## **Supporting Information**

# Simultaneous determination of interfacial molarities of alcohol, bromide ion, and water during alcohol induced microstructural transition: The difference between medium and long chain alcohols.

Kaixin Yao<sup>1</sup>, Lijie Sun<sup>1</sup>, Xiaoxuan Ding<sup>1</sup>, Yuzhao Wang<sup>1</sup>, Tianze Liu<sup>1</sup>, Changyao Liu<sup>1</sup>\*, Jiajing Tan<sup>2</sup>, Li Zhao<sup>1</sup>, Baocai Xu<sup>1</sup>, Larry Romsted<sup>3</sup>

 Department of Applied Chemistry, Beijing Technology and Business University, No. 11 Fucheng Road, Beijing, 100048, People's Republic of China

2. Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, P.R. China

3. Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road Piscataway, New Jersey 08854

## **Table of Contents**

Section I : Reological measurements	S2
Section II : TEM images	<b>S</b> 2
Section III : Turbidity measurements	<b>S</b> 3
Section IV: Chemical trapping with $1$ -ArN <sub>2</sub> <sup>+</sup> in aqueous TMABr solutions.	<b>S</b> 3
Section V: Interfacial molarities	<b>S</b> 7
Section VI: Packing parameter estimation	<b>S</b> 8

## Section I : Reological measurements

**Figure S1.** The steady shear viscosity as a function of shear rate for the aqueous solutions of 0.1 M CTAB containing 0.1 M KBr and (A) 5 - 45 mM C<sub>8</sub>OH or (B) 5 - 45 mM C<sub>4</sub>OH.



## Section II : TEM images

**Figure S2.** TEM images of 0.1 M CTAB/0.1 M KBr containing 5 mM C<sub>8</sub>OH (A & B)and 40 mM C<sub>8</sub>OH (C & D).



#### Section III : Turbidity measurements.

Turbidity was obtained using an UV-visible spectrophotometer, UV-3600 230VCE, Shimadzu Corporation, at 25°C. The resolution was 0.1nm. The wavelength was 500nm.

Figure S3. The changes of turbidity with the concentration of added butanol or octanol at 25°C.



#### Section IV: Chemical trapping with 1-ArN<sub>2</sub><sup>+</sup> in aqueous TMABr solutions.

Aqueous TMABr stock solutions were prepared via a routine procedure in which the weights of both the salt and the water were obtained by measuring them in weighed 10 mL volumetric flasks. TMABr was weighed in a 10 mL flask and sufficient water was added to dissolve it and then it was diluted to the mark. The weight of water was determined by difference between the total weight minus the total weight of salt and the flask. The stock solutions were used to prepare sets of TMABr solutions containing incremental amounts of the stock solutions in 2 mL volumetric flasks. The solution acidity was set by adding 20 µL of 0.1 M HBr to give a final HBr concentration of 1 mM. The weight of water in each 2 mL flask was obtained from the calculated weight of water in the aliquot of the stock solution plus the weight of water added to fill the 2 mL flask to the mark. These weights were used to calculate the molarities of Br<sup>-</sup> and H<sub>2</sub>O because the solutions were concentrated and salt occupies a significant fraction of the total solution volume. To initiate the dediazoniation reactions, 20  $\mu$ L of freshly prepared stock solutions of 1-ArN<sub>2</sub>BF<sub>4</sub> in ice-cold MeCN were added to give a final probe concentration of 5 x  $10^{-3}$  M. 100 µL of cyclohexane were layered on top of the solutions to prevent the evaporation of volatile 1-ArBr and 1-ArOH products. The volumetric flasks were sealed with Parafilm and equilibrated at 25 °C for 2 days. Prior to HPLC analysis, the product mixture was diluted 5-fold with MeOH to dissolve both the cyclohexane and the aqueous salt solution. Conditions for product separation on the HPLC were the following: an 80% MeOH/20% H2O (v/v) mobile

phase; flow rate = 0.6 mL/min; detector wavelength = 230 nm; the injection volume was  $50 \mu$ L. Percent yields were obtained from average values of peak areas from triplicate or duplicate injections with the calibration curves obtained for the particular product. Product yields are in **Table S1**.

