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Phase-transfer catalyst separation and re-use by solvent resistant nanofiltration membranes†

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This communication describes the use of nanofiltration (NF) membranes for efficient separation and recycling of phase-transfer catalysts, using the conversion of bromoheptane into iodoheptane with tetraoctylammonium bromide as the PT catalyst, as an example; a solvent flux of > 10 L m^{-2} h^{-1} was achieved with > 99% catalyst recycle and no loss in PT catalyst activity over a cycle of three consecutive reactions.

Phase-transfer (PT) catalysis, introduced by Starks,[1] is an alternative to the use of polar aprotic solvents (DMF, DMSO) for reactions involving a water-soluble nucleophilic reagent and an organic soluble electrophilic reagent (*e.g.* anions and organic substrates). However, one of the major technical problems inhibiting the use of phase-transfer catalysis in industrial applications is the need to separate the product and the phase-transfer catalyst.[2]

NF is a relatively new membrane process with a nominal molecular weight cut-off[3] (MWCO) in the range from 200–1000 Da. Recently NF membranes capable of performing separations in organic solvents have become available.[4] The molecular weight of many phase-transfer catalyts is in the range of 300–1000 Da. Therefore, it is of interest to investigate the potential application of NF membranes to separation of lipophilic phase-transfer catalysts from reaction mixtures, and subsequent recycling of the catalysts. We demonstrate the successful recycle and re-use of a catalyst in consecutive reactions using a solvent resistant NF membrane.

The model phase-transfer catalytic reaction employed in this study is given in eqn. (1), where PTC stands for phase-transfer

$$\mathrm{Br-C_7H_{15org} + KI_{aq} \xrightarrow{PTC} I-C_7H_{15org} + KBr_{aq}} \qquad (1)$$

catalyst. The model reaction involves the conversion of bromoheptane into iodoheptane using an aqueous phase containing potassium iodide[5] and is a classic example of a nucleophilic, aliphatic substitution reaction. Toluene, a common solvent in industry and a typical solvent used in phase-transfer catalysis, was used as the organic solvent. The PTC used was tetraoctylammonium bromide (TOABr). At the conclusion of the reaction, the lipophilic TOABr and the iodoheptane product both partition entirely into the organic phase.

Firstly, separation of PTC from a synthetic 'post-reaction' solution containing 0.1 M bromoheptane, 0.1 M iodoheptane and 0.01 M TOABr in toluene was studied using two polyimide solvent resistant NF membranes (142A and 142C, nominal MWCO of 220 and 400 Da respectively; W. R. Grace, USA).[6] The retention of the PTC, and the passage of the product molecule through the membrane, is necessary in order for the separation of product and catalyst to occur. Results are summarised in Table 1 and show that any residual reactant and the product pass through both membranes, which retain the catalyst for re-use. The 20–22% rejection[7] of reactant and product by 142A does not constitute a significant fraction of product being retained, and so 142A was chosen for further experiments involving repeated reactions. The flux in the presence of the reaction mixture is lower than for pure toluene, suggesting some degree of membrane fouling.

Two series of reactions were carried out, which differed only in the details of the process used to separate and recycle the PTC. In Case 1[8] a new membrane disc was used for each separation. In Case 2,[9] the same membrane disc was used for the series of separations. This latter procedure, with multiple membrane use, mimics more closely the likely procedure which would be used industrially. The time profiles for reactant (bromoheptane) and product (iodoheptane) during the Case 1 series of reactions, is shown in Fig. 1. After 5 h at 50 °C, with vigorous stirring, the yield was 97%. The phases were then separated, and the organic phase was filtered using 142A. After 35 mL of the original 40 mL of organic liquid had passed through the membrane, the residual 5 mL containing the PTC was recycled to the next reaction.

At the conclusion of the second reaction, this cycle was repeated, giving a total of three reactions and three catalyst separations. With pleasure we observed that the conversions of bromoheptane after 5 h in the second and third reactions were 90 and 96% respectively, indicating that the catalyst was recycled without any loss of activity.[10] Similar data were obtained in a second reaction cycle with catalyst recovery as per Case 2. A control confirmed no conversion of bromoheptane was observed in 6 hours in the absence of TOABr.

Flux data for filtrations from the two reaction cycles is summarised in Table 2. The permeate flux of the reaction mixture decreased to between 7 and 15 L m^{-2} h^{-1} by the end of the nanofiltration step, where a film of viscous material, assumed to be TOABr, was observed attached to the membrane surface. The solubility of TOABr in toluene is 380 g L^{-1}, and the starting concentration in the reaction mixture is 27 g L^{-1}, so it is expected that after 35 mL of organic phase has been removed, a maximum concentration of 218 g L^{-1} will result. This should be below the solubility limit of TOABr in toluene. However, it is possible that effects of the counter ion and the

Table 1 Separation of catalyst from a synthetic solution [Br–C_7H_{15} (0.1 M) + I–C_7H_{15} (0.1 M) + TOABr (0.01 M) + toluene]

		Flux/L m^{-2} h^{-1}		Rejection (%)		
Membrane	Nominal MWCO	Pure	Solution	Br–C_7H_{15} (MW 179)	I–C_7H_{15} (MW 226)	TOABr (MW 546)
142A	220	65	25	20	22	>99
142C	400	88	32	8	5	>99

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† Electronic supplementary information (ESI) available: experimental procedures and results. See http://www.rsc.org/suppdata/cc/b1/b103645a/

