

Suppl. Inf.

Theoretical equations

In the theory of regular solution, the excess energy (E^{excess}) due to the mixing of A and B reads

$$E^{excess} = (E_A + E_B) - E^{*,pure} \quad \text{Eq. SI1}$$

$$= \frac{q}{2} [(x_B \varepsilon_{AB} + x_A \varepsilon_{AA}) N_A + (x_A \varepsilon_{AB} + x_B \varepsilon_{BB}) N_B] - \frac{q}{2} \varepsilon_{AA} N_A - \frac{q}{2} \varepsilon_{BB} N_B$$

with respect to the energy of pure A (E_A) and pure B (E_B):

$$E_A = \frac{q}{2} \varepsilon_{AA} N_A \quad \text{Eq. SI2}$$

$$E_B = \frac{q}{2} \varepsilon_{BB} N_B \quad \text{Eq. SI3}$$

The model depends on the following parameters: ε_{AA} , energy if A is in the vicinity of A; ε_{BB} , energy if B is in the vicinity of B; ε_{AB} , energy if A is in the vicinity of B; q , the coordination number (number of closest neighbors); $x_{A/B}$, mole fraction of A or B.

Considering $x_A + x_B = 1$ and by dividing by $N_{tot} = N_A + N_B$, we obtain:

$$\frac{2E^{excess}}{q \cdot N_{tot}} = [(N_A \varepsilon_{AB} x_B - N_A \varepsilon_{AA} x_B) + (N_B \varepsilon_{AB} x_A - N_B \varepsilon_{BB} x_A)] \quad \text{Eq. SI4}$$

and finally,

$$\frac{E^{excess}}{N_{tot}} = q \left(\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \right) x_A x_B = qW x_A x_B = \alpha x_A x_B \quad \text{Eq. SI5}$$

With $\alpha = q \left(\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \right)$ and q the coordination number (number of closest neighbours and $\varepsilon_{\alpha\beta}$ the energy at contact of α and β .

$\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) = W$ is related to the cohesive energy per unit volume of the solvent used and does not take into account wetting by entropic effects.²¹ W represents the mixing cost in terms of internal energy. More precisely:

- If $W > 0$, so $\varepsilon_{AB} > \varepsilon_{AA} + \varepsilon_{BB}$: Mixing A and B is unfavorable for the mixed system
- If $W < 0$, so $\varepsilon_{AB} < \varepsilon_{AA} + \varepsilon_{BB}$: Mixing A and B is favorable for the mixed system

The corresponding Gibbs energy reads:

$$\frac{G^m}{n_{tot}} = x_{m,1}(\mu_{m,1}^{0,pure} + RT \cdot \ln x_{m,1}) + x_{m,2}(\mu_{m,2}^{0,pure} + RT \cdot \ln x_{m,2}) + \alpha x_{m,1}x_{m,2}$$

Eq.
SI6

With n_{tot} the total amount of ligands in the mixture.

It leads to,

$$G^m = n_{m,1} \cdot \mu_{m,1}^{0,pure} + n_{m,1} \cdot RT \cdot \ln \frac{n_{m,1}}{n_{m,1} + n_{m,2}} + n_{m,2} \cdot \mu_{m,2}^{0,pure} + n_{m,2} \cdot RT \cdot \ln \frac{n_{m,2}}{n_{m,1} + n_{m,2}} + \alpha n_{m,1} n_{m,2}$$

Eq.
SI7

$n_{m,1}$ and $n_{m,2}$ are the amount of ligand 1 and 2 in the mixture.

by definition,

$$\mu_{m,1} = \frac{\partial G_m}{\partial n_{m,1}}$$

Eq.
SI8

hence,

$$\begin{aligned} \mu_{m,1} = \frac{\partial G_m}{\partial n_{m,1}} &= \frac{\partial}{\partial n_{m,1}} n_{m,1} \cdot \mu_{m,1}^{0,pure} + n_{m,1} \cdot RT \cdot \ln \frac{n_{m,1}}{n_{m,1} + n_{m,2}} + n_{m,2} \cdot \mu_{m,2}^{0,pure} \\ &\quad + n_{m,2} \cdot RT \cdot \ln \frac{n_{m,2}}{n_{m,1} + n_{m,2}} + \alpha n_{m,1} n_{m,2} \end{aligned}$$

