

Supporting Information

Light-induced destabilisation of oil-in-water emulsions using light-active bolaform surfactants

Soumodeep Biswas^a, S Karishma^a, Balu Ramesh^b, Masilamani Jeganmohan^b, Ethayaraja Mani^{a*}

a: Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India-600036

b: Department of Chemistry, Indian Institute of Technology Madras, Chennai, India-600036

ethaya@iitm.ac.in

1. ¹H NMR characterization of LABS

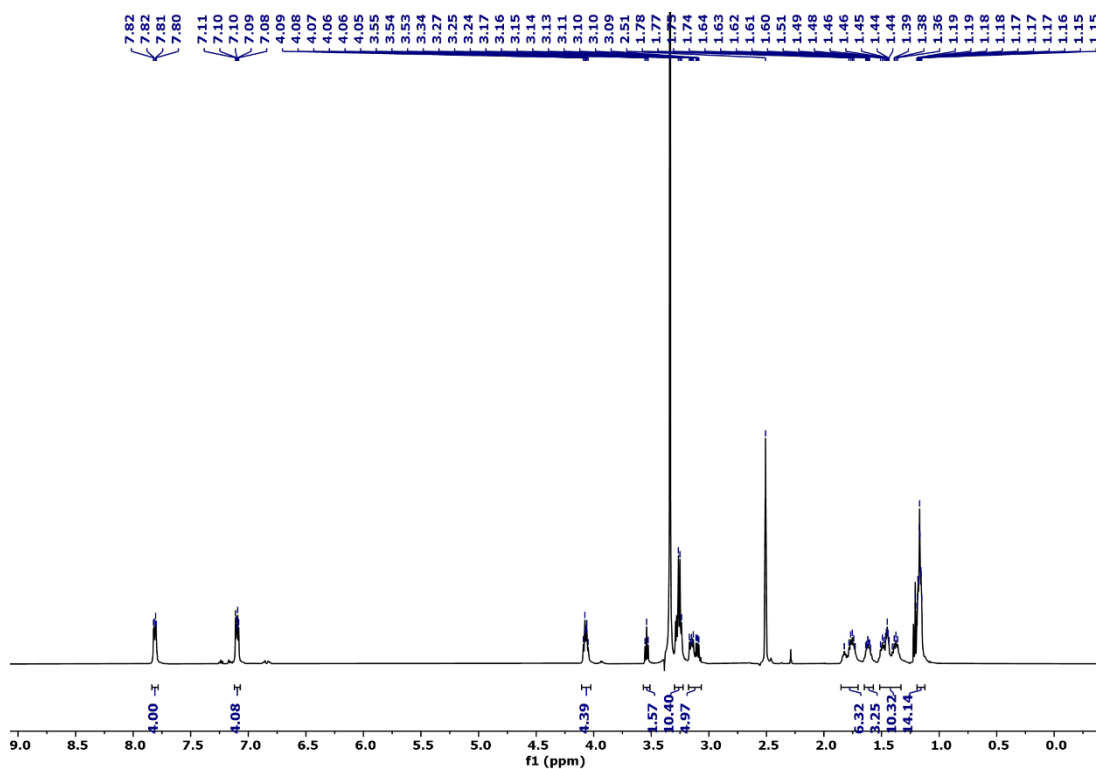


Figure S1. ¹H NMR spectrum of LABS

2. Estimation of CMC using UV-Vis spectroscopy

The CMC of the LABS was estimated to be 0.35 mM using UV-Vis spectroscopy. The figure below illustrates the CMC estimation.

