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Aqueous-biphasic hydroformylation of alkenes promoted by "weak" surfactants†‡

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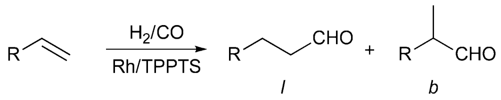
The aqueous-biphasic hydroformylation of higher alkenes catalyzed by Rh/TPPTS has been carried out in the presence of imidazolium, pyridinium and triethylammonium salts. High reaction rates are achieved with imidazolium and triethylammonium salts provided that their alkyl "tail" is $\geq C_8$. Fast and complete phase separation, and good retention of the metal in the aqueous phase could be achieved with an octyl "tail". Imidazolium salts were found to give the highest rate enhancement. The nature of the anion showed a moderate influence on the reaction. Evidence suggests that the additive can act as weak surfactant allowing emulsions to be formed and broken by simply switching the stirring on and off.

Introduction

The use of catalysts that allow the selective production of the desired product under mild conditions has been recognized as one of the main requirements for sustainable chemical development.[1] To achieve this aim, homogeneous catalyst are tools of choice, since they display high activity and their selectivity can be tailored through the use of specially designed ligands. Unfortunately, the catalyst being dissolved in the reaction medium makes its separation from the products often a challenging task. Beside economic considerations, the loss of catalyst in the product is not acceptable for environmental and toxicological reasons. Different strategies have thus been developed to tackle this problem.[2] Among them, aqueous-biphasic catalysis constitutes a very elegant approach.[3] By using water, a benign solvent, as a catalyst immobilizing phase, non-polar products are present in a different phase from the catalyst and can be simply removed by decantation. This methodology has proven its viability with the industrial Ruhr Chemie–Rhone Poulenc process, in which the rhodium catalyzed hydroformylation of propene or butene has been conducted since 1984 producing 800 000 t y^{-1} of C_4 and C_5 aldehydes (Scheme 1).[4] In this process, the rhodium catalyst is efficiently anchored in the aqueous phase *via* the water soluble ligand $P(3\text{-}C_6H_4SO_3Na)_3$, TPPTS, leading to very low metal leaching, *i.e.* ppb scale.[5] However, the scope of this methodology is greatly reduced by the low solubility of the substrate in the aqueous phase.



Scheme 1 The hydroformylation of alkenes catalyzed by a Rh/TPPTS complex under aqueous-biphasic conditions (R = CH_3: propene, R = C_4H_9: 1-hexene, R = C_6H_{13}: 1-octene and R = C_8H_{17}: 1-decene; *l* = linear, *b* = branched).

Poorly water soluble substrates react far too slowly under aqueous biphasic conditions for economically viable industrial application.

Numerous studies have been aimed at extending the scope of the aqueous-biphasic methodology to more hydrophobic substrates. Ligands for which the solubility can be reversibly switched by pH or temperature variation, or by addition/removal of CO_2 have been used to transfer the catalyst between the aqueous and the organic phase.[6–8] This allows the reaction to be carried out under homogeneous conditions, *i.e.* without mass transfer limitation, while transferring the catalyst to the aqueous phase after reaction for easy separation by decanting. Supporting the aqueous phase onto porous oxide supports has been used to develop heterogeneous-like catalysts.[9] With those catalysts, the reaction rate was shown to be independent of the substrate water solubility.[10] A new reactor design has also been shown to enhance reaction rates for poorly water soluble substrates.[11] All these elegant new approaches show very promising results. However, they require a significant redesign of the process which makes them unsuitable for a rapid wider application of the aqueous-biphasic methodology.

Additives have also been used to improve the solubility of the substrate in the catalyst phase without the need for a complete change in the process. Cosolvents, such as lower alcohols, have been shown to increase the reaction rate for aqueous-biphasic hydroformylation.[12] However, they induce side reactions, such as acetal formation, and leaching of the cosolvent into the product phase complicates the product separation. Inverse phase transfer catalysts, such as modified cyclodextrins and calixarenes, were shown to enhance reaction rates in various reactions under

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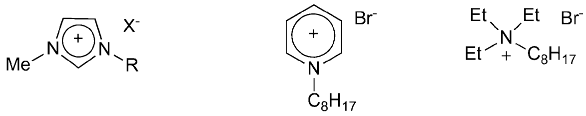
‡ Electronic supplementary information (ESI) available: Videos of the mixing and phase separation in the presence and absence of [OctMim]Br. See DOI: 10.1039/b822139a

aqueous-biphasic conditions.[13] Cationic surfactants can greatly enhance the reaction rate in aqueous-biphasic systems.[14] However, phase separation can become troublesome, since these systems are prone to emulsion.[15]