Eq. SI9

leading to,

$$\mu_{m,1} = \mu_{m,1}^{0,pure} + RT \cdot \ln x_{m,1} + \alpha(x_{m,2})^2$$

Eq. SI10

DMDOHEMA Molar ratio (%)	0	0.25	0.50	0.75	1
[HDEHP] (mol.L ⁻¹)	0.6	0.48	0.3	0.18	0
[DMDOHEMA] (mol.L ⁻¹)	0	0.12	0.3	0.42	0.6

Table SI 1. Molar concentration of the two extractant used for constant total concentration 0.6 mol.L⁻¹ for several DMDOHEMA molar ratio

	DMDOHEMA Molar ratio	Non-contacted	Contacted to Water	Contacted to water + nitric acid	Contacted to water + nitric acid + Eu
Extracted Water (mol.L⁻¹)	0	0.008	0.098	0.112	0.082
	0.25	0.013	0.178	0.176	0.150
	0.5	0.016	0.224	0.232	0.210
	0.75	0.02	0.205	0.264	0.268
	1	0.03	0.176	0.260	0.282
Extracted Nitric acid. (mol.L⁻¹)	0	-	-	0.012	0.001
	0.25	-	-	0.025	0.034
	0.5	-	-	0.040	0.065
	0.75	-	-	0.053	0.100
	1	-	-	0.066	0.119
Extracted Eu(NO₃)₃. (mol.L⁻¹)	0	-	-	-	0.018
	0.25	-	-	-	0.021
	0.5	-	-	-	0.019
	0.75	-	-	-	0.015
	1	-	-	-	0.006

Table SI 2. Concentration of extracted solute in the organic phase (HDEHP-DMDOHEMA 0.6 mol.L⁻¹ in dodecane) when the mixed system is contacted to water, water and acid (1 mol.L⁻¹), and water, acid (1 mol.L⁻¹) and europium nitrate (0.05 mol.L⁻¹).

Contacted to ...	m/z	HDEHP species	m/z	DMDOHEMA species	m/z	HDEHP-DMDOHEMA mixed species
water case : (a)	345	[LH.Na] ⁺	483.4	[D.H] ⁺	827.6	[D(LH).Na] ⁺
	667	[(LH) ₂ .Na] ⁺	505	[D.Na] ⁺	843.6	[D(LH).K] ⁺