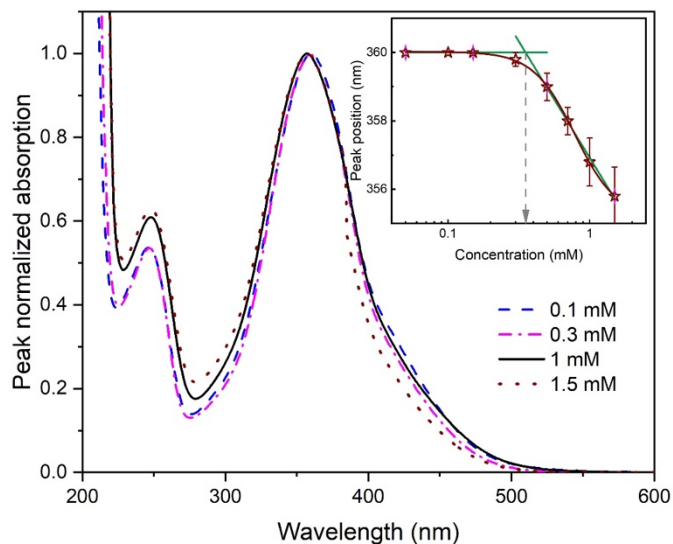


Figure S2: Plot of normalized UV-Vis absorbance of LABS solutions of concentrations 0.1, 0.3, 1 and 1.5 mM plotted against the wavelength in nm. The inset in the plot shows the peak positions in nm plotted against the concentration in mM. The shift in peak position used for estimating the CMC.

3. Surface excess concentration of LABS

Surface excess is calculated using Gibbs's isotherm given as [3]:

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln C}$$

Where, Γ is the surface excess of the surfactant in mol/m², γ is the interfacial tension in N/m, C is the concentration of the surfactant in the solution, R is the gas constant and T is absolute temperature.

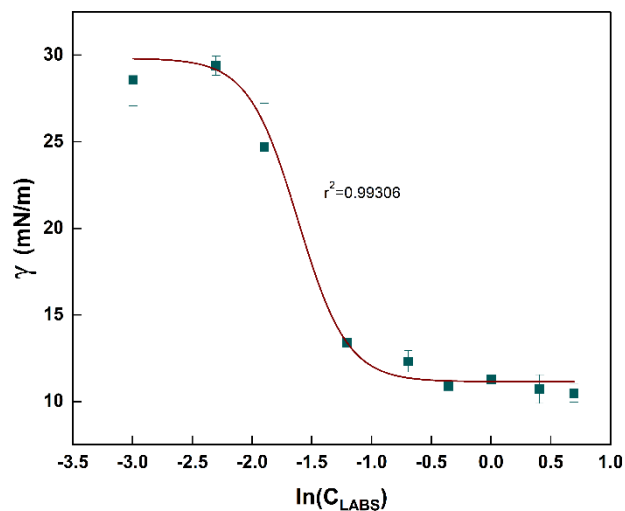


Figure S3: Interfacial tension values in mN/m at decane-LABS solution interface plotted against logarithm of concentration of LABS in solution

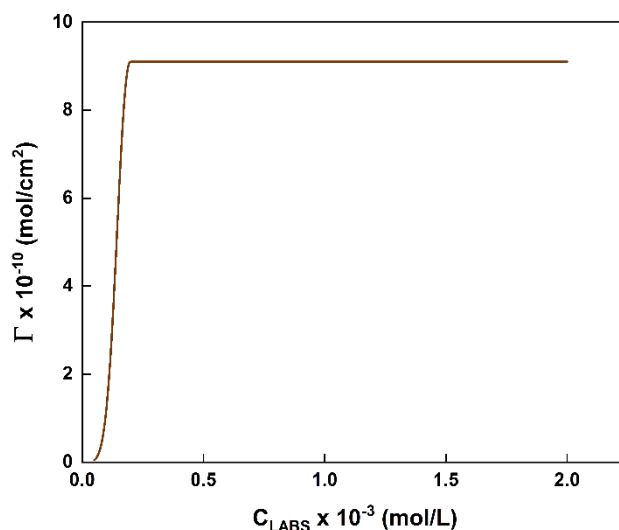
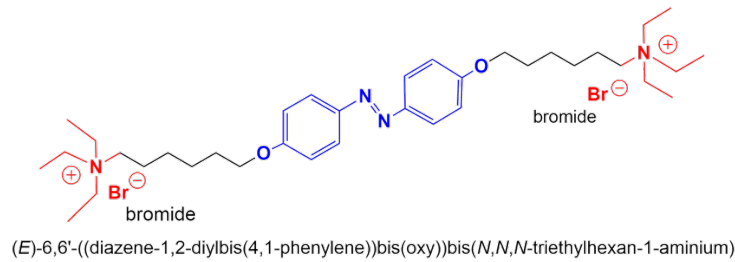


