Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Cooperative effects of ruthenium micellar catalysts and added surfactants in transfer hydrogenation of ketones in water

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Electronic Supplementary Information

Table S1. The main micellar properties of the surfactants **S** used in catalytic tests.

	CTAB	**HBAC**	**SDS**	**DSS**	**TX-100**	**TW20**	**ZW3-14**
cmc, mM	0.92; 0.15[a]	0.49	8.2; ~1.0[a]	11	0.3	0.06	0.38
T_k, °C	25; 16[b]	25	10	33; 49[a]	-	-	-
T_c, °C	-	-	-	-	65; ~50[a]	76	-
Ref	[1,2]	[3]	[4]	[4]	[5]	[4]	[6]

cmc – critical micelle concentration, T_k, °C – the Krafft temperature, T_c, °C – the clouding temperature. [a] in 1M NaCl solution. [b] in 0.01M NaCl solution.

Table S2. The micellar properties of $C_{16}H_{33}NMe_3^+X^-$ (CTA^+X^-: X = Cl, Br) mixed with surfactants **S**.

	CTAB	**HBAC**	**SDS**	**DSS**	**TX-100**	**TW20**	**ZW3-14**
cmc, mM	~1	~0.5	<0.1	0.06-0.08	<1	<1	~0.4-1
[a] χ_{CTA}^{mic}	~ χ_{CTA}^{sol}	~ χ_{CTA}^{sol}	~0.5	~0.5			~ χ_{CTA}^{sol}
T_k, °C	<25	<25	50	<50			-
T_c, °C					>>65	>>76	-
Mixed micelles	+	+	+	+	+	+	+
Ref	[7]	[7]	[7a, 8]	[9]	[6]	[6]	[10]

cmc – critical micelle concentration, T_k, °C – the Krafft temperature, T_c, °C – the clouding temperature. [a] χ_{CTA}^{mic} – molar fraction of CTA^+X^- in the mixed micelle **S**/CTA^+X^-, χ_{CTA}^{sol} – molar fraction of CTA^+X^- in the solution of **S** and CTA^+X^-.

Table S3. The micellar properties of $C_8H_{17}NMe_3^+Br^-$ (OTAB) mixed with surfactants **S**.

	CTAB	**HBAC**	**SDS**	**DSS**	**TX-100**	**TW20**	**ZW3-14**
cmc, mM	[b]	[b]	0.8		[b]	[b]	[b]
[a] χ_{OTA}^{mic}	<0.05	<0.05	~0.5	~0.5	<0.05	<0.05	<0.05
T_k, °C	~25	~25	18	<18	-	-	
T_c, °C					>65	>76	
Mixed micelles	-	-	+	+	-	-	-
Ref	[7]	[7]	[11, 8]	[12]	[6]	[6]	[10]

cmc – critical micelle concentration, T_k, °C – the Krafft temperature, T_c, °C – the clouding temperature. [a] χ_{OTA}^{mic} – molar fraction of OTAB in the mixed micelle **S**/OTAB, χ_{OTA}^{sol} – molar fraction of OTAB in the solution of **S** and OTAB. [b] the *cmc* of the mixed system is close to the *cmc* of the added surfactant **S**.

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Figure S1. Transfer hydrogenation conversions (%) of ketone **1** catalyzed by **RuL**^{16} (solid symbols) and **RuL**^{8} (empty symbols) in the presence of surfactants **S**: (**A**) and (**B**) anionic surfactants, (**C**) and (**D**) cationic, non-ionic and zwitter-ionic surfactants. Conditions: T = 60 °C, H_2O (4 mL), HCOONa (1.25 M), **1** (0.25 M), **RuL**^{n} (0.25 mM), **RuL**^{n}/**1**/HCO_2Na = 1/1000/5000. The ratio **S**/**RuL**^{n} is given in the brackets.

