Supporting Material

Dual Action of Hydrotropes at the Water/Oil Interface

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Section 1. Experimental and simulation details

Table S1 – Initial composition of the samples and composition of equilibrated phases at 20 °C

Sample	Initial composition, wt%			Oil phase at equilibrium, wt%			Water phase at equilibrium, wt%			Initial composition, mol%			Oil phase at equilibrium, mol%			Water phase at equilibrium, mol%		
	TBA	CHX	H_2O	TBA	CHX	H_2O	TBA	CHX	H_2O	TBA	CHX	H_2O	TBA	CHX	H_2O	TBA	CHX	H_2O
E0	0	49.98	50.02	0	99.99*	rest	0	0.006**	rest	0.0	17.62	82.38	0.00	99.95*	rest	0.00	0.00**	rest
E1	0.001	50.001	49.998	0.000	99.99*	rest	0.002	0.006**	rest	0.0004	17.6323	82.3673	0.000	99.95*	rest	0.0005	0.001**	rest
E2	0.01	50.00	49.99	0.001	99.99*	rest	0.016	0.005**	rest	0.004	17.634	82.362	0.001	99.96*	rest	0.004	0.001**	rest
E3	0.05	49.98	49.97	0.006	99.98*	rest	0.085	0.005**	rest	0.02	17.63	82.35	0.007	99.93*	rest	0.021	0.001**	rest
E4	0.10	49.94	49.95	0.01	99.97*	rest	0.18	0.006**	rest	0.04	17.62	82.34	0.011	99.90*	rest	0.04	0.001**	rest
E5	0.249	49.88	49.87	0.03	99.96*	rest	0.44	0.006**	rest	0.10	17.62	82.28	0.03	99.92*	rest	0.11	0.001**	rest
E6	0.506	49.76	49.74	0.07	99.92*	rest	0.90	0.006**	rest	0.20	17.60	82.20	0.08	99.87*	rest	0.22	0.001**	rest
E7	1.00	49.50	49.50	0.14	99.85*	rest	1.78	0.007**	rest	0.40	17.56	82.04	0.16	99.79*	rest	0.44	0.002**	rest
E8	2.00	48.98	49.02	0.32	99.63*	rest	3.52	0.009**	rest	0.81	17.48	81.71	0.36	99.40*	rest	0.88	0.002**	rest
E9	4.00	48.00	48.00	0.90	99.00*	rest	6.77	0.015**	rest	1.64	17.34	81.02	1.02	98.52	rest	1.73	0.003**	rest
E10	7.25	36.28	56.47	2.47	97.33*	rest	10.14	0.026**	rest	2.67	11.77	85.56	2.77	96.30	rest	2.67	0.006**	rest
E11	11.52	35.97	52.51	8.16	91.54	rest	13.89	0.046**	rest	4.44	12.22	83.34	9.07	89.56	rest	3.77	0.011**	rest
E12	11.01	44.49	44.49	8.16	91.54	rest	13.56	0.044**	rest	4.72	16.80	78.48	9.07	89.56	rest	3.67	0.010**	rest
E13	20.91	33.48	45.61	24.80	74.20	rest	17.64	0.083**	rest	8.78	12.39	78.83	26.31	69.33	rest	4.95	0.021**	rest
E14	28.89	31.38	39.73	38.26	58.44	rest	19.41	0.109**	rest	13.13	12.56	74.30	37.04	49.82	rest	5.54	0.027**	rest
E15	36.20	28.62	35.18	47.84	45.16	rest	20.18	0.123**	rest	17.56	12.23	70.21	41.10	34.17	rest	5.80	0.031**	rest
E16	37.74	31.13	31.13	47.83	45.16	rest	20.54	0.130**	rest	19.53	14.19	66.28	41.08	34.16	rest	5.92	0.033**	rest
E17	42.99	28.52	28.49	52.98	37.52	rest	21.48	0.140**	rest	23.20	13.55	63.25	42.35	26.41	rest	6.24	0.036**	rest
E18	47.98	25.99	26.03	56.72	30.78	rest	22.27	0.149**	rest	26.96	12.86	60.18	41.93	20.04	rest	6.52	0.038**	rest
E19	41.30	10.64	48.06	60.55	20.59	rest	23.53	0.15	rest	16.63	3.77	79.60	38.74	11.60	rest	6.97	0.04	rest
E20	42.20	7.09	50.71	60.65	13.40	rest	26.06	0.31	rest	16.41	2.43	81.16	33.84	6.58	rest	7.91	0.08	rest
E21	42.67	5.24	52.09	58.81	9.69	rest	29.71	0.66	rest	16.31	1.76	81.92	29.86	4.33	rest	9.38	0.18	rest
E22	42.93	4.25	52.82	53.84	6.54	rest	34.42	1.41	rest	16.26	1.42	82.32	24.19	2.59	rest	11.49	0.41	rest