**Figure S4** shows the plot between the normalized yields of 1-ArBr, % 1-ArBr<sub>N</sub>, and total bromide ion concentration, [Br<sub>t</sub>], in TMABr aqueous solutions. The data was also fitted into Equation S1, which was employed as the standard curve. The standard curve was used to estimate the interfacial bromide ion molarities according to the basic assumption of chemical trapping : when the yield are the same, the concentrations are the same.

$$\%1 - ArBr_N = 10.38 + 11.04[Br_t]$$
(S1)

**Figure S5** shows the plot of the selectivity between bromide ion and water,  $S_w^{Br}$  versus [Br<sub>t</sub>] in TMABr aqueous solutions. The data was also fitted into Equation S2, which was used to estimate the selectivity,  $S_w^{Br}$ , at the interfacial region of CTAB micelles.

$$S_{\rm w}^{\rm Br} = 13.40 - 1.38[{\rm Br}_{\rm t}]$$
 (S2)

[Br <sub>t</sub> ]	[H <sub>2</sub> O]	Peak Areas	Peak Areas $(10^6 \mu v \bullet s)^b$ Observed Yields (%) <sup>c</sup>		(o) <sup>c</sup>	Normalized Yields (%) <sup>d</sup>		$S_{\mathrm{w}}{}^{\mathrm{Br}\mathrm{e}}$	$[H_2O]/[Br_t]$	
М	М	1-ArOH	1-ArBr	1-ArOH	1-ArBr	Total	1-ArOH <sub>N</sub>	1-ArBr <sub>N</sub>	-	
0.011	55.5	12.040	0.131	95.0	0.582	95.6	99.4	0.608	30.9	5044.4
0.021	55.4	11.708	0.228	92.4	1.01	93.4	98.9	1.08	28.8	2639.1
0.036	55.3	11.980	0.366	92.8	1.59	94.4	98.3	1.68	26.3	1536.7
0.054	55.2	11.804	0.514	91.4	2.23	93.7	97.6	2.38	25.0	1022.3
0.071	55.1	12.253	0.602	94.9	2.61	97.5	97.3	2.68	21.4	775.8
0.088	55.0	11.940	0.741	92.5	3.22	95.7	96.6	3.36	21.7	624.6
0.1	54.9	12.015	0.836	91.0	3.55	94.5	96.2	3.75	21.4	548.8
0.2	54.2	11.717	1.400	88.7	5.94	94.7	93.7	6.27	18.1	271.0
0.3	53.5	11.240	1.831	85.1	7.77	92.9	91.6	8.36	16.3	178.4
0.5	52.2	10.629	2.777	85.5	12.5	98.0	87.2	12.8	15.3	104.4
1	48.8	9.185	3.968	73.9	17.9	91.8	80.5	19.5	11.8	48.8
1.5	45.4	7.722	5.198	63.4	23.9	87.3	72.6	27.4	11.43	30.3
2	42.1	7.795	6.332	62.7	28.5	91.3	68.7	31.3	9.57	21.0
2.5	38.7	6.670	7.496	54.8	34.5	89.2	61.4	38.6	9.75	15.5
3	35.3	6.031	8.435	49.5	38.8	88.3	56.1	43.9	9.23	11.8
3.5	32.0	5.518	9.366	45.3	43.1	88.4	51.3	48.7	8.68	9.13

**Table S1.** HPLC peak areas, observed and normalized (subscript N) product yields for dediazoniation of 1-ArN<sub>2</sub><sup>+</sup> in aqueous TMABr solutions at 25°C and 1 mM HBr, and values for total Br<sup>-</sup>, water concentration, selectivities,  $S_w^{Br}$ , and H<sub>2</sub>O/Br molar ratios.<sup>a</sup>

a. Reaction time ca. 48 hours. The concentrations of 1-ArN<sub>2</sub>BF<sub>4</sub> were around  $1 \times 10^{-3}$  M but vary in each experiment. 100 µl of cyclohexane was layered on top of TMABr solutions in 2 ml volumetric flasks to prevent the evaporation of 1-ArBr. Prior to HPLC analysis, the product mixture was diluted 5 fold with methanol to dissolve both the cyclohexane and the aqueous salt solution.

b. 50  $\mu$ L sample injections. Peak areas are average of triplicate injections. Eluting solvents: 80%MeOH/20%H<sub>2</sub>O; Flow rate: 0.6 ml/min; Detector wavelength: 230 nm.

c. HPLC calibration curves (y-peak area in µv's; x-concentraiton in molarity):

 $y(1-ArOH) = 1.300 \times 10^{10}x$  (R<sup>2</sup> = 0.9995);  $y(1-ArBr) = 2.321 \times 10^{10}x + 14530$  (R<sup>2</sup> = 0.9998).

