Electronic Supplementary Information

Aqueous biphasic hydroformylation in the presence of cyclodextrins mixtures: evidence of a positive synergistic effect.

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General procedure for surface tension measurements.

Surface tension measurements of aqueous solutions of chemically modified cyclodextrin(s) (the total concentration of cyclodextrins was equal to 42 mmol.L^{-1}) were performed at 20°C with the pendant drop method using an OCA-15 plus (DataPhysics) tensiometer. All equilibrium surface tension values were mean quantities of at least three measurements. The standard deviation of the mean never deviated ± 1.5% of the mean.

Fig. S1. Surface tension measurements of different RAME-α-CD / RAME-β-CD mixtures

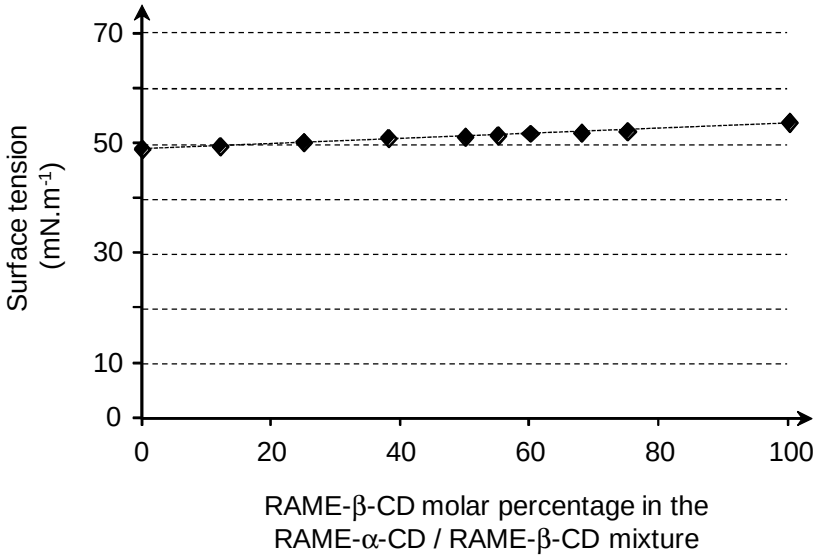


Fig. S2. Surface tension measurements of different RAME-α-CD / RAME-γ-CD mixtures

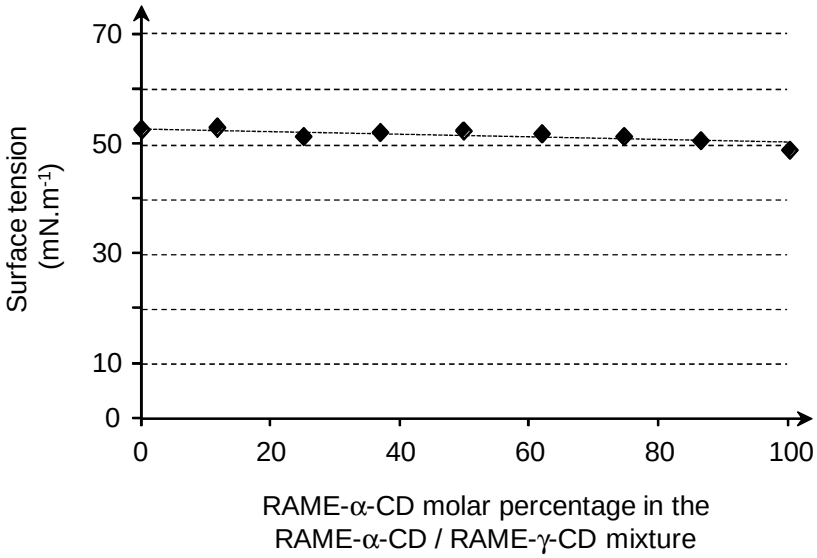
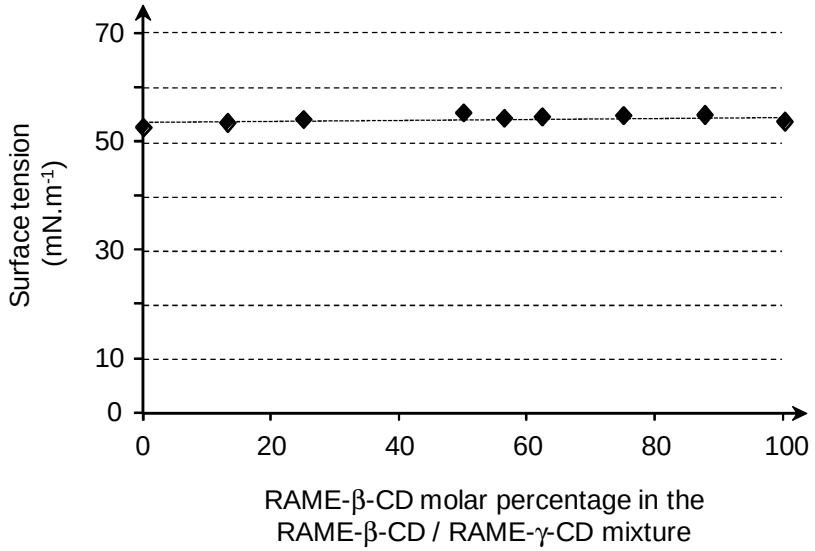