TBA – *tert*-butyl alcohol, CHX – cyclohexane, H_2O – water;

* – result of approximation based on our experimental data of separation boundary;

** – result of calculation of CHX concentration in terms of its solubility in water[1]

The standard uncertainties are $u(\omega_{TBA}) \leq 0.0025$ % mass for the samples E1-E5, for other components and samples $u(\omega) \leq 0.004$ % mass; phase composition ≤ 5 percent of TBA and CHX concentration values

Table S2 – Experimental values of refractive index n_D, density ρ, surface tension $\gamma_{l\text{-}g}$ and interfacial tension $\gamma_{l\text{-}l}$ of equilibrated phases in triple system of «water – TBA – CHX» at 20 °C

Sample	Oil phase			Water phase			Interfacial tension $\gamma_{l\text{-}l}$, mN/m
	n_D	ρ, g/ml	$\gamma_{l\text{-}g}$, mN/m	n_D	ρ, g/ml	$\gamma_{l\text{-}g}$, mN/m	
E0	1.4265	0.776	24.9	1.3332	0.998	72.6	48.8* 48.30±0.19**
E1	1.4266	0.779	25.1	1.3330	0.998	72.3	48.3*
E2	1.4265	0.778	25.1	1.3330	0.998	72.1	48.2*
E3	1.4264	0.778	25.1	1.3331	0.999	70.5	47.0*
E4	1.4264	0.778	25.1	1.3332	0.997	68.0	45.0*
E5	1.4266	0.778	25.1	1.3335	0.998	63.6	41.0*
E6	1.4266	0.777	25.1	1.3342	0.996	58.1	36.5*
E7	1.4265	0.776	24.8	1.3350	0.995	52.3	30.0*
E8	1.4265	0.776	24.8	1.3365	0.992	45.8	24.5*
E9	1.4263	0.775	24.8	1.3398	0.987	38.8	17.1*
E10	1.4230	0.776	24.8	1.3425	0.984	35.6	12.4*
E11	1.4200	0.776	24.3	1.3470	0.976	31.4	7.3*
E12	1.4224	0.776	24.2	1.3471	0.979	30.5	7.2*
E13	1.4110	0.778	23.1	1.3505	0.974	28.2	3.5* 3.26±0.14**
E14	1.4045	0.783	22.6	1.3520	0.971	26.4	2.3*
E15	1.3995	0.790	22.4	1.3530	0.969	26.3	1.7*
E16	1.4010	0.791	22.5	1.3542	0.969	26.1	1.7*
E17	1.3978	0.796	22.3	1.3551	0.967	25.9	1.3*
E18	1.3944	0.802	22.2	1.3556	0.966	25.5	1.0* 0.977±0.041**
E19	1.3899	0.820	22.0	1.3580	0.962	24.8	0.4* 0.515±0.020**
E20	1.3858	0.835	22.1	1.3589	0.953	24.1	0.1* 0.228±0.013**
E21	1.3823	0.853	-	1.3611	0.946	-	0.0457±0.0015**
E22	1.3790	0.868	-	1.3635	0.934	-	0.0025±0.0017**

* - Wilhelmy plate method

** - Spinning drop method

The standard uncertainties are u(n_D) = 0.0005, u(ρ) = 0.003 g/mL, u($\gamma_{l\text{-}g}$) = 0.3 mN/m (for Wilhelmy plate), u($\gamma_{l\text{-}l}$) = 0.3 mN/m (for Wilhelmy plate)