Figure S4: Surface excess concentration of LABS in mol/cm² plotted against concentration of LABS in bulk solution (mol/L)

4. Hydrophilic-lipophilic balance of LABS molecule

Hydrophilic-lipophilic-balance calculation [1,2]:

Hydrophilic	Group Number	Hydrophobic	Group Number
-o-	1.3	-CH-	-0.475
Quaternary amine	22	-CH ₂ -	-0.475
		benzyl	-2.85



Davies' method:

$$HLB_D = HLB_o + N * HLB_{alkyl} + N * HLB_{benzyl} + 7$$

HLB_o :- HLB of head group

HLB_{benzyl} :- The increment of the CH₂ segment.

$$HLB_o = HLB_{amine,l} + \sum HLB_j$$

HLB_j :- the increment of the jth elementary segment

$$HLB = (22 * 2 + (12 * -0.475)) + (12 * -0.475) + (1.3 * 2) + (2 * -2.85) + 7$$

$$HLB = 44 - 5.7 - 5.7 + 2.6 - 5.7 + 7$$

$$HLB = 36.5$$

(OR)

$$HLB = 7 + GN_{CH_2} * N_{CH_2,eff} + GN_{EO} * N_{EO,eff} + GN_{PO} * N_{PO,eff} + \sum \text{Other hydrophilic groups} + \sum \text{other lipophilic groups}$$

$$N_{CH_2,eff} = 0.965 * N_{CH_2} - 0.178$$

$$N_{CH_2} = 0.965 * 24 - 0.178$$

$$= 22.982$$

$$Hlb = (22 * 2 + (22.982 * -0.475)) + (1.3 * 2) + (-2.85 * 2) + 7$$

$$HLB = 44 - 10.9165 + 2.6 - 5.7 + 7$$

$$HLB = 35.68$$

5. Color scaling of the state diagram

The coloured scale state diagram in Fig 4(a) for emulsions was made by quantifying the emulsion volume at various combinations of concentrations of LABS and NaCl. The volume of emulsion was then scaled onto a colour scale ranging from blue to red, where blue would mean no emulsion formed and red would mean complete emulsification. The quantification and scaling methods are elaborated below:

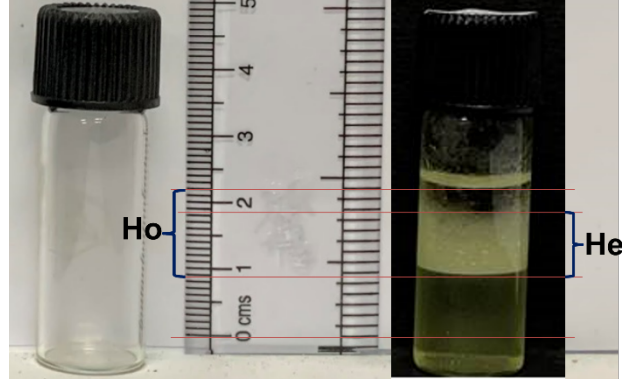


Figure S5: Image of the vial containing emulsion against a ruler scale and empty vial, used for estimating the height of emulsion formed for colour-scaled state diagram

The scaling is done as follows:

Let, α be the height fraction of the emulsion in the phase above the aqueous phase, such that:

$$\alpha = \frac{H_o}{H_e}, (1 \leq \alpha \leq 0)$$

The height fraction of the emulsion cream in the upper phase is then assigned a colour based on the following colour scaling:

$$\alpha = \frac{\lambda - 400}{750 - 400}$$

Where, the wavelength of red colour is 750 and blue colour is 400. Hence the wavelength of colour for any height fraction is given as:

$$\lambda = 350 \alpha + 400$$

6. Temporal evolution of temperature of the sample upon UV irradiation

Temperature of the emulsion was monitored while it was irradiated with UV light using a temperature gun. The results from the experiments are plotted in the figure below.