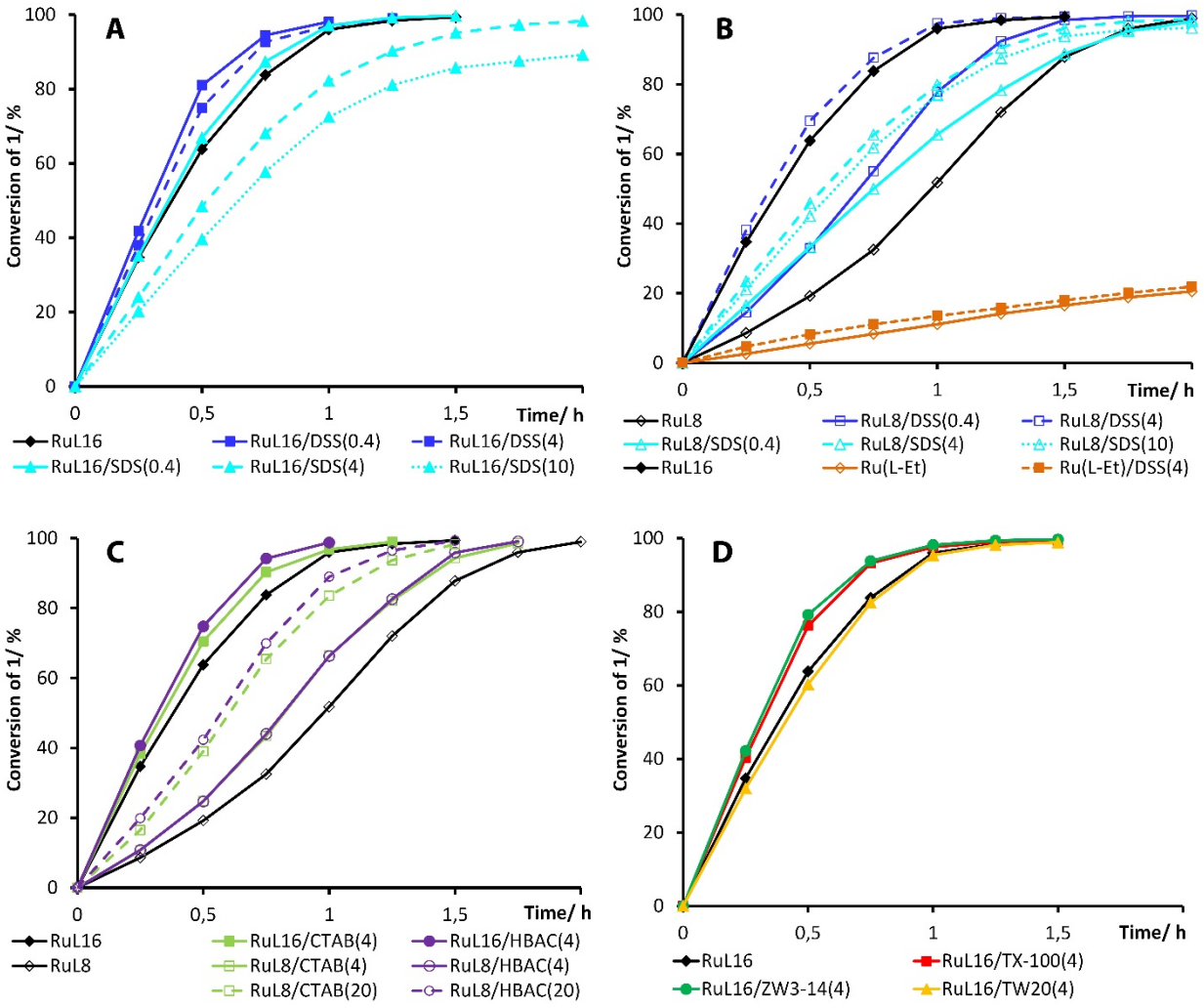

Figure S2. Transfer hydrogenation conversions (%) of ketone **2** catalyzed by **RuL**^{16} (solid symbols) and **RuL**^{8} (empty symbols) in the presence of surfactants **S**: (**A**) anionic surfactants, (**B**) and (**E**) cationic, non-ionic and zwitter-ionic surfactants. Conditions: *T* = 60 °C, H_2O (4 mL), HCOONa (1.25 M), **2** (0.25 M), **RuL**^{n} (0.625 mM), **RuL**^{n}/**2**/HCO_2Na = 1/400/2000. The ratio **S**/**RuL**^{n} is given in the brackets.