	1027	$[(LH)_2.(LNa).K]^+$	521.4	$[D.K]^+$	849.6	$[D(LNa).Na]^+$
	1350	$[(LH)_3.(LNa).K]^+$	743	$[D_3.Ca]^{2+}$	1326.1	$[D_2(LH).K]^+$
	1650	$[(LH)_5.K]^+$	988	$[D_2.Na]^+$	1649.2	$[D_2(LH)_2.K]^+$
	-	-	1003.8	$[D_2.K]^+$	-	-
1 mol.L⁻¹ HNO₃ Case : (b)	345	$[LH.Na]^+$	483.4	$[D.H]^+$	827.6	$[D(LH).Na]^+$
	667	$[(LH)_2.Na]^+$	502	$[D_2.Ca]^{2+}$	843.6	$[D(LH).K]^+$
	989	$[(LH)_3.Na]^+$	521.4	$[D.K]^+$	849.6	$[D(LNa).Na]^+$
	1312	$[(LH)_4.Na]^+$	743	$[D_3.Ca]^{2+}$	1165.8	$[D(LH)_2.K]^+$
	1650	$[(LH)_5.K]^+$	988	$[D_2.Na]^+$	1326	$[D_2(LH).K]^+$
	1972	$[(LH)_6.K]^+$	-	-	1488	$[D(LH)_3.K]^+$
	-	-	-	-	1648.2	$[D_2(LH)_2.K]^+$
	-	-	-	-	1810.3	$[D(LH)_4.K]^+$
	-	-	-	-	1971.5	$[D_2(LH)_3.K]^+$
	-	-	-	-	1977.5	$[D_2(LH)_2(LNa).K]^+$
	-	-	-	-	2315.7	$[D_2(LH)_3(LNa).K]^+$
	-	-	-	-	2653.9	$[D_2(LH)_4(LNa).K]^+$
1 mol.L⁻¹ HNO₃- 0.05 mol.L⁻¹ Eu(NO₃)₃ case : (c)	345	$[LH.Na]^+$	483.4	$[D.H]^+$	827.6	$[D(LH)Na^+]$
	667	$[(LH)_2.Na]^+$	502	$[D_2.Ca]^{2+}$	843.6	$[D(LH)K^+]$
	989	$[(LH)_3.Na]^+$	521.4	$[D.K]^+$	849.6	$[D(LNa)Na^+]$
	1312	$[(LH)_4.Na]^+$	743	$[D_3.Ca]^{2+}$	960.7	$[D_3LEu^{2+}]$
	1440	$[(LH)_2L_2Eu]^+$	988	$[D_2.Na]^+$	1149.8	$[D(LH)_2Na^+]$
	1650	$[(LH)_5.K]^+$	-	-	1165.8	$[D(LH)_2K^+]$
	1762	$(LH)_3L_2Eu^+$	-	-	1277.8	$[DL_2Eu^+]$
	2084	$(LH)_4L_2Eu^+$	-	-	1326.0	$[D_2(LH)K^+]$
	-	-	-	-	1488.0	$[D(LH)_3K^+]$
					1600.0	$[D(LH)L_2Eu^+]$
					1648.2	$[D_2(LH)_2K^+]$
					1760.2	$[D_2L_2Eu^+]$
					1922.2	$[D(LH)_2L_2Eu^+]$
					1977.5	$[D_2(LH)_2(LNa)K^+]$
					2082.4	$[D_2(LH)L_2Eu^+]$
					2244.4	$[D(LH)_3L_2Eu^+]$
					2315.7	$[D_2(LH)_3(LNa)K^+]$

Table SI 3. Identification of major peaks for samples containing only HDEHP (x=0), only DMDOHEMA (x=1) and mixed HDEHP DMDOHEMA (x=0.5) for the mixed system contacted to water (a), nitric acid solution 1mol.L⁻¹ (b) and 50 mmol.L⁻¹ of europium nitrate in nitric acid solution (c).