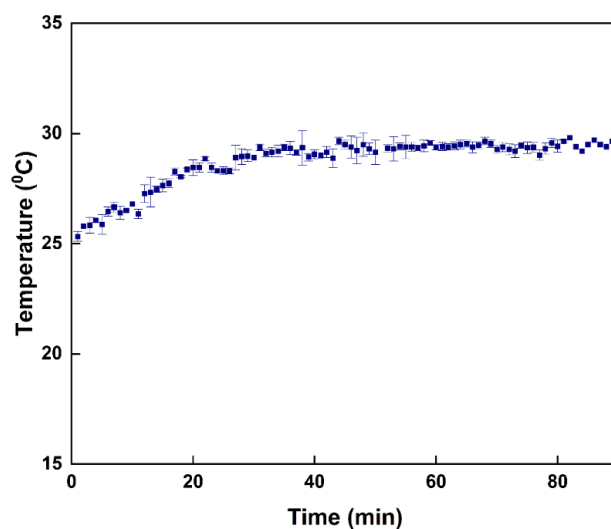


Figure S6: Temperature of the emulsion in °C plotted against the time of illumination in min

7. Destabilization experiment at low surfactant concentration

O/W emulsion made with n-decane, 0.3mM LABS and 0.2M NaCl solution;

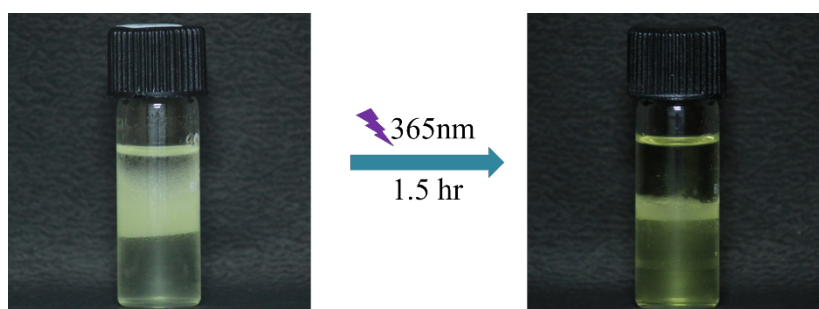


Figure S7: Photographs of vials taken before and after exposure to UV light; the vials contain emulsion prepared with 0.3 mM LABS and 0.2 M NaCl solution and decane taken in equal volumes. The vial on the right shows partial phase separation after 90 minutes of exposure

O/W emulsion made with n-decane, 0.3mM LABS and 0.2M NaCl solution, and 7% ethanol.

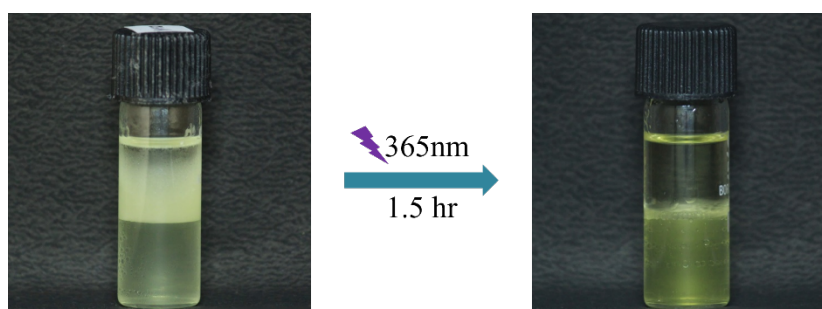


Figure S8: Photographs of vials taken before and after exposure to UV light; the vials contain emulsion prepared with 0.3mM LABS and 0.2 M NaCl solution and decane taken in equal volumes; 7% ethanol

was added before emulsifying the contents in the vials. The vial on the right shows almost complete phase separation after 90 minutes of exposure

8. Time study of extent of phase separation during illumination

O/W emulsion made with n-decane, 0.5mM LABS and 0.2M NaCl solution, and 7% ethanol. The emulsion is exposed for various durations to UV light and the extent of phase separation is observed.