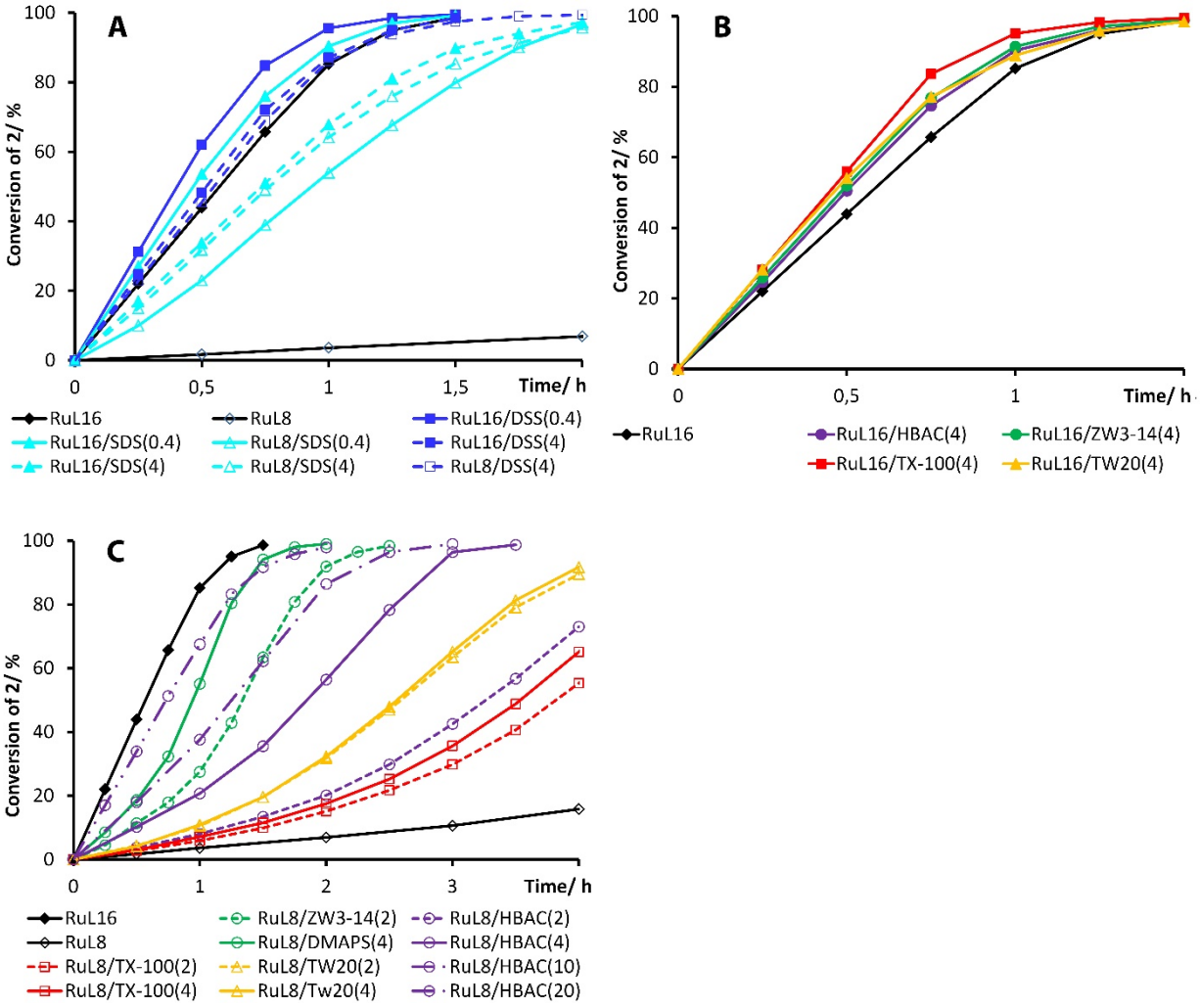

Figure S3. Transfer hydrogenation conversions (%) of ketone **3** catalyzed by **RuL**^{16} (solid symbols) and **RuL**^{8} (empty symbols) in the presence of surfactants **S**: (**A**) anionic surfactants, (**B**) cationic, non-ionic and zwitter-ionic surfactants. Conditions: *T* = 60 °C, H_2O (4 mL), HCOONa (1.25 M), **3** (0.25 M), **RuL**^{n} (0.625 