Table S3 – Experimental results of determination of separation boundary in the system of water – TBA – CHX by gravimetric titration at 20 °C

Composition in two-phase region, wt%			Composition in one-phase region wt%		
H_2O	TBA	CHX	H_2O	TBA	CHX
60.81	36.59	2.60	60.78	36.63	2.59
37.08	55.05	7.87	37.01	55.14	7.85
65.73	32.66	1.61	65.51	32.89	1.61
40.89	52.36	6.75	40.75	52.52	6.72
32.65	57.22	10.13	32.51	57.40	10.09
26.53	59.70	13.77	26.43	59.86	13.71
19.37	60.19	20.44	19.30	60.33	20.37
10.16	54.49	35.35	10.12	54.69	35.19
56.90	40.04	3.06	56.50	40.45	3.04
48.96	46.49	4.55	48.83	46.64	4.53
43.04	51.39	5.57	42.82	51.64	5.54
12.95	57.06	30.00	12.86	57.34	29.80
7.96	50.38	41.66	7.92	50.60	41.48
6.06	46.05	47.89	6.04	46.25	47.71
57.02	39.98	3.00	56.81	40.20	2.99
16.86	60.57	22.57	16.80	60.71	22.49
46.53	48.39	5.07	46.33	48.62	5.05
22.11	61.30	16.60	22.03	61.43	16.54
4.81	43.53	51.66	4.79	43.74	51.47
3.05	36.31	60.64	3.04	36.47	60.49
3.91	40.77	55.32	3.89	40.99	55.12
1.93	30.81	67.26	1.93	31.08	67.00
1.18	24.39	74.42	1.18	24.58	74.25
0.43	14.52	85.05	0.43	14.77	84.81
75.08	24.57	0.35	74.98	24.67	0.35
69.96	29.22	0.82	69.82	29.36	0.82
52.19	44.09	3.73	52.03	44.25	3.72
14.72	59.73	25.55	14.69	59.80	25.51
2.46	33.75	63.79	2.46	33.91	63.63
1.57	27.25	71.17	1.57	27.38	71.05
0.82	19.43	79.75	0.82	19.62	79.56
28.39	60.05	11.57	28.31	60.15	11.54
43.41	50.88	5.72	43.22	51.09	5.69

Separation boundary is between the corresponding two-phase and one-phase compositions

Table S4 – Compositions, interfacial tension, and correlation length for the samples studied by DLS method

Sample	Wt% (H_2O;TBA;CHX)	γ (mN/m)	ξ (nm)
DLS_{11}	48.07; 41.32; 10.62	0.515	1
DLS_{12}	50.64; 41.94; 7.42	0.228	2
DLS_{13}	52.17; 42.63; 5.20	0.0457	3
DLS_{14}	52.92; 42.84; 4.24	0.0025	6
DLS_{21}	27.4; 47.2; 25.4	(1)	1
DLS_{22}	48.5; 41.3; 10.2	(0.515)	1.5
DLS_{23}	51.9; 41.0; 7.1	(0.228)	2
DLS_{24}	53.5; 42.2; 43.3	(0.0457)	4
DLS_{25}	54.3; 42.0; 3.7	(0.0025)	9.5

Data shown in parentheses are interpolations because these DLS samples were not of the exactly same concentrations as the samples for γ measurements