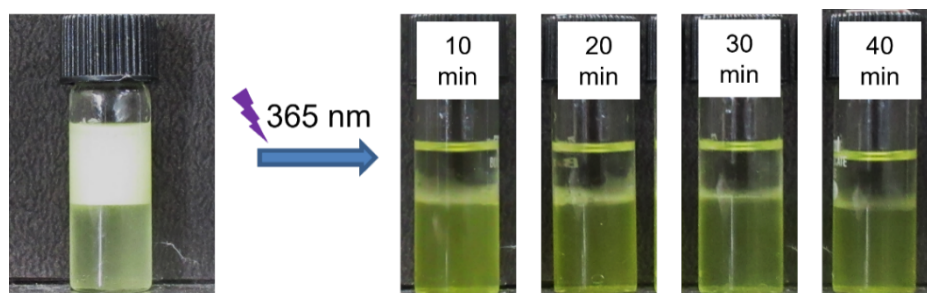


Figure S9: Photographs of the vials containing emulsions before illumination (on the left) and after illuminating for different durations. The illumination is performed by transferring the emulsions into a petri-dish and transferring it back into the vial after illumination for better visualization of phase separation.

9. Destabilization in the absence of salt

O/W emulsion made with n-decane and 0.3mM LABS solution, and 7% ethanol

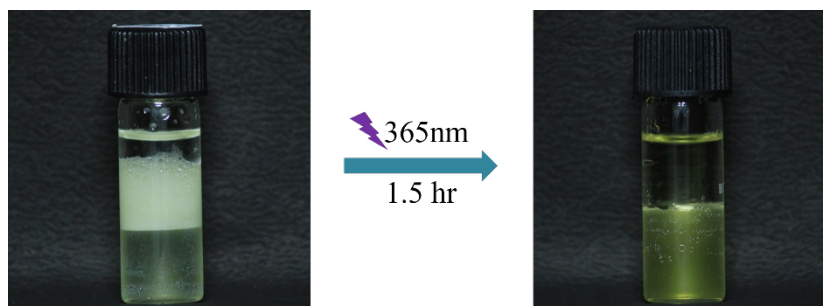


Figure S10: Photographs of vials taken before and after exposure to UV light; the vials contain emulsion prepared with 0.3 mM LABS solution and decane taken in equal volumes; 7% ethanol was added before emulsifying the contents in the vials. The vial on the right shows complete phase separation after 90 minutes of exposure

10. Effect of chemical nature of volatile compound

O/W emulsion made with n-decane, 0.5mM LABS and 0.2 M NaCl solution, and 7% methanol.

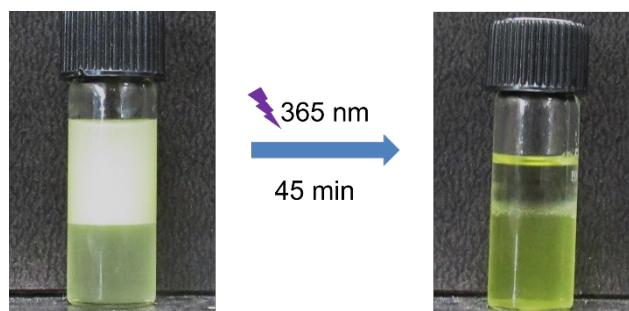


Figure S11: Photographs of vials taken before and after exposure to UV light; the vials contain emulsion prepared with 0.5 mM LABS and 0.2 M NaCl solution and decane taken in equal volumes (2 ml each); 7% methanol was added before emulsifying the contents in the vials. The vial on the right shows complete phase separation after 45 minutes of exposure.