mM), **RuL**^{n}/**3**/HCO_2Na = 1/400/2000. The ratio **S**/**RuL**^{n} is given in the brackets.

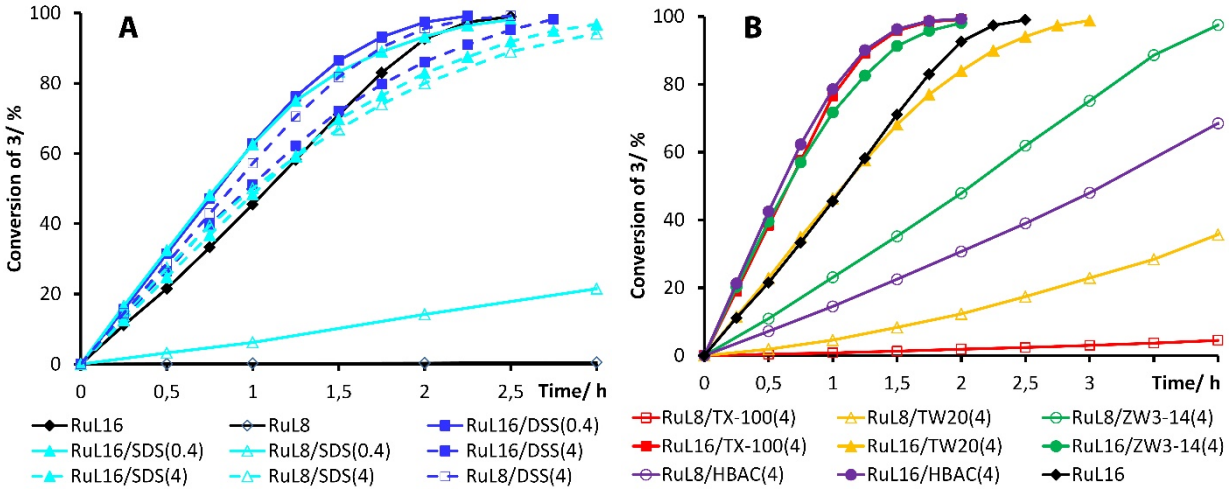

Figure S4. DOSY NMR spectra for the complex **RuL**^{8} in D_2O in the presence of 2 equiv. of surfactants **S**: (A) **S** = HBAC, (B) **S** = ZW3-14, (C) **S** = TX-100, (D) S = TW20. Axis *x* – chemical shift (ppm), axis *y* – diffusion coefficient (log D).