In a preliminary communication, we have described the use of imidazolium salts as promoters for aqueous-biphasic hydroformylation of higher alkenes catalyzed by Rh/TPPTS.[16] In this paper we describe details of that system and discuss the influence of the additive structure on the reaction (Fig. 1), especially the influence of the apolar tail of the cationic group and the ionic head group, as well as the influence of the anion. Moreover, we provide further evidence of the additive acting as a "weak" surfactant.



[HexMim]Br R = C_6H_{13} ; X = Br
[OctMim]Br R = C_8H_{17}; X = Br
[DecMim]Br R = $C_{10}H_{21}$; X = Br
[OctMim]Cl R = C_8H_{17}; X = Cl
[OctMim]TfA R = C_8H_{17}; X = CF_3CO_2
[OctMim]TfO R = C_8H_{17}; X = CF_3SO_3

[OctPyr]Br

[OctNEt$_3$]Br

Fig. 1 Structure of the different additives used in this study.

Results and discussion

Use of [OctMim]Br in the aqueous-biphasic hydroformylaton of alkenes

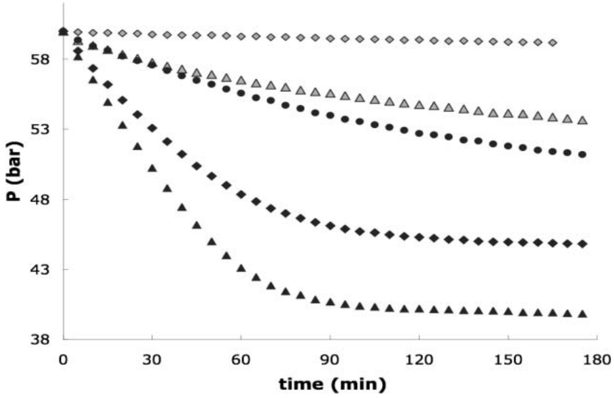


Fig. 2 Gas uptake plots from a ballast vessel for the hydroformylation of various alkenes in the absence (grey) and presence (black) of [OctMim]Br (0.5 mol dm^{-3}). ▲1-Hexene, ◆ 1-octene, ● 1-decene (for conditions see Table 1 footnote *a*, P/Rh = 10).

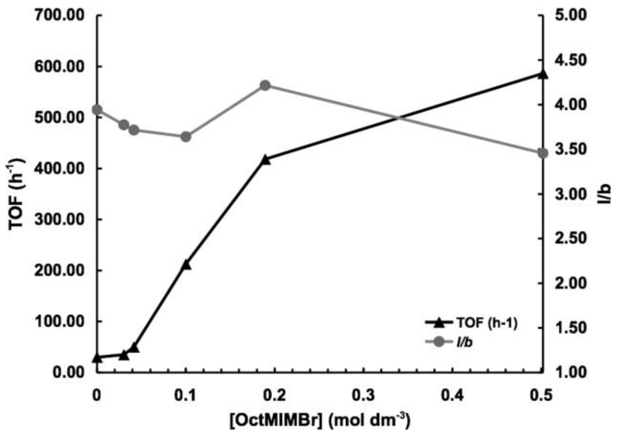


Fig. 3 Effect of the concentration of [OctMim]Br on the average TOF and the *l*/*b* ratio for the hydroformylation of 1-octene (closed reactor).

In the absence of additives, the hydroformylation of medium chain alkenes is very slow (see Fig. 2). For example, 1-octene gives only 1.9% conversion to aldehydes in 3 h (initial turnover frequency, TOF = 10 h^{-1}, under the conditions of Table 1). On adding [OctMim]Br, the rate increases dramatically above 0.033 mol dm^{-3} (Fig. 3), reaching 1100 h^{-1} at a concentration of 0.5 mol dm^{-3} with a decrease of linear selectivity (linear to branched ratio (*l*/*b*) = 2.9 *vs.* 4.9 in the absence of additive) (Table 1). Importantly, on opening the autoclave the two phases were fully separated and clear, the lower aqueous