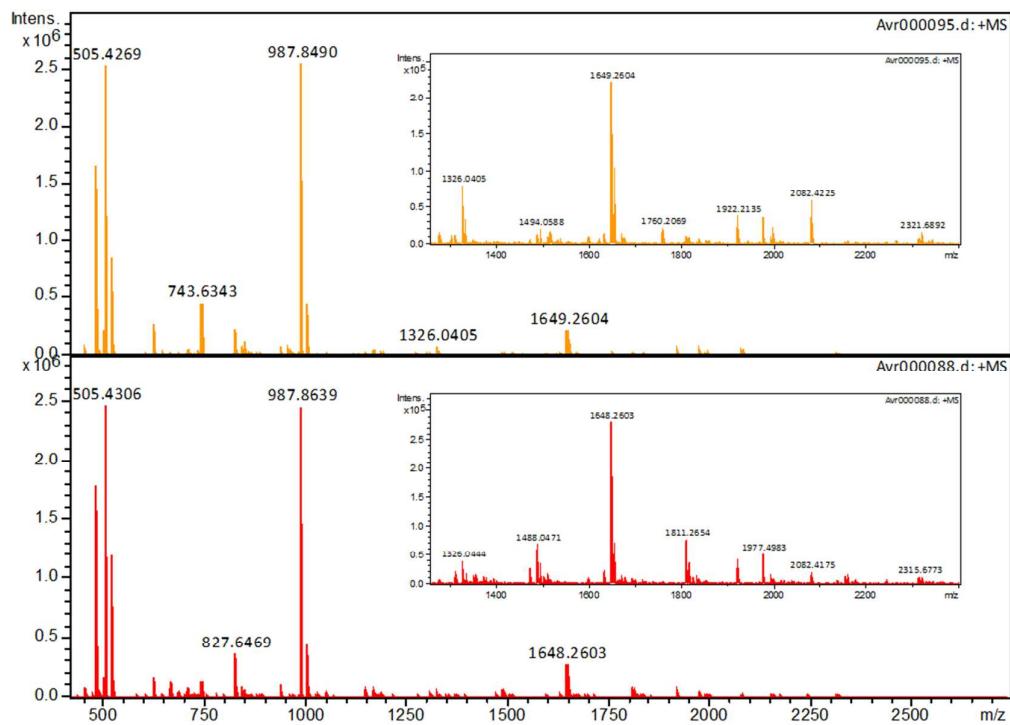


Figure SI 1. ESI-MS spectra recorded for DMDOHEMA ratio of 0.25 and 0.5 after contact with 1 mol.L⁻¹ HNO₃ and 50mmol.L⁻¹

CAC determination for HDEHP-DMDOHEMA by drop shop tensiometer analysis for samples contacted to:

- water (*a*)
- to water and acid (1M HNO₃) (*b*)
- to water, acid (1M HNO₃) and cation (0.05M Eu(NO₃)₃) (*c*)

