Electronic Supplementary Information

Transfer Hydrogenation of Acetophenone in Organic-Aqueous Biphasic System Containing Double Long-chain Surfactants

Experimental

The triphenylphosphinetrisulfonate (P(m-C₆H₄SO₃Na)₃, TPPTS) was prepared according to the method described in the literature.¹ Water-soluble ruthenium complex, RuCl₂(TPPTS)₂, was synthesized according to the literature.²,³ Water, iso-propanol and acetophenone were commercial and degassed before use.

Cetyltrimethylammonium bromide (CTAB), Dihexadecyldimethylammonium bromide (DDAB₁₆), sodium dodecyl sulfate (SDS) and polysorbate 80 (Tween 80) were commercial and without further purification. The double long-chain surfactants with different chain length were prepared according to the literature.⁴ The surface tension of surfactant solutions was measured by the Kruss Surface Tensiometer K100.

The transfer hydrogenation was conducted in a Schlenk tube (10ml) with a magnetic stirrer. A typical procedure as follows: the reactor was flushed with argon three times, and then, the ruthenium catalyst, TPPTS, surfactant solution, KOH, water, iso-propanol and acetophenone were added into it respectively. After a given reaction time, the mixture was extracted with chloroform and the organic phase was washed with water, dried with MgSO₄ and evaporated to dryness, and then detected by GC.

The composition of product was analyzed on an Agilent 6890 gas chromatograph equipped with a PEG-20M capillary column (30m×0.25mm×0.25mm) and flame ionization detector (FID).

Synthesis of the double long-chain cationic surfactants

1 C₁₆H₃₃N(CH₃)₂C₂H₅Br: 3.3 ml (9.81mmol) of C₁₆H₃₃N(CH₃)₂ and 1.3 ml (17.4mmol) of C₂H₅Br were performed with 80 ml of acetone as a solvent under argon atmosphere. The reaction was heated to 75°C and refluxed for 24 hours. The resulting products were extracted by ether and further purified by recrystallization from a mixture of acetone and ether. The yield was 3.31 g (89%). mp 208-212°C. ¹H NMR(CDCl₃, 400Hz): δ: 0.881(3H, t), 1.258-1.64(31H, m), 3.405(6H, s), 3.517(2H, t), 3.723(2H, q) ppm.
2 $\text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2\text{C}_4\text{H}_9\text{Br}$: 2.6 ml (7.7mmol) of $\text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2$ and 1.5 ml (13.9mmol) of $\text{C}_4\text{H}_9\text{Br}$ react with 80 ml acetone according to the same procedure as that followed for 1. Overall yield was 1.63 g (52%). mp 58-62°C, $^1\text{H}$ NMR(CDCl$_3$, 400Hz): δ: 0.897-1.037(6H, t), 1.000-1.698(32H, m), 3.398(6H, s), 3.488(2H, t), 3.527(2H, q) ppm.

3 $\text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2\text{C}_8\text{H}_{17}\text{Br}$: 2.5 ml (7.4mmol) of $\text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2$ and 1.6 ml (9.2mmol) of $\text{C}_8\text{H}_{17}\text{Br}$ react with 80 ml acetone according to the same procedure as that followed for 1. Overall yield was 0.78 g (23%). mp 163-165°C, $^1\text{H}$ NMR(CDCl$_3$, 400Hz): δ: 0.883(6H, t), 1.231-1.699(40H, m), 3.401(6H, s), 3.535(4H, t) ppm.

4 $\text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2\text{C}_{12}\text{H}_{25}\text{Br}$: 3.1 ml (9.18mmol) of $\text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2$ and 2.5 ml (10.4mmol) of $\text{C}_{12}\text{H}_{25}\text{Br}$ react with 80 ml acetone according to the same procedure as that followed for 1. Overall yield was 2.76 g (58%). mp 173-175°C, $^1\text{H}$ NMR(CDCl$_3$, 400Hz): δ: 0.897(6H, t), 1.230-1.696(48H, m), 3.396(6H, s), 3.533(4H, t) ppm.

References