 $\begin{array}{l} \text{d. } \%1\text{-}ArBr_{N} = 100 \;(\%1\text{-}ArBr)/(\%1\text{-}ArOH + \%1\text{-}ArBr); \; \% \; 1\text{-}ArOH_{N} = 100 \;(\%1\text{-}ArOH)/(\%1\text{-}ArOH + \%1\text{-}ArBr). \\ \text{e. } S_{w}^{Br} = [H_{2}O](\%1\text{-}ArBr)/[Br_{t}](\%1\text{-}ArOH) \end{array}$ 

**Figure S4** Plot between the normalized yields of 1-ArBr, %1-ArBr<sub>N</sub>, and total bromide ion concentration, [Br<sub>t</sub>], in TMABr aqueous solutions ([HBr] = 1 mM) (a) containing 0 to 3.5 M [Br<sub>t</sub>]; and (b) containing 1.5 to 3.5 M [Br<sub>t</sub>] fitted to equation %1-ArBr<sub>N</sub> = 10.38 + 11.04[Br<sub>t</sub>].



**Figure S5** Plot between  $S_w^{Br}$  and  $[Br_t]$ , in TMABr aqueous solutions ([HBr] = 1 mM) (a) containing 0 to 3.5 M  $[Br_t]$ ; and (b) containing 1.5 to 3.5 M  $[Br_t]$  fitted to equation  $S_w^{Br} = 13.40 - 1.38[Br_t]$ .



#### Section V: Interfacial molarities

**Table S2.** Estimated values of interfacial molarities of water,  $H_2O_m$ , bromide ions,  $Br_m$ , and butanol, C<sub>4</sub>OH<sub>m</sub>, in aqueous solutions of 0. 1 M CTAB/0.1 M KBr containing 0 – 54.6 mM **Butanol** (C<sub>4</sub>OH) at 25°C. [HBr] = 1 mM.<sup>a</sup>

$[C_4OH]$	$\mathrm{Br_m}^{\mathrm{a}}$	$H_2O_m{}^b$	$C_4OH_m^c$
(mM)	(M)	(M)	(M)
0.0	2.69	39.0	0.00
10.9	2.75	38.3	0.06
21.8	2.75	38.3	0.14
32.8	2.71	38.6	0.18
43.7	2.69	38.7	0.23
54.6	2.66	38.9	0.29

a.  $Br_m = (\% 16 - ArBr_N - 10.38)/11.04$ 

b.  $H_2O_m = S_w^{Br} \times Br_m(\%16\text{-}ArOH_N)/(\%16\text{-}ArBr_N)$ 

c.  $C_4OH_m = H_2O_m x (\% 16-ArOBu_N)/[S_w^{ROH} x (\% 16-ArOH_N)]; S_w^{ROH} \approx 1$  according to ref<sup>1</sup>.

**Table S3.** Estimated values of interfacial molarities of water,  $H_2O_m$ , bromide ions,  $Br_m$ , and Octanol,  $C_8OH_m$ , in aqueous solutions of 0. 1 M CTAB/0.1 M KBr containing 0 – 55 mM **Octanol (C\_8OH)** at 25°C. [HBr] = 1 mM.<sup>a</sup>