Table S5 - Composition of each system studied with MD

System	TBA in water		# molecules in simulation			overall wt% compositions			total # atoms
	mol%	mass%	H_2O	CHX	TBA	H_2O	CHX	TBA	
S0	0.00	0.00	1600	250	0	57.81	42.19	0.00	10900
S1	0.01	0.05	1650	220	8	60.87	37.92	1.21	10680
S2	0.11	0.46	1650	220	26	59.25	36.91	3.84	10950
S3	0.18	0.73	1650	220	34	58.56	36.48	4.96	11070
S4	0.44	1.80	1650	220	44	57.72	35.95	6.33	11220
S5	0.67	2.68	1600	220	50	56.47	36.27	7.26	11110
S6	1.89	7.34	1500	220	64	53.74	36.82	9.43	10920
S7	2.64	10.04	1500	220	80	52.50	35.97	11.52	11160
S8	3.48	12.92	1500	220	96	51.32	35.16	13.51	11400
S9	4.47	16.14	1500	220	114	50.05	34.30	15.65	11670
S10	5.54	19.44	1500	220	132	48.85	33.47	17.69	11940
S11	7.23	24.29	1400	220	156	45.61	33.48	20.91	11900
S12	12.09	36.13	1300	220	230	39.71	31.39	28.90	12610
S13	18.59	48.44	1260	220	316	35.12	28.65	36.24	13740
S14	24.05	56.59	1200	220	410	30.65	26.25	43.09	14910
S15	29.79	63.59	1100	220	484	26.71	24.95	48.34	15620
S16	34.24	68.20	1000	220	550	23.31	23.95	52.74	16210
S17	38.91	72.40	1000	220	650	21.27	21.86	56.88	17710
S18	44.61	76.83	900	220	750	17.95	20.50	61.55	18810

Table S6 - Simulated values of interfacial tension in ternary system of water – TBA – CHX at 25 °C

System	TBA in water mol%	TBA in water wt%	Interfacial tension $\gamma_{l\text{-}l}$ (mN/m)		
S0	0.00	0.00	48.92	±	0.03
S1	0.01	0.07	47.37	±	0.48
S2	0.11	0.38	40.48	±	0.48
S3	0.18	0.70	35.67	±	0.46
S4	0.44	2.48	28.71	±	0.52
S5	0.67	2.47	26.39	±	0.49
S6	1.89	8.40	21.54	±	0.58
S7	2.64	8.58	15.31	±	0.56
S8	3.48	11.67	13.13	±	0.66
S9	4.47	15.42	10.46	±	0.63
S10	5.54	18.38	9.37	±	0.63
S11	7.23	23.27	7.41	±	0.63
S12	12.09	36.49	4.58	±	0.76
S13	18.59	48.23	2.52	±	0.78
S14	24.05	56.59	1.56	±	0.38
S15	29.79	63.62	-0.71	±	1.36
S16	34.24	68.20	1.44	±	0.67
S17	38.91	72.40	-1.77	±	0.47
S18	44.61	76.83	0.12	±	1.19

Table S7 – Theoretical values related to the thickness of the interface (Eq. 4), the interfacial tension is included as a reference

System	γ (mN/m)			Thickness, 2ζ (nm)			$\Delta\rho_o$ (molec/nm^3)		
S1	47.374	±	0.485	0.324	±	0.000	27.100	±	0.004
S2	40.480	±	0.484	0.359	±	0.001	27.018	±	0.004
S3	35.668	±	0.462	0.387	±	0.000	26.966	±	0.004
S4	28.711	±	0.519	0.422	±	0.002	26.688	±	0.015
S5	26.387	±	0.492	0.449	±	0.004	26.509	±	0.011
S6	21.540	±	0.579	0.606	±	0.005	25.886	±	0.024
S7	15.313	±	0.559	0.573	±	0.007	25.273	±	0.020
S8	13.132	±	0.662	0.624	±	0.015	24.520	±	0.032
S9	10.459	±	0.631	0.658	±	0.021	23.687	±	0.012
S10	9.373	±	0.632	0.685	±	0.016	22.761	±	0.047

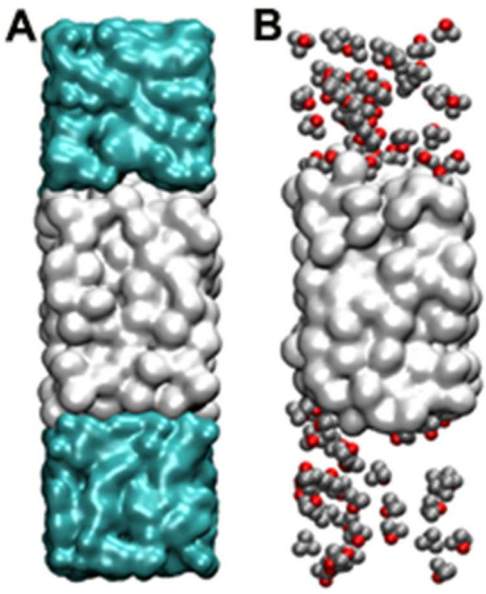

Figure S1. Initial simulation box setup, (A) bulk water is shown in cyan and bulk cyclohexane in white; (B) TBA in aqueous solution at the beginning of the simulation (explicit molecule; C atoms in gray, O atoms in red), *water not shown for clarity*