Table 1 Aqueous-biphasic hydroformylation of alkenes in the presence of different 1-alkyl-3-methyl-imidazolium salts[a]

Entry	Alkene	Additive	P/Rh	Aldehydes (%)	Isomerised Alkenes (%)	*l*/*b*[b]	TOF$_0$/h^{-1} [c]	[Rh]$_{org}$ (ppm)[d]	Phase separation
1	1-Octene	—	10	2	1.5	4.9	10	n.d.[f]	<10 min[e]
2	1-Octene	[HexMim]Br	50	8	2	8.7	47	0.13	<10 min[e]
3	1-Octene	[OctMim]Br	10	92	6	2.9	1100	126	<10 min[e]
4	1-Octene	[OctMim]Br	50	92	3	3.2[g]	900	0.49	<10 min[e]
5	1-Octene	[DecMim]Br	50	94	1.4	3.0[g]	1200	0.31	stable emulsion
6	1-Hexene	—	10	38	4	4.5	300	n.d.[f]	<10 min[e]
7	1-Hexene	[HexMim]Br	10	20	0	7.8	150	0.30	<10 min[e]
8	1-Hexene	[HexMim]Br	50	37	0	13.7	200	0.21	<10 min[e]
9	1-Hexene	[OctMim]Br	10	90	9	2.8[h]	1550	27	<10 min[e]
10	1-Octene	[OctMim]Cl	50	81	3	3.2	650	n.d.	<10 min[e]
11	1-Octene	[OctMim]TfA	50	83	4	3.1	650	0.13	<10 min[e]
12	1-Decene	—	10	1	30[i]	3.1	n.d.[j]	n.d.[f]	<10 min[e]
13	1-Decene	[OctMim]Br	10	63	18[i]	2.5	340	23	<10 min[e]

[a] Reaction conditions: $T = 100$ °C; $P = 20$ bar ($CO/H_2 = 1:1$); stirring rate = 1000 rpm; 3 h; [additive]$_{aq}$ = 0.5 mol dm^{-3}; [Rh]$_{aq}$ = 1.25 10^{-3} mol dm^{-3}; alkene: 2 cm^3; H_2O: 8 cm^3. [b] Mole of linear aldehyde/mole of all the branched aldehydes. [c] Initial turnover frequency (mole of alkene converted per mole of rhodium per hour); calculated from the tangent at the origin of the gas uptake curve obtained. [d] Concentration of rhodium detected in the organic phase by ICP-MS. [e] The phases were fully separated by the time the autoclave was vented and opened, *ca.* 10 min after the reaction was stopped. [f] Not determined. [g] 2-Ethylheptanal detected. [h] 2-Ethylpentanal detected. [i] Including 12% of isomers present in the starting material. [j] The reaction is too slow for the gas uptake to be measured.

phase being orange and the organic phase being colourless (see Fig. 4).

Fig. 4 Photograph of the separated phases after hydroformylation of 1-octene in the presence of [OctMim]Br (0.5 mol dm^{-3}).

Analysis of the organic phase by ICP-MS showed that, despite the lack of colour, the organic phase contained 126 ppm of rhodium—an unacceptable level of leaching. These reactions were carried out with a P : Rh ratio of 10, whilst commercial processes operate with very much higher ratios (>100). Reasoning that a higher ratio might improve the *l*/*b* ratio, but might also enhance the catalyst retention, we carried out a reaction with P/Rh = 50. The reaction rate was not much affected, but the *l*/*b* ratio increased to 3.2. Crucially, the [Rh] in the organic phase dropped dramatically to 0.49 ppm. These results are summarised in Fig. 5.

