

## Supplementary material

### 1. Experimental

#### 1.1 Materials and methods

Commercial stripped bulk or emulsified corn oil (Acros Organics) was used to minimize the effect of endogenous antioxidants. It was kept at low temperature in the dark to minimize lipid peroxidation. Caffeic acid (CA, Riedel de Haën),  $\alpha$ -Tocopherol (TOC, Sigma-Aldrich) and the emulsifier Tween 20 were of the highest purity available and used as received. All solutions were prepared with Milli-Q grade water. Aqueous buffered solutions were prepared from citric acid/sodium citrate (CA) or acetic acid/acetate (TOC). Final concentrations were 0.04 M and their pH was determined from potentiometric measurements.

The chemical probe 16-ArN<sub>2</sub>BF<sub>4</sub>, was prepared in high yield and purity from commercial 4-hexadecylaniline (Aldrich, 97%) by diazotization following a published method.(20, 27) Solutions of the coupling agent *N*-(1-naphthyl)ethylenediamine (NED, Aldrich,) were prepared in a 50:50 (v/v) BuOH:EtOH mixture to give [NED] = 0.02 M. Details can be found elsewhere. (20, 26, 27, 31)

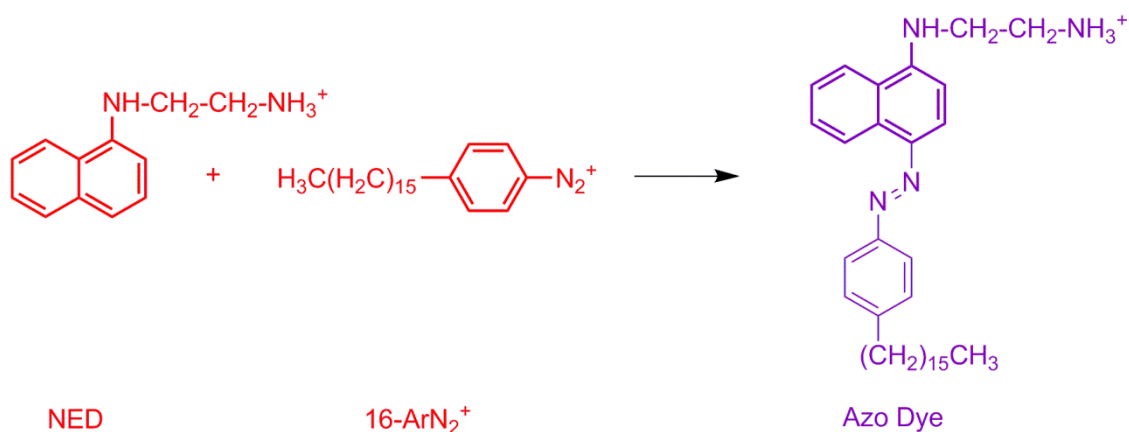
#### 1.2 Emulsion preparation.

Emulsions of different oil to water ratios were prepared by employing stripped corn oil, acidic water (0.04 M citrate(CA) or acetate (TOC) buffers, pH = 3.6) and Tween 20 as emulsifier. The mixture was stirred at high speed at room temperature with the aid of a Polytronic PT-100 homogeneizer and the resulting emulsions were visually stable

for at least 6 hours, a time much longer than that required to complete the chemical reaction between  $16\text{-ArN}_2^+$  and the AO.

### 1.3 Kinetic experiments. Determining the observed rate constant, $k_{\text{obs}}$ , for the reaction between AOs and $16\text{-ArN}_2^+$ in corn oil emulsions

Values of the observed (or measured) rate constants,  $k_{\text{obs}}$ , were determined in the intact corn oil emulsions by following a published derivatization (azo dye formation) procedure as described elsewhere.(20, 27, 31, 35, 39) The method exploits the rapid reaction of  $16\text{-ArN}_2^+$  with a suitable coupling agent (NED) that leads to the formation of an stable azo dye whose absorbance is proportional to the concentration of unreacted  $16\text{-ArN}_2^+$ , Scheme 4. The half-life of this reaction is less than 10 seconds, much lower than that of the reaction between  $16\text{-ArN}_2^+$  and the antioxidant.



Scheme 4. C-coupling reaction between  $16\text{-ArN}_2^+$  and the coupling agent *N*-(1-naphthyl)ethylenediamine (NED) to give a stable azo dye.

Figure 6 is illustrative and shows typical kinetic plots obtained in 1:9 (v:v) oil to water emulsions at different temperatures. Duplicate or triplicate experiments gave  $k_{obs}$  values within  $\pm 7-9\%$ .