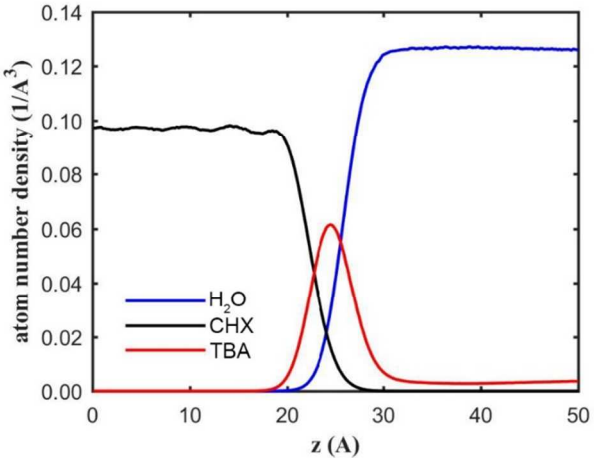

Figure S2. Sample atom density profile (ADP) for the S3 system

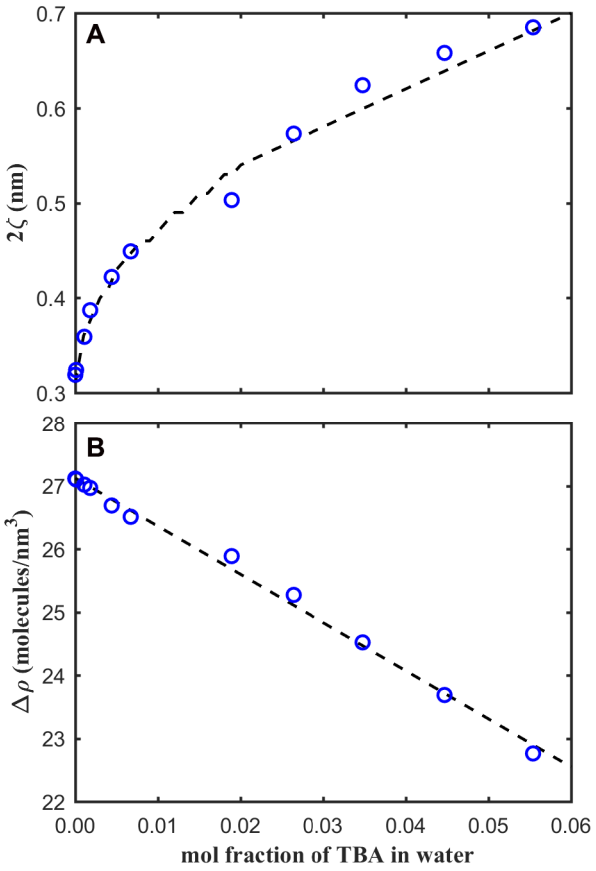

Figure S3. Thickness of the interface and difference in bulk densities as a function of TBA concentration (from MD simulations)

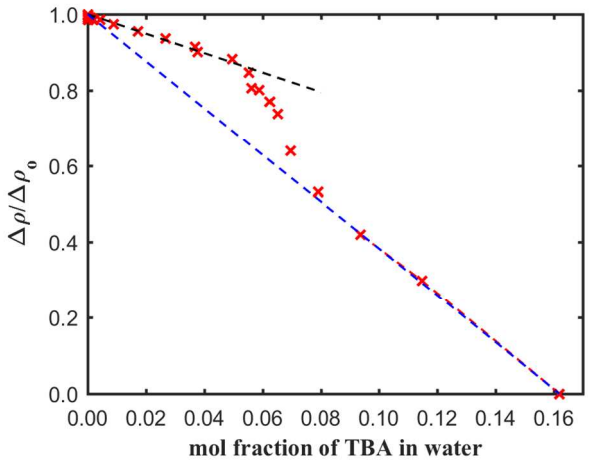

Figure S4. Experimental values of normalized density difference of coexisting phases as a function of TBA concentration