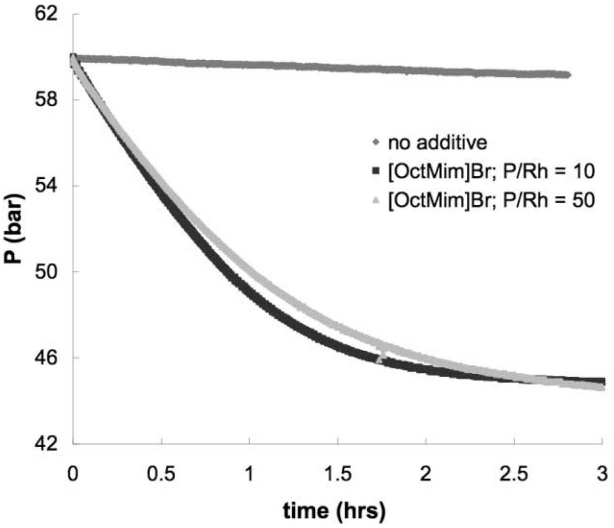


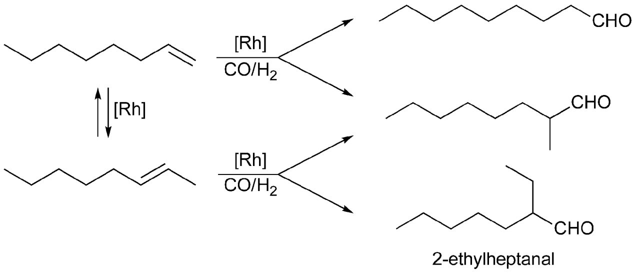
Fig. 5 Effect of the presence of [OctMim]Br and different P/Rh ratio on the gas uptake from a ballast vessel during the aqueous-biphasic hydroformylation of 1-octene (for conditions see Table 1 footnote *a*).

Similar improvements were obtained using 1-hexene and 1-decene (Table 1 and Fig. 2). For the former, the reaction was complete in <1.5 h (compared to 38% conversion after 3 h in the absence of additive); whilst for 1-decene there was no observable gas uptake in the absence of additive, but the reaction to aldehydes had proceeded to 71.4% in 3 h, allowing for the isomerised alkenes in the starting 1-decene, in the presence of [OctMim]Br (0.5 mol dm^{-3}).

In all cases, the observed amount of isomerised alkene was enhanced by the presence of the additive, but not relative to the amount of aldheyde formed. For 1-octene and 1-decene, isomerisation was supressed relative to hydroformylation. For 1-hexene and for 1-octene with Rh/P = 10, the gas uptake plots from a ballast vessel (Fig. 2 and 5) were linear over substantial parts of the reaction. This is probably because the gas transfer became rate determining. This would also explain why the initial rate of hydroformylation of 1-octene is only slightly different when using Rh/P = 10 or 50. Normally, hydroformylation reactions are inhibited by the presence of excess phosphine (negative order in [P]), but, if the reaction is gas transport limited, this order will not be observed. The gas uptake curve for 1-octene with P/Rh = 50 fits to first order kinetics, so the reaction is probably limited by the intrinsic kinetics, rather than by mass transport, at the higher loading of phosphine.

Variation of the apolar chain on the additive

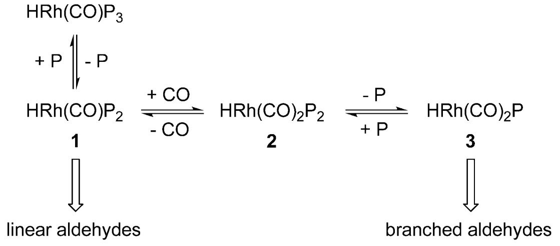
In order to try to understand the origin of the dramatic rate increase for the 1-octene hydroformylation when using [OctMim]Br as additive, as well as to see whether further improvements are possible, we studied the effect of varying the chain length of the alkyl substituent on the methyl imidazolium salt. [DecMim]Br, having a C_{10} side chain, enhances the reaction rate even further but leads to the formation a stable emulsion (Table 1, entry 5). The effect of [HexMim]Br, bearing a slightly shorter chain, C_6, is intriguing. It shows little influence on the reaction rate. However, it has a dramatic effect on the linear selectivity (Table 1, entries 1–2). The *l*/*b* ratio for the C_9 aldehyde reaches 8.7 in the presence of [HexMim]Br albeit with a 50 fold excess of ligand. This marked difference in linear selectivity can be attributed to different parameters. When comparing [HexMim]Br with [OctMim]Br it should be kept in mind that the linear selectivities are observed at very different conversion. At low conversion, the linear alkenes are mainly transformed, yielding linear aldehydes if the catalyst is selective. On the other hand, internal alkenes, which build up in the reaction mixture due to competitive isomerisation (Scheme 2), are hydroformylated to yield branched products when high conversion is reached, and only small amounts of terminal alkenes remain in the reaction mixture. This may explain the low linear selectivity observed in presence of [OctMim]Br and [DecMim]Br (Table 1, entries 4–5). Supporting this, 2-ethylheptanal arising from the hydroformylation of 2-octene (Scheme 2), was detected in reactions carried out to high conversion. However, when the reaction in the presence of [OctMim]Br was run for a shorter time (1.2 h), *i.e.* to lower conversion (58.7% aldehydes), the



Scheme 2 Hydroformylation–isomerisation of 1-octene.

l/*b* ratio was 3.3. This suggests that the low linear selectivity is due to a poorer selectivity of the catalytic system in the presence of [OctMim]Br, rather than to the hydroformylation of isomerised alkenes. Thus, the difference in linear selectivity observed between [OctMim]Br and [HexMim]Br seems genuine and does not arise from a conversion artefact.