O/W emulsion made with n-decane, 0.5mM LABS and 0.2 M NaCl solution, and 7% tetrahydrofuran;

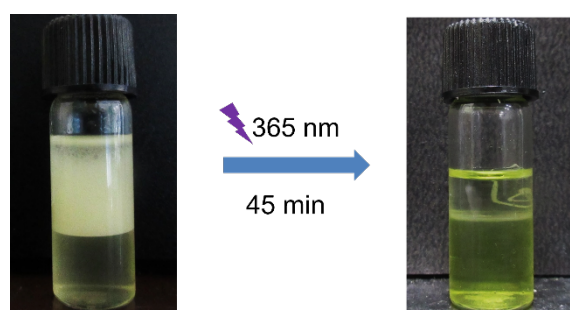


Figure S12: Photographs of vials taken before and after exposure to UV light; the vials contain emulsion prepared with 0.5 mM LABS and 0.2 M NaCl solution and decane taken in equal volumes (2 ml each); 7% tetrahydrofuran was added before emulsifying the contents in the vials. The vial on the right shows complete phase separation after 45 minutes of exposure.

11. Effect of chemical nature of electrolyte

O/W emulsion made with n-decane, 0.5mM LABS and 0.2M KCl solution, and 7% ethanol

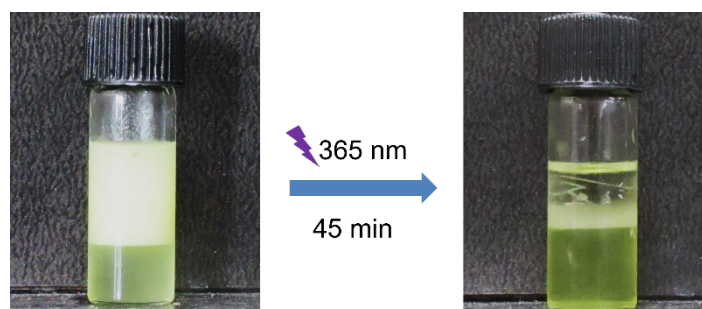


Figure S13: Photographs of vials taken before and after exposure to UV light; the vials contain emulsion prepared with 0.5 mM LABS and 0.2 M KCl solution, 7% ethanol and decane taken in equal volumes. The vial on the right shows complete phase separation after 45 minutes of exposure.

O/W emulsion made with n-decane, 0.5mM LABS and 0.2M MgCl₂ solution, and 7% ethanol.

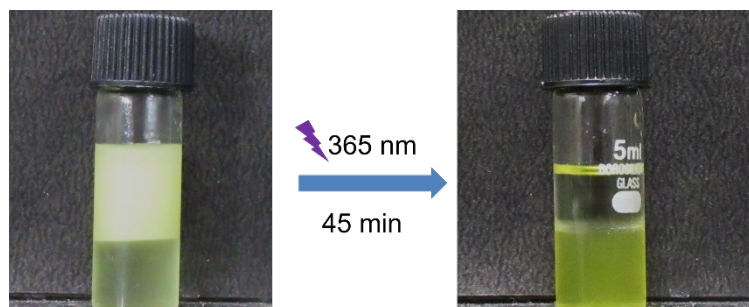


Figure S14: Photographs of vials taken before and after exposure to UV light; the vials contain emulsion prepared with 0.5 mM LABS and 0.2 M MgCl₂ solution, 7% ethanol and decane taken in equal volumes. The vial on the right shows complete phase separation after 45 minutes of exposure.

References:

1. Guo, X., Rong, Z., Ying, X., Calculation of hydrophile-lipophile balance for polyethoxylated surfactants by group contribution method, *J. Colloid Interface Sci.*, **2006**, 298 (1) , pp. 441-450
2. Ho, O.B., Electrokinetic Studies on Emulsions Stabilized by Ionic Surfactants: The Electroacoustophoretic Behavior and Estimation of Davies' HLB Increments, *J. Colloid Interface Sci.*, **1998**, 198 (2) , pp. 249-260
3. Tajima, K., Radiotracer Studies on Adsorption of Surface Active Substance a Aqueous Surface. II. The Effect of Excess Salt on the Adsorption of Sodium Dodecylsulfate, *Bulletin of the Chemical Society of Japan*, **1970**, 43:10, 3063-3066