dilution. The concentrations of all REEs (La^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+}, Yb^{3+}) were generated randomly and uniformly within a given range. According to the procedure already described in references [1,2], standard known concentrations of single REE or mixture of them were prepared as shown in **Table S1**.

Table S1. *Calibration concentrations of REEs.*

C (mmol/L)	La	Nd	Eu	Dy	Er	Yb
1	2.2	10.8	7.5	0.7	2.9	2.9
2	12.0	4.5	3.2	1.5	11.7	2.1
3	8.4	1.3	11.1	6.6	7.05	10.8
4	4.9	4.2	0.4	11.9	4.9	0.6
5	3.0	1.2	7.8	12.4	1.1	8.1
6	5.2	6.9	5.6	3.1	4.7	11.7
7	11.2	6.4	8.0	5.0	7.5	5.7
8	6.8	0.7	10.8	12.0	10.3	1.7
9	2.9	2.0	5.1	11.5	2.7	11.1
10	4.6	1.9	2.6	5.5	11.1	10.5
11	3.4	2.7	3.8	9.6	8.5	7.1
12	5.7	10.8	9.0	10.6	10.8	6.3
13	3.0	5.5	4.5	6.3	12.4	6.8

14	0.2	2.2	3.7	4.2	3.9	7.9
15	8.2	8.1	0.9	8.0	4.2	10.8
16	7.5	1.7	6.7	9.1	4.3	9.0
17	1.5	1.0	1.5	9.2	3.0	6.4
18	7.8	9.0	10.5	11.1	6.2	11.5
19	3.6	8.6	10.2	1.8	9.7	4.1
20	1.1	1.3	8.2	3.0	12.1	5.6
21	0.4	4.0	11.6	4.8	9.5	9.6
22	3.9	8.7	4.6	8.4	0.7	2.5
23	1.1	10.9	12.0	0.3	10.8	8.3
24	7.7	11.5	0.2	7.8	5.4	0.2
25	1.5	5.8	9.9	2.1	2.1	1.1
26	8.5	3.9	9.7	1.1	5.3	7.8
27	11.4	8.8	5.1	1.8	10.2	7.5
28	5.1	3.9	8.4	6.6	7.2	1.9
29	9.9	1.5	2.1	8.4	5.2	3.4
30	4.8	0.3	5.0	1.0	9.4	2.3
31	4.3	9.9	4.2	10.2	12.0	9.1
32	7.3	1.1	3.4	3.3	2.0	0.7
33	11.7	6.0	0.2	0.1	2.7	8.2
34	2.1	0.6	0.6	2.7	5.7	11.7
35	1.2	7.2	10.1	8.2	5.6	2.6
36	8.0	8.8	6.2	8.7	10.7	2.1
37	6.5	2.2	8.6	2.4	10.0	6.0
38	8.2	10.3	3.9	6.9	8.4	9.3
39	9.0	5.4	10.7	8.1	1.7	0.3
40	12.2	10.8	2.4	5.7	3.7	1.6
41	1.0	4.9	7.9	9.9	0.2	3.9
42	12.5	12.5	12.5	12.5	12.5	12.5

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Figure S1 shows the calibration curves obtained from measuring the solutions listed in **Table S1**. To assess the accuracy of the calibration, the results were cross-validated using the scikit learn library in Python. We obtained an average root mean square error of 0.05 mM. This value fluctuates depending on the element and the phase considered. The remaining measurement error likely arises from matrix effects, which induce unwanted correlation between REE peaks.

