Supplementary Information

How Acidity Rules Synergism and Antagonism in Liquid-Liquid Extraction by Lipophilic Extractants—Part I: Determination of Nanostructures and Free Energies of Transfer

S. Dourdain[1], M. Špadina[1,2], J. Rey[1], K. Bohinc[2], S. Pellet-Rostaing[1], Jean-François Dufrêche,[1] and T. Zemb[1]

Model used to FIT SANS data

The following standard equations of scattering for an ellipsoidal core-shell model are applied:

$$I(q) = n_P P(q) S(\mathrm{q})$$

With,

$$n_p = \frac{N_{\mathrm{A}(}C - \mathrm{CAC})}{N_{\mathrm{ag}}}$$

$$P(Q) = \langle F^2(Q,\mu)\rangle = \int_0^1 [F(Q,\mu)]^2 d\mu$$

$$\langle F\ (Q,\mu)\rangle^2 = \left[\int_0^1 [F(Q,\mu)]\ d\mu\right]^2$$

$$F(Q,\mu) = V_{core}.\Delta\rho_1.3\frac{\sin x_1 - x_1\cos x_1}{(x_1)} + V_{ag}.\Delta\rho_2.3\frac{\sin x_2 - x_2\cos x_2}{Qx_2}$$

With,

$x1 = Q\sqrt{a^2\mu^2 + b^2(1-\mu^2)}$

$x2 = Q\sqrt{(a+\Delta R)^2\mu^2 + (b+\Delta R)^2(1-\mu^2)}$

$V_{core} = \frac{4}{3}\pi ab^2$

$V_{ag} = \frac{4}{3}\pi(a+\Delta R)(b+\Delta R)^2$

$n = \frac{a}{b}$

a : principal semi-axis of the ellipsoid

b : equatorial semi-axis of the ellipsoid

ΔR : thickness of the shell

$\Delta\rho_1 : \rho_{core} - \rho_{shell}$

$\Delta\rho_2 : \rho_{shell} - \rho_{diluant}$

Considering,

$$\rho_{core} = \frac{\varphi_{Dpol}\rho_{Dpol} + \varphi_{Hpol}\rho_{Hpol} + \varphi_{H_2O}\rho_{H_2O} + \varphi_{U02pol}\rho_{UO2pol} + \varphi_{Fe}\rho_{Fe}}{\varphi_{Dpol} + \varphi_{Hpol} + \varphi_{H_2O} + \varphi_{UO2} + \varphi_{Fe}}$$

$$\rho_{shell} = \emptyset_D\rho_{Dapol} + \emptyset_H\rho_{Hapol}$$

Where:

- R_{ag}, R_{core} the core and aggregate radii deduced from the volumes;
- ρ the scattering length densities of the species;
- $\varphi_{Dpol}, \varphi_{Hpol}$ the volume fraction of HDEHP and DMDOHEMA polar part;
- $\emptyset_D, \emptyset_H$ the molar ratio of HDEHP and DMDOHEMA;
- $\rho_{Dapol}, \rho_{Hapol}$ the scattering length density of apolar of HDEHP and DMDOHEMA apolar part;
- V_{core}, V_{ag} the core and the aggregate volumes calculated from extraction data, the molecular volume of the different species, and weighted by the mean aggregation number (variable to adjust to fit the data)

Structure factor:

An excluded volume structure factor *S*(*Q*) was taken into account, modelled by a non-sticky hard-sphere expression defined as :

$$S(q) = \left[1 + 24f_p\frac{G(f_p, R_{HS}q)}{R_{HS}q}\right]^{-1}$$

$$G(q) = \alpha\frac{(\sin A - A\cos A)}{A^2} + \beta\frac{(2A\sin A - (2 - A^2)\cos A - 2)}{A^3} + \gamma\frac{(-A^4 cosA + 4[(3A^2 - 6)cosA + (A^3 - 6A)sinA + 6]}{A^5}$$

With:

$$\alpha = \frac{(1 + 2f_p)^2}{(1 - f_p)^4}$$

$$\beta = -6f_p\frac{(1 + \frac{f_p}{2})^2}{(1 - f_p)^4}$$

$$\gamma = \frac{f_p\alpha}{2}$$

$$A = 2qR_{HS}$$

A: Volume fraction of the particle
q: Scattering vector
R_{HS}: Hard-sphere radii

For neutron and X-ray scattering, taking these equations of scattering, it can be shown that the intensity when *Q* tends to zero behaves as follows:

$$I_{SANS/SAXS}(q \to 0) \propto \frac{N_{A(}C - CAC)}{N_{ag}} . (V_{ag}\Delta\rho_{ag})^2$$

Where N_A is Avogadro number, C is the total concentration of ligands, CAC, is the critical aggregation concentration, N_{ag}, is the aggregation number equal to the average number of ligands in each aggregate, V_{ag} is the aggregate volume and where $\Delta\rho_{ag} = (\rho_{ag} - \rho_{solvant})$ is the scattering length density contrast.