Fig. S3. Surface tension measurements of different RAME-β-CD / RAME-γ-CD mixtures



Calculation of the free RAME-β-CD percentage compared to the total amount of free CD when inclusion complexes between TPPTS and RAME-β-CD were taken into account (relative to the figure 3).

The percentage of free RAME-β-CD in a considered catalytic experiment has been determinate by using the following equation:

$$\text{free RAME-β-CD (\%)} = \frac{[\text{RAME-β-CD}]_T - [\text{COMPLEX}]}{[\text{CD}]_T - [\text{COMPLEX}]} \times 100$$

where $[CD]_T$ represents the total CD concentration ($[CD]_T$ = 42 mM), $[RAME\text{-β-CD}]_T$ the RAME-β-CD concentration in the considered catalytic experiment (*i.e.* $[CD]_T$ × molar fraction of RAME-β-CD in the considered catalytic experiment) and [COMPLEX] the RAME-β-CD:TPPTS complex concentration.

The RAME-β-CD:TPPTS complex concentration in the considered catalytic experiment can been easily calculated from the following equation:

$$[\text{COMPLEX}] = \frac{1}{2} \times \left(\frac{1}{K_{\text{RAME-β-CD:TPPTS}}} + [\text{RAME-β-CD}]_T + [\text{TPPTS}]_T \right) - \frac{1}{2} \times \sqrt{\left(\frac{1}{K_{\text{RAME-β-CD:TPPTS}}} + [\text{RAME-β-CD}]_T + [\text{TPPTS}]_T \right)^2 - 4 \times [\text{RAME-β-CD}]_T \times [\text{TPPTS}]_T}$$

where $K_{\text{RAME-β-CD:TPPTS}}$ stand for the RAME-β-CD:TPPTS complex association constant which is equal to 805 M^{-1} at 20°C in the case of commercial RAME-β-CD possessing a degree of substitution equal to 1.8[i].

The value of $[TPPTS]_T$ has been calculated by considering the free TPPTS amount *i.e.* two equivalents of TPPTS on the five introduced for one rhodium. Indeed, three equivalents of TPPTS are involved in the formation of the catalytic precursor $HRh(CO)(TPPTS)_3$. So, the $[TPPTS]_T$ is equal to 7.3 mM (*i.e.* 2/5 of the concentration of the catalytic experiments which is equal to 18.3 mM).

[i] F.X. Legrand, M. Sauthier, C. Flahaut, J. Hachani, C. Elfakir, S. Fourmentin, S. Tilloy, E. Monflier, *J. Mol. Catal. A: Chem.* 2009, **303**, 72.