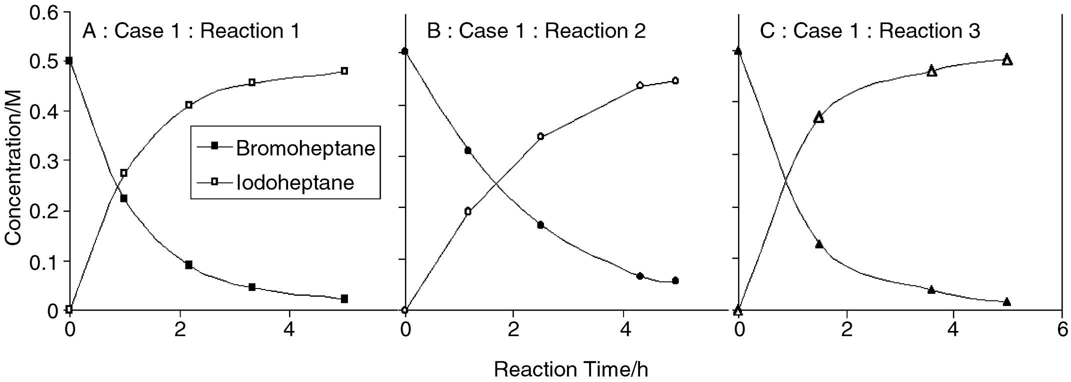

Fig. 1 Evolution of bromoheptane and iodoheptane concentration over time in the reaction in the presence of 0.05 M TOABr at 50 °C. The aqueous phase: 40 ml 0.5 M KI; the organic phase: 40 ml 0.5 M bromoheptane + 0.05 M TOABr. Stirring speed: 400 rpm. (A) Reaction 1; (B) Reaction 2 with the TOABr separated from the Reaction 1 mixture; (C) Reaction 3 with the TOABr separated from the Reaction 2 mixture.

Table 2 Separation of catalyst from reaction product mixture by 142A (MWCO = 220) membrane

						Rejection (%)					
	Reaction time/h	Conversion (%)[a]		Solution flux/L m^{-2} h^{-1}		TOABr MW 546)		1–C_7H_{15} (MW 226)		Br–C_7H_{15} (MW 179)	
		Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
Reaction 1	5	97	98	12	9.1	>99	>99	12	11	10	11
Reaction 2	5	90	97	14	8.5	>99	>99	18	15	14	18
Reaction 3	5	96	96	15	7.0	>99	>99	5	8	13	7

[a] Case 1: the 5 ml of retentate was washed out with pure toluene and then recovered by toluene evaporation; each filtration was carried out with a fresh membrane disc. Case 2: the retentate was washed out each time with fresh organic reactant solution containing no catalyst, and consecutive filtrations were carried out with the same membrane disc.

reactant/product in the system lower the TOABr solubility, causing the catalyst to come out of solution at the membrane surface.

For both reaction and filtration, Case 1 and Case 2 gave similar results with no noticeable difference. In Case 2, (in which the same membrane disc is used for all filtrations) the membrane is effectively 'washed' at the end of each filtration with the reaction mixture going into the next batch. In Case 1, the membrane is washed with pure toluene at the end of each filtration. Subsequently, prior to each separation, the pure toluene flux was measured and found to be between 50 and 60 L m^{-2} h^{-1}. Mass balances on the PTC over each separation cycle showed that effectively all of the PTC was recovered during separation and subsequent membrane washing. We conjecture that the decrease in flux during a post-reaction filtration is due to PTC which precipitates out on the surface of the membrane, as described above possibly due to concentration effects. Apparently this flux can be restored, and the catalyst reclaimed, by simple washing with the reaction solvent. This is likely to be an important factor in making catalyst recovery by NF a viable process.

Using the polyimide solvent resistant nanofiltration membranes, it is possible to retain essentially all the PTC and to repeat reactions in a cycle of at least 3 reactions, without adding any further catalyst. Membrane fouling occurs during filtration of the catalyst, but appears to be reversible when the membrane is washed with the reaction solvent. Finally, we conclude that the membrane retention of homogenous phase-transfer catalysts is feasible and offers exciting opportunities for further work in coupling of NF membrane separators with phase-transfer catalysis reactors.

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Notes and references

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5 Reaction details: the reaction was carried out in a glass vessel of 100 mL with 40 mL aqueous phase (2 M KI) and 40 mL organic phase (0.5 M bromoheptane + 0.05 M TOABr in toluene). The temperature was kept at 50 ± 1 °C using an oil bath and stirring speed was 400 rpm. After the reaction was completed, the organic phase (40 mL) was transferred into a SEPA filtration cell and the cell was pressurized to 30 bar at room temperature. The SEPA cell was stirred at 300 rpm.
6 Values stated are supplied by W. R. Grace, Colombia, Maryland, USA, using various alkane solutes in toluene.
7 R_x defines the rejection of component x, this can be obtained from the following eqn. $1 - (C_{p,x}/C_{r,x})$ where $C_{p,x}$ is the concentration of x in the permeate and $C_{r,x}$ is the concentration of x in the retentate.
8 Case 1: the 5 ml of retentate left in the cell was washed out with pure toluene and the toluene was evaporated at 50 ± 1 °C (overnight in fume cupboard). This catalyst was then added to 35 mL 0.5 M bromoheptane in toluene (no fresh TOABr added) and mixed with 40 mL of 2 M KI aqueous phase. The reaction and nanofiltration were carried out as the above.
9 Case 2: the 5 ml of retentate left in the cell was washed out with 35 mL of 0.5 M bromoheptane in toluene to form the organic phase for the subsequent reaction. This organic phase was then mixed with 40 mL of 2 M KI aqueous phase. The reaction and nanofiltration were carried out as for the first reaction.
10 Reactants, products and catalyst were analysed using GC.