[C <sub>8</sub> OH]	$\mathrm{Br_m}^{\mathrm{a}}$	$H_2O_m{}^b$	$C_8OH_m^{\ c}$
(mM)	(M)	(M)	(M)
0.0	2.69	39.0	0.00
6.35	2.65	39.2	0.15
12.7	$2.61 (\pm 0.01)^d$	39.5 (±0.1)	0.20 (±0.01)
15.9	2.58 (±0.01)	39.7 (±0.1)	0.22 (±0.01)
19.0	2.54 (±0.01)	40.0 (±0.1)	0.26 (±0.01)
22.2	2.50 (±0.01)	40.3 (±0.1)	0.31 (±0.01)
25.4	2.47 (±0.01)	40.5 (±0.1)	0.40 (±0.01)
31.8	2.39	41.0	0.48
34.9	2.36	41.2	0.55
38.9	2.35	41.3	0.52
55.0	2.20	42.1	0.89

a.  $Br_m = (\% 16 - ArBr_N - 10.38)/11.04$ 

b.  $H_2O_m = S_w^{Br} \times Br_m(\% 16\text{-}ArOH_N)/(\% 16\text{-}ArBr_N)$ 

c.  $C_8OH_m = H_2O_m x (\% 16-ArOOc_N)/[S_w^{ROH} x (\% 16-ArOH_N)]; S_w^{ROH} \approx 1$  according to ref<sup>1</sup>.

d. The values in the bracket are the standard deviation obtained from three parallel experiments.

#### Section VI: Packing parameter estimation

**Table S4.** Estimated values of interfacial CTAB molarities,  $CTAB_m$ , interfacial C<sub>4</sub>OH molarities, C<sub>4</sub>OH<sub>m</sub>, faction of CTAB in the mixed micelle,  $\alpha$ (CTAB), fraction of C<sub>4</sub>OH in the mixed micelle,  $\alpha$ (C<sub>4</sub>OH), weighted effective headgroup area, a<sub>0</sub>, weighted tail volume, V<sub>H</sub>, weighted tail length, l<sub>c</sub>, packing parameter for mixed aggregates, P, in aqueous solutions of 0. 1 M CTAB/0.1 M KBr containing 10.9 – 54.6 mM C<sub>4</sub>OH at 25°C. ( $\beta$  = 0.75)

$[C_4OH]$	<b>CTAB</b> <sub>m</sub>	$C_4OH_m$	α(CTAB)	$\alpha(C_4OH)$	$a_0$	$V_{\mathrm{H}}$	$l_{c}$	Р
(mM)	(M)	(M)			$(nm^2)$	$(nm^3)$	(nm)	
0	3.59	0	1.00	0.00	0.54	0.46	2.17	0.39
10.9	3.67	0.06	0.98	0.02	0.53	0.45	2.15	0.40
21.8	3.67	0.14	0.96	0.04	0.52	0.45	2.12	0.40
32.8	3.61	0.18	0.95	0.05	0.52	0.44	2.10	0.41
43.7	3.59	0.23	0.94	0.06	0.51	0.44	2.08	0.41
54.6	3.55	0.29	0.92	0.08	0.51	0.43	2.06	0.42

**Table S5.** Estimated values of interfacial CTAB molarities,  $CTAB_m$ , interfacial C<sub>8</sub>OH molarities, C<sub>8</sub>OH<sub>m</sub>, faction of CTAB in the mixed micelle,  $\alpha$ (CTAB), fraction of C<sub>8</sub>OH in the mixed micelle,  $\alpha$ (C<sub>8</sub>OH), weighted effective headgroup area, a<sub>0</sub>, weighted tail volume, V<sub>H</sub>, weighted tail length, l<sub>c</sub>, packing parameter for mixed aggregates, P, in aqueous solutions of 0. 1 M CTAB/0.1 M KBr containing 0 – 55 mM C<sub>8</sub>OH at 25°C. ( $\beta = 0.75$ )

[C <sub>8</sub> OH]	CTAB <sub>m</sub>	$C_8OH_m$	α(CTAB)	$\alpha(C_8OH)$	$a_0$	$V_{\mathrm{H}}$	$l_c$	Р
(mM)	(M)	(M)			$(nm^2)$	$(nm^3)$	(nm)	
0	3.59	0	1.00	0.00	0.54	0.46	2.17	0.39
6.35	3.53	0.15	0.96	0.04	0.52	0.45	2.13	0.40
12.7	3.48	0.2	0.95	0.05	0.52	0.45	2.12	0.41
15.9	3.44	0.22	0.94	0.06	0.51	0.45	2.11	0.41
19	3.39	0.26	0.93	0.07	0.51	0.44	2.10	0.42
22.2	3.33	0.31	0.91	0.09	0.50	0.44	2.09	0.42
25.4	3.29	0.40	0.89	0.11	0.49	0.43	2.06	0.43
31.8	3.19	0.48	0.87	0.13	0.48	0.43	2.04	0.44
34.9	3.15	0.55	0.85	0.15	0.47	0.43	2.02	0.45
38.9	3.13	0.52	0.86	0.14	0.47	0.43	2.03	0.44
55	2.93	0.89	0.77	0.23	0.43	0.41	1.94	0.49