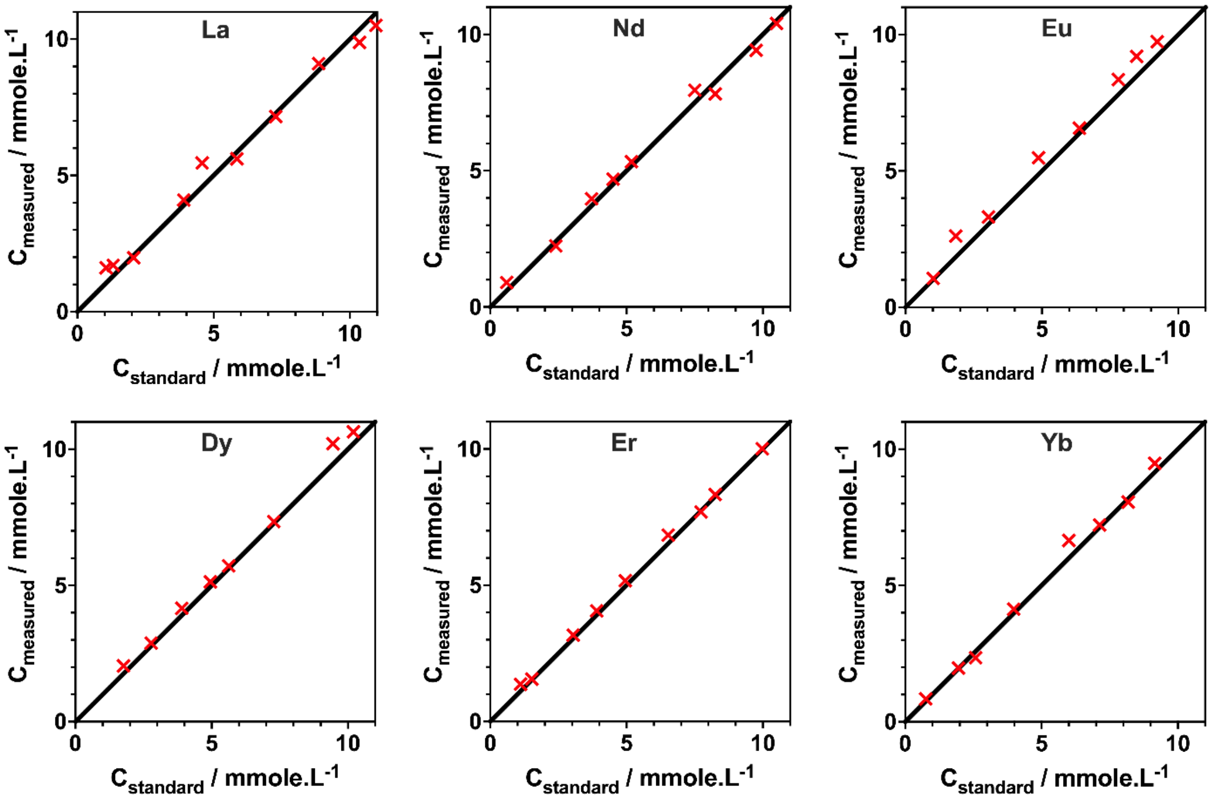

Figure S1. *Calibration curves of the XRF.*

2- Self-diffusion coefficients: raw data

Table S2. *the composition of the samples for DOSY measurements along the two dilution lines as shown in* ***Error! Reference source not found.****.*

wt %	NaSal	H_2O	EA
1	0.403	0.312	0.285
2	0.3734	0.3628	0.2638
3	0.3365	0.4258	0.2377
4	0.30263	0.48144	0.21593
5	0.25432	0.566	0.17968
6	0.21743	0.6294	0.15317
7	0.16625	0.7163	0.11745
8	0.12189	0.792	0.08611
9	0.06399	0.8908	0.04521

10	0.06624	0.93376	0
11	0.1001	0.1001	1.8229
12	0.10796	0.10795	0.78409
13	0.15237	0.15237	0.69526
14	0.19816	0.19816	0.60368
15	0.24979	0.24979	0.50042
16	0.30391	0.30391	0.39218
17	0.3517	0.3517	0.2966
18	0.39991	0.39991	0.20018
19	0.4485	0.4485	0.10299
20	0.5	0.5	0

Table S3. *Self-diffusion coefficients and reduced Self-diffusion coefficients of water, EtOAc, and NaSal along the two dilution lines as shown in* ***Error! Reference source not found.****.*