In order to assess the influence of [HexMim]Br on the reaction selectivity at higher conversion, we investigated the hydroformylation of 1-hexene, which shows some activity even in the absence of additive. For this substrate, [HexMim]Br showed an inhibition effect on the reaction rate, but again led to higher linear selectivity compared with the neat biphasic system at similar conversion (Table 1, entries 6–7). Moreover, no isomerised alkenes were detected in the reaction mixture. When using a larger ligand excess, the *l*/*b* ratio increased to 13.7. Surprisingly, the reaction rate also increased, whereas excess ligand usually has an inhibiting effect on the reaction rate. When using [OctMim]Br, high reaction rate could be achieved but with poor linear selectivity and significant isomerisation of the substrate. The high linear selectivity observed for the hydroformylation of 1-hexene seems very likely to be due to the presence of [HexMim]Br. One explanation for this could be the increase of the ionic strength of the aqueous phase in the presence of [HexMim]Br. Hanson and coworkers reported that the linear selectivity of the aqueous-biphasic hydroformylation of 1-octene catalyzed by Rh/TPPTS can be improved upon addition of Na_2HPO_4 (0.5 mol dm^{-3}).[17] They showed by variable temperature ^{31}P-NMR studies that the dissociation energy of TPPTS from [HRh(CO)$(TPPTS)_3$] increases with the ionic strength of the solution. Dissociation of TPPTS is required to form the low phosphine coordinated complex **3** responsible for the formation of branched aldehydes (Scheme 3). Therefore, in aqueous media with high ionic strength the equilibria lie in favour of **1**, leading to a higher proportion of linear products. In our system, [HexMim]Br, presumably dissociated in the water phase, may increase the ionic strength, which would explain its effect on the reaction selectivity, although we note that [HexMim]Br is not expected to be as structure directing towards the water as is Na_2HPO_4. The low linear selectivity observed with [OctMim]Br and [DecMim]Br may be due to the formation of micelles. Conductivity measurements show that [OctMim]Br has a critical micelle concentration (CMC) of 2.16×10^{-2} mol dm^{-3} at 25 °C, *i.e.* well below the concentration used in the catalytic experiments. These longer chain additives, which form aggregates under the reaction conditions, do not significantly increase the ionic strength of the water and, hence, have no promoting effect on the linear selectivity. The increased ionic strength might also possibly be responsible for the lower rate obtained when using [HexMim]Br and 1-hexene, since this would reduce the solubility of 1-hexene in the aqueous phase. However, the slight increase in rate at high phosphine loadings would not be accounted for by this explanation.



Scheme 3 Equilibria involved in the formation of the different active catalytic species.

Variation of the "ionic head"

Having established that, in our system, the optimum balance between high reaction rate and good phase separation is obtained with an additive bearing a C_8 alkyl chain, we investigated the effect of structural variation of the additive "ionic head" while keeping the length of the "tail" to 8 carbon atoms. We investigated the use of water soluble *N*-octylpyridinium bromide, [OctPyr]Br, and *N*-octyl-*N*,*N*,*N*-triethylammonium bromide, [OctNEt$_3$]Br, as additives for the aqueous-biphasic hydroformylation of 1-octene with a 50 fold excess of TPPTS over rhodium (Fig. 6). From the gas uptake curves obtained, it appears that changing the structure of the "ionic" head of the additive dramatically changes its influence on the reaction rate. Surprisingly, [OctPyr]Br showed very little effect on the reaction rate. Moreover, opposite to what was observed with [HexMim]Br, it also had almost no influence on the regioselectivity, the *l*/*b* values observed being typically 4.1. On the other hand, the addition of [OctNEt$_3$]Br to the system allowed 1-octene to be transformed with a TOF_0 of 350 h^{-1} and a *l*/*b* value of *ca.* 3.0. None of those additives showed detrimental effects on the phase separation. The phases were fully separated by the time the autoclave was opened, *ca.* 10 min after the reaction was stopped. The smaller effect on the reaction rate observer for [OctNEt$_3$]Br compared with [OctMim]Br may arise from steric interactions. We propose (see below) that the accelerating effect observed with [OctMim]Br arises from the formation of an emulsion. Li has attributed the increased rate of hydroformylation reactions in the presence of cationic surfactants to the high concentration of Rh/TPPTS at the positively charge surface of the micelle.[14] This brings the catalyst and the substrate, solubilised in the core of the micelles, in close proximity and, hence, accelerates the reaction through a local concentrating effect. When using [OctNEt$_3$]Br, the ethyl groups may lead to a more sterically crowded micelle surface than the