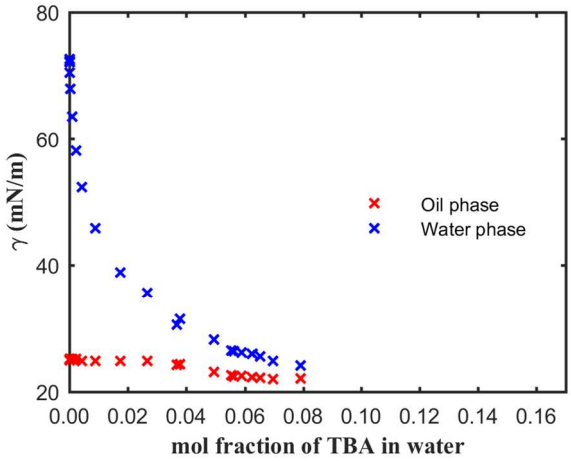

Figure S5. Surface tension between the water phase and the oil phase with air, respectively, as a function of TBA concentration.

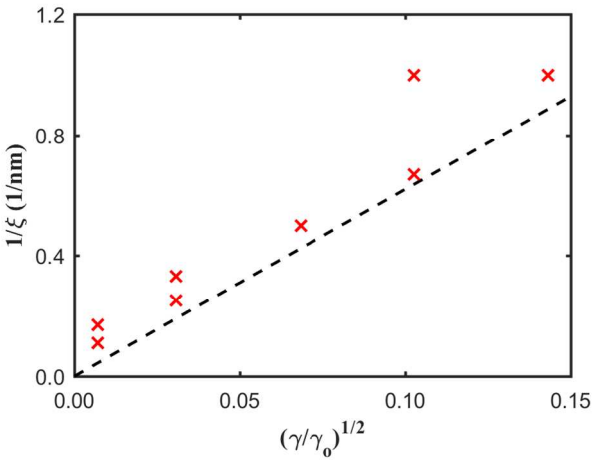

Figure S6. Linear relation between the inverse of the interface thickness (2ξ) and the square root of the reduced interfacial tension. The dashed line is the scaling prediction for the relation between these two properties.

Section 2. Comparison of adsorption isotherms

Von Szyszkowski more than 100 years ago suggested an empirical equation for the adsorption isotherm:

$$\frac{\gamma}{\gamma_0} = 1 - A\log(1 + Bc) \tag{S1}$$

where A and B are constants, and c is the molar concentration. According to Ross and Morrison,[3] surface pressure can be expressed as:

$$\gamma_0 - \gamma = RT\Gamma_m \ln\left(\frac{f_2^\alpha x_2^\alpha}{a_2 f_2^s} + \frac{f_1^\alpha\left(1 - x_2^\alpha\right)}{a_1 f_1^s}\right) \tag{S2}$$

where Γ_m – maximum adsorption, f_1 and f_2 – activity coefficients, a_1 and a_2 – constants, superscripts α and s denote the bulk and surface phases, respectively, and subscripts 1 and 2 denote the solvent and solute, respectively. Equation (S2) could be simplified when the following approximations are valid:

$$\frac{f_1^\alpha}{f_1^s} \approx 1 \;;\; \frac{f_2^\alpha}{f_2^s} \approx const \;;\; a_1 = \frac{f_1^{0\alpha}}{f_1^{0s}} \approx 1,$$

where the additional superscript 0 denotes the pure solvent. After simplifications, equation (S2) becomes:

$$\frac{\gamma}{\gamma_0} = 1 - A\ln\left(Bx_2^\alpha + 1\right) \tag{S3}$$

where A and B are constants. Note: equation (S3) is essentially the same as equation (S1).

Our experimental results can be described by equation (S3) up to the molar fraction of TBA of about 0.07 (see Fig. S7 below). At higher concentration the interfacial tension approximated by equation (S3) becomes negative, which is obviously unphysical. The fitting constants for equation (S3) are A = 0.2382; B = 838.2.