	Self-diffusion coefficient D_i / m^2/s			Reduced self-diffusion coefficient D_i^* / m^2/s		
Sample	H_2O	EtOAc	NaSal	H_2O	EtOAc	NaSal
1	$4.69\cdot10^{-10}$	$2.51\cdot10^{-10}$	$1.15\cdot10^{-10}$	$2.06\cdot10^{-01}$	$8.04\cdot10^{-02}$	$1.49\cdot10^{-01}$
2	$4.70\cdot10^{-10}$	$2.49\cdot10^{-10}$	$1.18\cdot10^{-10}$	$2.06\cdot10^{-01}$	$7.97\cdot10^{-02}$	$1.53\cdot10^{-01}$
3	$6.94\cdot10^{-10}$	$2.93\cdot10^{-10}$	$1.60\cdot10^{-10}$	$3.05\cdot10^{-01}$	$9.38\cdot10^{-02}$	$2.08\cdot10^{-01}$
4	$8.65\cdot10^{-10}$	$3.34\cdot10^{-10}$	$2.04\cdot10^{-10}$	$3.80\cdot10^{-01}$	$1.07\cdot10^{-01}$	$2.65\cdot10^{-01}$
5	$1.17\cdot10^{-09}$	$3.97\cdot10^{-10}$	$2.83\cdot10^{-10}$	$5.13\cdot10^{-01}$	$1.27\cdot10^{-01}$	$3.68\cdot10^{-01}$
6	$1.28\cdot10^{-09}$	$4.58\cdot10^{-10}$	$3.35\cdot10^{-10}$	$5.63\cdot10^{-01}$	$1.47\cdot10^{-01}$	$4.35\cdot10^{-01}$
7	$1.53\cdot10^{-09}$	$5.88\cdot10^{-10}$	$4.45\cdot10^{-10}$	$6.73\cdot10^{-01}$	$2.88\cdot10^{-01}$	$5.79\cdot10^{-01}$
8	$1.72\cdot10^{-09}$	$7.02\cdot10^{-10}$	$5.47\cdot10^{-10}$	$7.54\cdot10^{-01}$	$2.25\cdot10^{-01}$	$7.11\cdot10^{-01}$
9	$2.08\cdot10^{-09}$	$9.01\cdot10^{-10}$	$7.23\cdot10^{-10}$	$9.14\cdot10^{-01}$	$2.89\cdot10^{-01}$	$9.40\cdot10^{-01}$
10	$2.28\cdot10^{-09}$	n.d	$7.69\cdot10^{-10}$	$1.00\cdot10^{+00}$	$0.00\cdot10^{+00}$	$1.00\cdot10^{+00}$
11	$1.79\cdot10^{-09}$	$2.47\cdot10^{-09}$	$4.94\cdot10^{-10}$	$7.88\cdot10^{-01}$	$7.92\cdot10^{-01}$	$6.43\cdot10^{-01}$
12	$1.00\cdot10^{-09}$	$1.89\cdot10^{-09}$	$4.94\cdot10^{-10}$	$4.40\cdot10^{-01}$	$6.06\cdot10^{-01}$	$6.43\cdot10^{-01}$
13	$8.06\cdot10^{-10}$	$1.52\cdot10^{-09}$	$2.86\cdot10^{-10}$	$3.54\cdot10^{-01}$	$4.86\cdot10-^{01}$	$3.71\cdot10^{-01}$
14	$6.97\cdot10^{-10}$	$1.17\cdot10^{-09}$	$2.58\cdot10^{-10}$	$3.06\cdot10^{-01}$	$3.75\cdot10^{-01}$	$3.36\cdot10^{-01}$
15	$6.36\cdot10^{-10}$	$8.12\cdot10^{-10}$	$2.24\cdot10^{-10}$	$2.79\cdot10^{-01}$	$2.60\cdot10-^{01}$	$2.91\cdot10^{-01}$
16	$6.02\cdot10^{-10}$	$5.42\cdot10^{-10}$	$1.95\cdot10^{-10}$	$2.64\cdot10^{-01}$	$1.74\cdot10^{-01}$	$2.54\cdot10^{-01}$

17	$6.59\cdot10^{-10}$	$3.71\cdot10^{-10}$	$1.68\cdot10^{-10}$	$2.90\cdot10^{-01}$	$1.19\cdot10^{-01}$	$2.19\cdot10^{-01}$
18	$6.28\cdot10^{-10}$	$2.62\cdot10^{-10}$	$1.45\cdot10^{-10}$	$2.76\cdot10^{-01}$	$8.39\cdot10^{-02}$	$1.89\cdot10^{-01}$
19	$5.74\cdot10^{-10}$	$1.92\cdot10^{-10}$	$1.30\cdot10^{-10}$	$2.52\cdot10^{-01}$	$6.17\cdot10^{-02}$	$1.69\cdot10^{-01}$
20	$6.28\cdot10^{-10}$	n.d	$1.19\cdot10^{-10}$	2.7610^{-01}	$0.00\cdot10^{+00}$	$1.55\cdot10^{-01}$

3- Detailed calculation for SAXS fitting

The following standard equations of scattering were applied with a spherical form factor P(q) and a structure factor S(q) assumed to be equal to 1:

$$I(q) = n_p P(q) S(q)$$

With n_p number of scattering particles (aggregates) per unit volume:

$$n_p = \frac{N_A(C - LAC)}{N_{agg}}$$

And

$$P(q) = 3V_{agg}^2(\Delta\rho)^2 \cdot \left(\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right)^2$$

$$\Delta\rho = \rho_{agg} - \rho_{solvent}$$

Where:

- N_A Avogadro number;
- N_{agg} Aggregation number, *i.e.*, number of NaSal molecules per aggregate;
- r_{agg} aggregate radii;
- V_{agg} aggregate volume;
- ρ_{agg} is the scattering length density of the aggregte, $\rho_{solvent}$ is the scattering length density of the external solvent

Finally,

$$I(q) = \frac{N_A(C - LAC)}{N_{agg}} \cdot 3V_{agg}^2\left(\rho_{agg} - \rho_{solvent}\right)^2 \cdot \left(\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right)^2$$

References

[1] Kirsanov, D.; Panchuk, V.; Agafonova-Moroz, M.; Khaydukova, M.; Lumpov, A.; Semenov, V.; Legin, A., A sample-effective calibration design for multiple components. Analyst 2014, 139 (17), 4303-4309.

[2] El Maangar, A.; Theisen, J.; Penisson, C.; Zemb, T.; Gabriel, J.-C. P., A microfluidic study of synergic liquid–liquid extraction of rare earth elements. Physical Chemistry Chemical Physics 2020, 22 (10), 5449-5462.