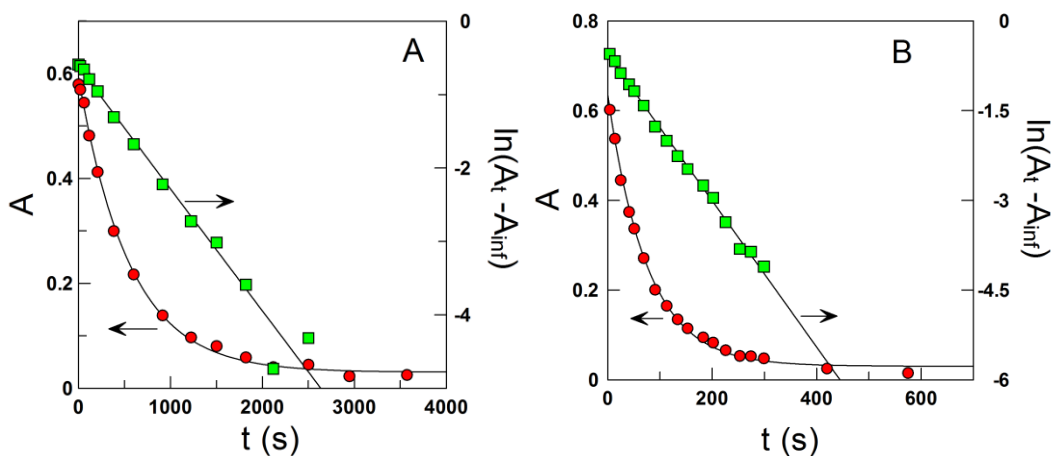


Figure 6. Plots of the variation of the absorbance ( $\lambda = 572 \text{ nm}$ ) and  $\ln$  plots according to the integrated first order equation in 1:9 (v:v) oil to water emulsions at two selected temperatures and emulsifier concentrations obtained in emulsions composed of stripped corn oil, acidic water (citric/citrate buffer, (0.04 M, measured pH = 3.66) and Tween 20. A)  $T = 15 \text{ }^\circ\text{C}$ ,  $\Phi_1 = 0.020$ . B)  $T = 35 \text{ }^\circ\text{C}$ ,  $\Phi_1 = 0.0387$ .  $[\text{CA}] = 4.55 \times 10^{-3} \text{ M}$ ,  $[\text{16-ArN}_2^+] \approx 2,9 \times 10^{-4} \text{ M}$ ,  $[\text{NED}] = 0.02 \text{ M}$ .

#### 1.4 Partition constants $P_w^0$ of TOC and CA in binary stripped corn oil-water mixtures in the absence of emulsifier.

Values of the partition constant  $P_w^0$  were determined, as in previous works,(29, 31, 39) as the ratio of the concentrations of antioxidant between the oil and water regions by employing equation 16,

$$P_W^o = \frac{(AO_o)}{(AO_w)} = \frac{n_{AO_o}}{n_{AO_w}} \cdot \frac{V_w}{V_o} \quad (16)$$

where n is the number of moles of antioxidant in a given phase (determined from the calibration curves) and  $V_w$  and  $V_o$  are the aqueous and oil region volumes.(27, 49)

TOC has a very low solubility in water,  $< 5 \times 10^{-5} \text{ M}$ ,(50) which means that less than 1% of the total TOC is located in the aqueous region of the emulsions. This creates considerable uncertainty in the determination of  $P_W^o$  values because small errors in the denominator of Eq. (16) may have a large effect on the value of  $P_W^o$ . Because the values of  $P_W^o$  for TOC are not reliable, they are not reported.

Conversely, CA is essentially oil insoluble and an average value (six runs) of  $P_W^o = 0.044 \pm 0.009$  was obtained at  $T = 25 \text{ }^\circ\text{C}$ . This very low  $P_W^o$  value is in keeping with the hydrophilic nature of this antioxidant very close to that reported by Rodis et al.(51)  $P_W^o = 0.0770$  between olive oil and water.

Change in temperature did not lead to a substantial changes in the fractions of antioxidant in the aqueous phase (for CA,  $P_W^o = 0.058$  at  $T = 15 \text{ }^\circ\text{C}$ ). Thus, one can expect the concentrations of TOC in the aqueous region and that of CA in the oil region of corn emulsions to be negligible at any temperature. Therefore, TOC will mostly distribute between the oil and interfacial region of the emulsions meanwhile CA will be mostly distributed between the aqueous and interfacial region of the emulsions.