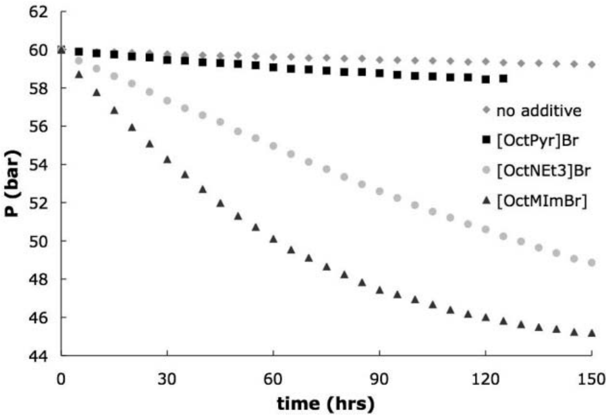


Fig. 6 Effect of the variation of the additive ionic "head" on the gas uptake from a ballast vessel during the aqueous-biphasic hydroformylation of 1-octene. (for conditions see Table 1 footnote *a*).

planar imidazolium cation and, thus, hinder the contact between the substrate and the catalyst.

Variation of the anion

Having investigated some of the possible structural variations of the cationic part of the additive, we tested the effect of changing the nature of the anion. It is well established that the nature of the anion has a dramatic impact on the water solubility of 1-alkyl-3-methylimidazolium salts. We synthesized 1-octyl-3-methyl imidazolium salts with bromide, chloride, trifluoroacetate and triflate anions, since they are likely to yield water soluble salts. Unfortunately, the triflate salt, [OctMim]TfO, proved to be insoluble in water and therefore unsuitable for our purpose. All the other salts were fully miscible with water at the investigated concentrations. [OctMim]Cl and [OctMim]TfA both led to higher reaction rates compared to the reactions carried out without additive. However, they were less efficient than their bromide analogues in speeding up the reaction (Table 1, entries 4, 10 and 11). The reaction selectivities were similar to those observed in the presence of [OctMim]Br. The rhodium leaching was found to be very low when using [OctMim]TfA. However, the crude reaction solution obtained in the presence of this additive had a strong "vinegary" smell, presumably arising from the hydrolysis of the CF_3CO_2 anion.

Origin of the promoting effect

Based on the comparison of the results regarding rate improvement, phase separation and rhodium leaching obtained for the hydroformylation of 1-octene in the presence of [HexMim]Br, [OctMim]Br and [DecMim]Br, we proposed that the rate improvement most probably arises because the additive is acting as a surfactant.[16] To test this hypothesis further, we visualised the mixing behaviour of aqueous-octene biphasic systems with and without added [OctMim]Br at room temperature and atmospheric pressure, using a yellow dye to colour the organic phase (Fig. 7). From the photographs and the videos available in the ESI‡ it can be seen that, while the system is poorly mixed without additive, a much more homogeneous system is obtained in the presence of [OctMim]Br after only 6 s of stirring. When the stirring is stopped, the phases instantly separate when no additive is present. In the presence of [OctMim]Br, the two phases take longer to separate, but after 20 s a biphasic system is obtained with a clear interface. The persisting yellow coloration of the aqueous phase indicates that some of the 1-octene dyed phase remains trapped in the water.

These results, together with those obtained using different alkyl chains on the imidazolium salt, support our proposal that [OctMim]Br acts as a weak surfactant. It promotes the formation of an emulsion whilst being stirred but the emulsion is too unstable and breaks quickly after the stirring is stopped. Consistent with this hypothesis, the effect of the additive is only noticeable above the CMC (Fig. 3).