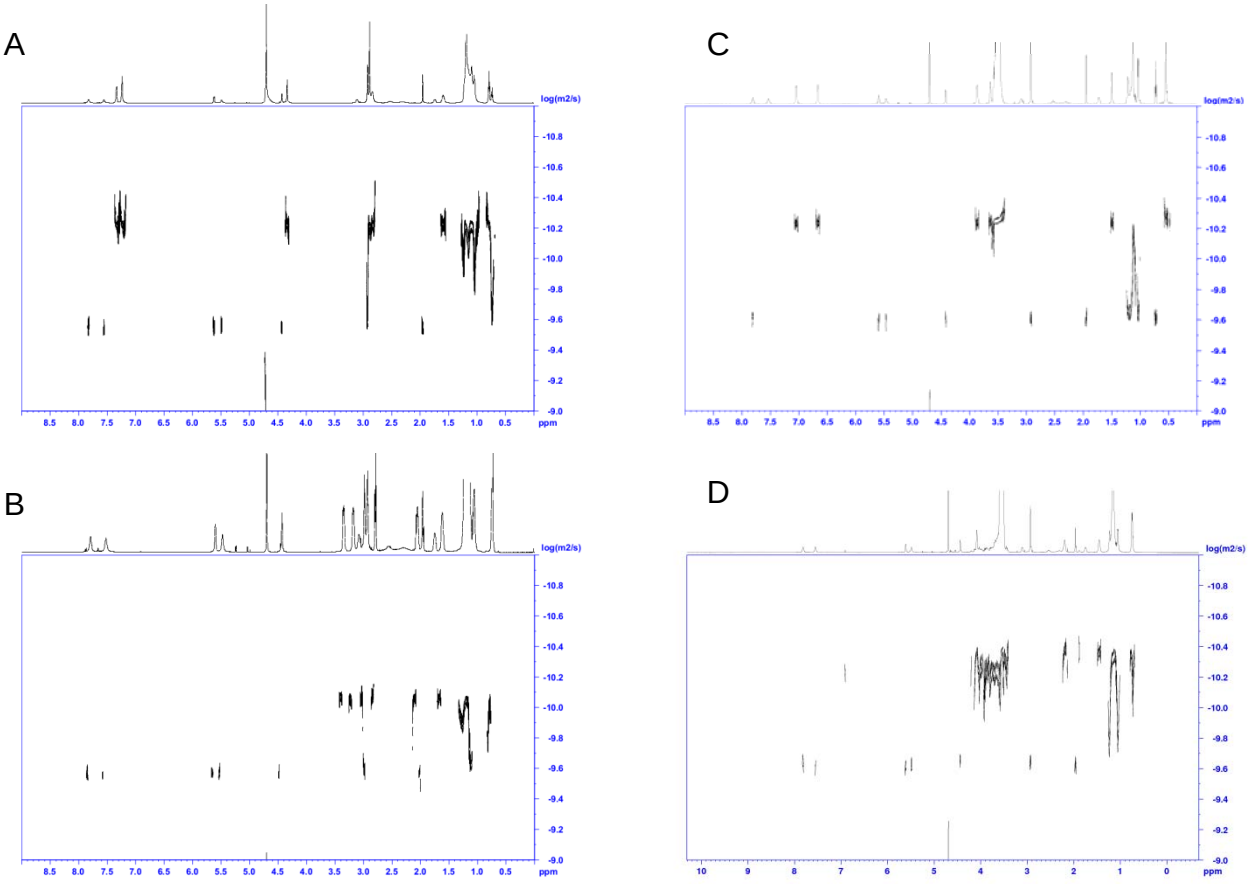

Figure S5. Diffusion-dependent signal attenuation of the complex **RuL**^{8} (squares) and the surfactants **S** (triangles) in D_2O solution: (A) **S** = HBAC, (B) **S** = ZW3-14, (C) **S** = TX-100, (D) S = TW20. The continuous lines represent the fit to the experimental data using the diffusion coefficients given in the Table 3. The signals with the following chemical shifts were used for the computation of the signal decay curves: 5.60 ppm (**RuL**^{8}), 7.22 ppm (HBAC), 3.34 ppm (ZW3-14), 3.86 ppm (TX-100), 1.45 ppm (TW20).