**Table S6.** Estimated values of interfacial CTAB molarities,  $CTAB_m$ , interfacial C<sub>8</sub>OH molarities, C<sub>8</sub>OH<sub>m</sub>, faction of CTAB in the mixed micelle,  $\alpha$ (CTAB), fraction of C<sub>8</sub>OH in the mixed micelle,  $\alpha$ (C<sub>8</sub>OH), weighted effective headgroup area, a<sub>0</sub>, weighted tail volume, V<sub>H</sub>, weighted tail length, l<sub>c</sub>, packing parameter for mixed aggregates, P, in aqueous solutions of 0. 1 M CTAB/0.1 M KBr containing 0 – 55 mM C<sub>8</sub>OH at 25°C. ( $\beta = 1$ )

[C <sub>8</sub> OH]	CTAB <sub>m</sub>	C <sub>8</sub> OH <sub>m</sub>	α(CTAB)	$\alpha(C_8OH)$	$a_0$	$V_{\rm H}$	lc	Р
(mM)	(M)	(M)			$(nm^2)$	$(nm^3)$	(nm)	
0	2.69	0	1.00	0.00	0.54	0.46	2.17	0.39
6.35	2.65	0.15	0.95	0.05	0.52	0.45	2.12	0.41
12.7	2.61	0.2	0.93	0.07	0.51	0.44	2.10	0.42

15.9	2.58	0.22	0.92	0.08	0.50	0.44	2.09	0.42
19	2.54	0.26	0.91	0.09	0.50	0.44	2.08	0.42
22.2	2.50	0.31	0.89	0.11	0.49	0.43	2.06	0.43
25.4	2.47	0.4	0.86	0.14	0.48	0.43	2.03	0.44
31.8	2.39	0.48	0.83	0.17	0.46	0.42	2.00	0.45
34.9	2.36	0.55	0.81	0.19	0.45	0.42	1.98	0.46
38.9	2.35	0.52	0.82	0.18	0.46	0.42	1.99	0.46
55	2.20	0.89	0.71	0.29	0.41	0.40	1.88	0.52

The equations used to calculate the above values were as follow:

$CTAB_m = Br_m/\beta$ (Br <sub>m</sub> are estimated from CT experiments)	(S3)
$\alpha(\text{CTAB}) = \text{CTAB}_m / (\text{CTAB}_m + \text{C}_n\text{OH}_m)$ (n = 4 or 8; C <sub>n</sub> OH <sub>m</sub> are estimated from CT experiments)	(S4)
$\alpha(C_nOH) = 1 - \alpha(CTAB)  (n = 4 \text{ or } 8)$	(S5)
$a_0 = a_0(CTAB)^*\alpha(CTAB) + a_0(C_nOH)^*\alpha(C_nOH)  (n = 4 \text{ or } 8)$	(S6)
$V_{\rm H} = V_{\rm H}({\rm CTAB})^* \alpha({\rm CTAB}) + V_{\rm H}({\rm C_nOH})^* \alpha({\rm C_nOH}) \ (n = 4 \text{ or } 8)$	(S7)
$l_c = l_c (CTAB)^* \alpha (CTAB) + l_c (C_n OH)^* \alpha (C_n OH)  (n = 4 \text{ or } 8)$	(S8)
$\mathbf{P} = \mathbf{V}_{\mathrm{H}} / (\mathbf{a}_0 \mathbf{l}_{\mathrm{c}})$	(S9)

# Reference

1. J. Yao, L. S. Romsted, *Langmuir*, 2000, **16**, 8771-8779.