Conclusions

We have studied the use of several structurally related additives in the aqueous-biphasic hydroformylation of higher alkenes. By careful choice of the cationic head group and its alkyl side chain, high reaction rates can be obtained without impairing the phase separation or the metal retention. These additives could greatly improve the scope of the aqueous-biphasic methodology. The structural features of the additive play an important role. The length of the side chain appears to be the most critical feature. The nature of the cationic head group also has an important influence on the reaction rate, but for reasons that remain rather unclear at the moment. Regarding the anion, its effect is less marked, although care should be taken with regard to its stability under the reaction conditions. The most promising additive is based on the 1-octyl-3-methylimidazolium cation. We propose that it affects the reaction by forming emulsions with poor stability that improve the contact between the catalyst and the substrate, but break after settling for a short time. These unstable emulsions seem to be very promising media for aqueous-biphasic systems, since switching between a pseudo monophasic system (good for high reaction rates) and a biphasic system (good for catalyst product separation) is just a matter of switching the stirrer on and off.

Experimental

General

All experiments were carried out under dry argon on a vacuum line using standard Schlenk techniques.

Gases, argon and syngas, were purchased from BOC gases. Water was distilled, degassed by vacuum, and stored under argon. Triphenylphosphine trisulfonate sodium salt, TPPTS,

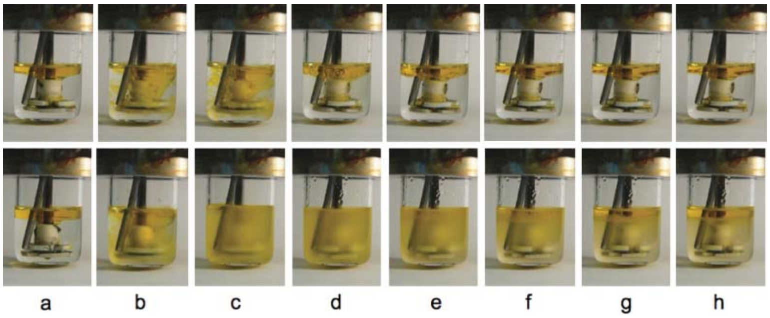


Fig. 7 Photographs of an octene–water biphasic system (octene: 2 cm^3, dyed; water: 8 cm^3) without additive (top line) and with [OctMim]Br (0.5 mol dm^{-3}, bottom line). (a) At $t = 0$ s; (b) after 2 s stirring; (c) after 6 s stirring; (d) after 12 s stirring (stirring is stopped); (e) after 2 s settling; (f) after 6 s settling; (g) after 12 s settling and (h) after 20 s settling (stirring rate = 1000 rpm). Videos are available in the ESI.‡

(Aldrich, 96% or prepared according to ref. 18), [Rh(acac)(CO)$_2$] (Strem chemical, 99%), deuterium oxide (Aldrich, 99.9 atom% D) and silver trifluroacetate (Aldrich, 98%) were used as received. Alkenes, 1-hexene (Aldrich, 99%), 1-octene (Aldrich, 98%) and 1-decene (Aldrich, 95%) were purified from peroxide by extraction with aqueous $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ followed by filtration trough basic alumina and stored in the dark under argon.

Ethyl acetate (Fischer, technical grade) was dried over magnesium sulfate and distilled over P_2O_5. Acetonitrile (Fischer, technical grade) was distilled over CaH_2. *N*-methylimidazole (Acros Organics, 99%) was distilled over sodium. Pyridine (Aldrich, 99%) was distilled over KOH. Triethylamine (Aldrich 98%) was refluxed overnight with KOH and then distilled. 1-Bromohexane (Aldrich, 98%) was dried over CaH_2 and distilled over P_2O_5. 1-Bromooctane (Aldrich, 99%) was distilled over K_2CO_3. 1-Chlorooctane (Aldrich, 99%) was distilled over CaH_2 under vacuum. 1-Bromodecane (Aldrich, 98%) was dried over CaH_2 and distilled over P_2O_5 under vacuum.

Gas chromatography analyses were carried out using a Hewlett-Packard 5890 series gas chromatograph equipped with a flame ionisation detector (FID) fitted with a Supelco MDN-35 (35% phenyl-/65% methyl-polysiloxane) capillary column for quantitative analysis. The temperature programme used was: 50 °C (4 min), Δ 20 °C min^{-1} to 130 °C (2 min), Δ 20 °C min^{-1} to 260 °C (13.5 min). The temperature of the injector and the detector were both 250 °C. The split ratio used was 100 : 1. Helium was used as the carrier gas with a flow of 1 ml min^{-1}.