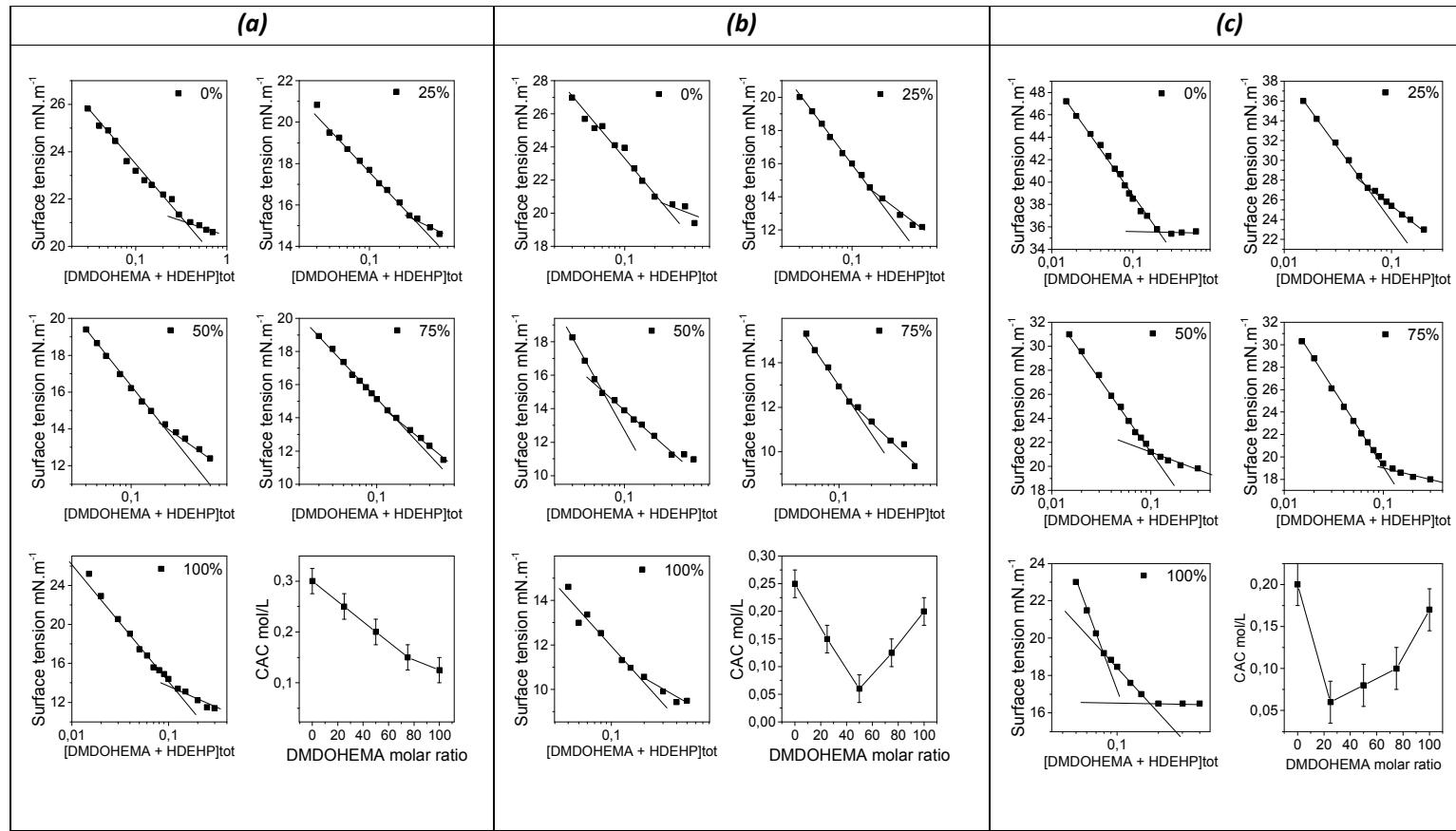


Figure SI 2. Surface tension of extractant system HDEHP-DMDOHEMA in dodecane at different DMDOHEMA molar ratio 0, 0.25, 0.5, 0.75 and 1 contacted to aqueous phase containing water (*a*), water and acid (HNO₃ 1M) (*b*), and water, acid (HNO₃ 1M) and europium nitrate (0.05M Eu(NO₃)₃) (*c*). Critical aggregation concentration plotted versus DMDOHEMA molar ratio (*f*)

Conditions	DMDOHEMA molar ratio	0	0.25	0.50	0.75	1
Theoretical area per head-group (\AA^2)		29.8	30.855	31.91	32.965	34.02
contacted to water	a_{exp}^{hg} (\AA^2)	213.24	189.65	121.40	132.74	74.83
	η	0.140	0.165	0.263	0.248	0.455
	ϵ_{hg}^m	-1.652	-1.440	-0.664	-0.768	0.702
contacted to water and nitric acid 1M	a_{exp}^{hg} (\AA^2)	138.11	121.40	85.74	118.26	172.20
	η	0.216	0.254	0.372	0.279	0.198
	ϵ_{hg}^m	-1.009	-0.726	0.098	-0.551	-1.150
contacted to water, nitric acid 1M and 0.05M Eu(NO_3) ₃	a_{exp}^{hg} (\AA^2)	90.65	65.22	79.30	82.14	115.28
	η	0.329	0.473	0.402	0.401	0.295
	ϵ_{hg}^m	0.204	0.847	0.313	0.305	0.437

Table SI 4. Parameter used for entropic contribution derivation and results of the calculation for each DMDOHEMA molar ratio 0, 0.25, 0.5, 0.75 and 1 for the mixed system contacted with water, contacted with water & nitric acid (1M) and contacted with water, nitric acid (1M) & Eu(NO_3)₃ (0.05M).

Conditions	DMDOHEMA molar ratio	0	0.25	0.5	0.75	1
contacted to water	a_{exp}^{hg} (\AA^2)	213.24	189.65	121.40	132.74	74.83
	a_0 (\AA^2)	213.24	178.6375	144.035	109.4325	74.83
	$\epsilon_{elastic/kT}$	0.000	0.047	0.308	0.298	0.000
contacted to water and nitric acid 1M	a_{exp}^{hg} (\AA^2)	138.11	121.4	85.74	118.26	172.199
	a_0 (\AA^2)	138.11	146.6323	155.1545	163.6768	172.199
	$\epsilon_{elastic/kT}$	0.000	0.382	4.098	1.272	0.000
contacted to water, nitric acid 1M and 0.05M Eu(NO_3) ₃	a_{exp}^{hg} (\AA^2)	90.65	65.223	79.3	82.14	115.28
	a_0 (\AA^2)	90.65	96.807	102.965	109.122	115.28
	$\epsilon_{elastic/kT}$	0.000	1.115	0.515	0.646	0.000

Table SI 5. Elastic energy of the interfacial film between oil and water as a function of the DMDOHEMA molar ratio when the mixed system is contacted to water and to an acidic solution.