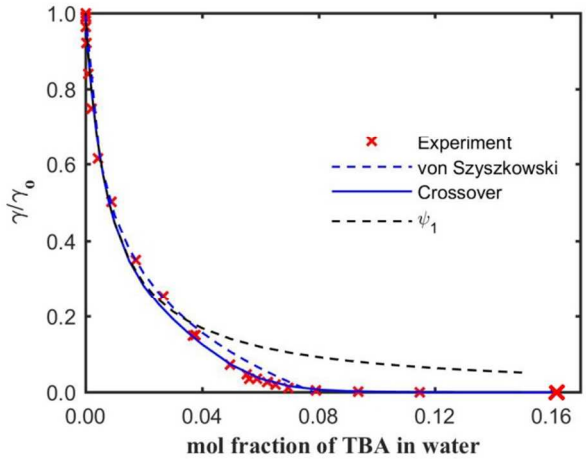

Figure S7. Approximation of experimental results by von Szyszkowski isotherm (Eq. S3) and crossover Eq. (7). The critical point at [0.1622; 0.0] is indicated by a bigger cross marker.

According to the Gibbs theory, we can describe the behavior of solute as adsorption, if we assume that the activity is not much different from the concentration ($f \approx 1$), and the model parameters can be chosen such that the mole fraction (x) replaces the molar concentration (c).

$$\Gamma = -\frac{fc}{RT}\frac{d\gamma}{d(fc)} \tag{S4}$$

Thus, the von Szyszkowski equation in the form of (S5) can be transformed into equation (S6) which is equivalent to the Langmuir adsorption model:

$$\frac{\gamma}{\gamma_0} = 1 - a_1 \ln(1 + a_2 x) \tag{S5}$$

$$\Gamma = -\frac{x d\gamma}{RTdx} = -\frac{a_1 \gamma_0}{RT}\left(\frac{a_2 x}{1 + a_2 x}\right) \tag{S6}$$

As pointed out by Ross and Morrison,[3] the observed adsorption isotherm of Langmuir-von Szyszkowski type does not imply the ideal behavior of solute in bulk or interface, but merely indicates that the deviations from ideality in bulk and interface are close to each other. Nevertheless, this adsorption model implies that the adsorption asymptotically approaches to a constant value (Γ_m), and cannot include the decrease of adsorption corresponding to the vanishing of interfacial tension at the critical point.

In some simulations, we observed the tendency of TBA molecules to temporarily form the associates at the interface between the water and oil phases. This suggests that adsorption model should take into account the interactions of adsorbate molecules at the interface. The Frumkin adsorption model (that phenomenologically accounts this effect) reads[4]:

$$\Gamma = -\frac{d\gamma}{RTd(\ln x)} = -\frac{x d\gamma}{RTdx} = -\frac{a_1 \gamma_0}{RT}\left(\frac{a_2 x}{1 + a_2 x}\right) e^{-a_3 x} \tag{S7}$$

We compared the adsorption (obtained by taking the derivative of the interfacial tension with respect to ln$x$ after initial smoothing the data by a spline-fit function[5]) with the crossover model, and the adsorption models of Langmuir-von Szyszkowski (fitted parameters are a_1=0.2382; a_2=838.2) and Frumkin (fitted parameters are a_1=36.66; a_2=81.01; a_3=24.26). The results are shown in Figure S8. Note that only the crossover function approaches zero at the critical point in agreement with the experiment.

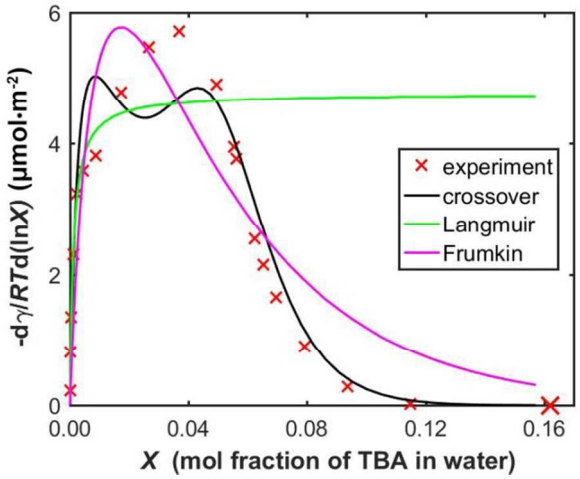

Figure S8. Approximation of experimental adsorption data by crossover isotherm, Langmuir–von Szyszkowski isotherm (Eq. S6) and Frumkin isotherm (Eq. S7). The critical point at [0.1622; 0.00] is indicated by a bigger cross marker.

Section 3. Simulation model limitations and justification

Our simulation model does not accurately represent the solvation interactions between TBA (solute) in the bulk cyclohexane (CHX) solvent. At low hydrotrope concentrations, one could argue TBA will be present in smaller fractions at the interface than those represented in our model because it partitions to both phases. However, there is good agreement between simulation and experiment below 0.7 mol% of TBA in water, and even up to concentrations below 6 mol% with minor adjustments using Eq. 5 in the main manuscript (system S10). Which indicates the interactions between TBA and CHX are not critical at these low concentrations because the hydrotrope would rather interact with water or remain at the interface between the two liquids. Moreover, the amount of TBA at the interface does not depend on its solubility in CHX at higher concentrations, i.e. when the interface is saturated. The plot below shows the interface starts to saturate in TBA with system S5 (0.7 mol% TBA in water at equilibrium) and does not change much after this point (black data points). Therefore, our representation of the interfacial profiles is still representative of the real systems (up to system S10).

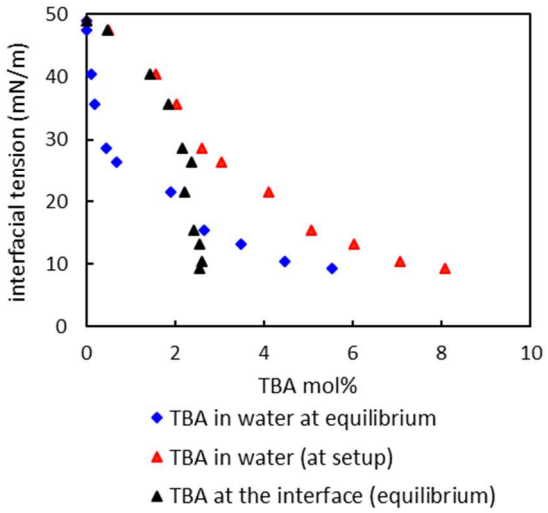

Figure S9. Concentration of TBA at the beginning of the simulation (red), at equilibrium in the aqueous phase (blue) and at the interface (black) for the simulation systems S1 to S10 shown with their corresponding interfacial tension.

As far as the simulation force field (FF) itself, CHARMM36 General FF[6] was optimized to reproduce the interactions between alcohols and water. However, the accuracy of interactions between alcohols and an organic solvent may suffer due to the response of partial charges on atoms upon a change of environment in the organic phase. The current model contains a too high of a charge penalty when bringing TBA into the organic phase. This would be consistent with all pairwise additive models. Alternate FFs, such as TraPPE-UA FF[7] or HH-Alkane[8] are united atom FF optimized to reproduce the properties of pure alcohols and to represent better the interactions between water and alkanes, respectively. The TraPPE-UA FF did not perform well for binary mixtures of alcohols and water in terms of predicting the correct pressure of the system, which also suggests that the interfacial tension between liquids may not reproduce experimental results. On the other hand, the HH-Alkane FF, developed as a refined form of the TraPPE-UA, still does not accurately reproduce experimental values of the alkanes' solubility in water and was not tested for alcohols.

With all this in mind, the main issue with the TraPPE-UA FF is that it is not optimized with respect to water. The alkane-TBA interaction might be improved compared to our model but we cannot use this FF for explicit hydrogen water. In addition, we did not want to mix UA and AA FFs as this can be dangerous as inconsistency in optimization procedures between FFs. The charges used on the alcohols for UA FF will not match well with how this was obtained with the AA FF. In summary, we believe we are getting the correct interfacial behavior at low TBA concentration, but are missing the difficult-to-predict partitioning in the organic phase.

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