^{13}C, ^{1}H and ^{31}P NMR spectra were recorded on Bruker AM 300/400 NMR spectrometers or a Varian 300 NMR spectrometer. Broadband decoupling was used for ^{13}C and ^{31}P NMR spectra. ^{1}H and ^{13}C NMR spectra were referenced internally to deuterated solvents; which were referenced relative to TMS, $\delta = 0$ ppm, CDCl$_3$, $\delta_H = 7.27$ ppm and $\delta_C = 77.23$ ppm, and D$_2$O $\delta_H = 4.53$ ppm. ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. Coupling constants are given in Hz.

Catalyst preparation

Catalyst solutions were prepared as follows: weighed amounts of [Rh(acac)(CO)$_2$] and TPPTS were dissolved in a known volume of water containing the additive at the desired concentration. CO/H$_2$ was then gently bubbled through the resulting yellow solution at 60 °C for 1 h. δ_P (300 MHz; D$_2$O) −4.55 (br s).

To check that the procedure was efficient to form the catalytically active complex *in situ*, the same procedure was followed but with higher concentration to allow detection by ^{31}P{^{1}H} NMR spectroscopy. δ_P (300 MHz; D$_2$O) −4.55 (br s) and 44.78 (d, $^1J_{P\text{-}Rh}$ 155). Literature values: δ_P (D$_2$O) 42.8 (d, $^1J_{P\text{-}Rh}$ 156)[19a] and δ_P (300 MHz; D$_2$O) −5.7 (s) 44.7 (d, $^1J_{P\text{-}Rh}$ 156).[19b]

Hydroformylation of alkenes

Typical procedure for the hydroformylation of alkenes at constant pressure: an autoclave fitted with a mechanical stirrer, thermocouple pocket and pressure transducer, and attached to a ballast vessel *via* a catalyst injector and a mass flow controller, was degassed by pressurizing three times with CO/H$_2$ and releasing the pressure. Catalyst solution (8 cm^3) was transferred into the autoclave and degassed by pressurizing three times with CO/H$_2$ and releasing the pressure. The autoclave was pressurized with CO/H$_2$ (1 : 1, 16 bar) and heated to 100 °C (Stirrer speed = 1000 rpm). Meanwhile, the substrate injector was charged with the substrate (2 cm^3). Once the reactor had reached 100 °C, the substrate was injected using an overpressure of CO/H$_2$ and the pressure was brought to 20 bar. CO/H$_2$ was then fed from the ballast vessel to maintain the pressure in the autoclave at 20 bar, and the pressure in the ballast vessel was monitored electronically. At the end of the reaction the autoclave was quickly cooled and depressurized. The content of the autoclave was transferred to a vial for visual inspection of the phase separation. The organic phase was analysed by GC for organics and by ICP-MS for rhodium. The results presented (Fig. 2, 5, and 6 and Table 1) are the average of at least 3 runs under each set of conditions.

Typical procedure for hydroformylation of 1-octene in a closed reactor: an autoclave, fitted with a mechanical stirrer, thermocouple pocket, pressure transducer, gas inlet and injection port, was degassed by 3 alternate vacuum–N$_2$ cycles. The stock catalyst solution (8 cm^3) and 1-octene (2 cm^3) were transferred into the autoclave. The autoclave was purged three times with pressurised CO/H$_2$. The autoclave was pressurized with CO/H$_2$ (1 : 1, 20 bar) and heated, with stirring, to 100 °C. After 2 h, the autoclave was quickly cooled depressurised and the content analysed using GC for the organic products. The results presented (Fig. 3) are the average of at least 3 runs under each set of conditions.

Synthesis of the additives

1-Hexyl-3-methylimidazolium bromide, [HexMim]Br. *N*-Methylimidazole (10 cm^3, 10.30 g, 0.125 mol), 1-bromohexane (21 cm^3, 24.70 g, 0.150 mol) and ethyl acetate (30 cm^3) were heated under reflux for 24 h in an atmosphere of argon. The biphasic system obtained was separated and the upper organic phase discharged. The bottom product phase was washed with ethyl acetate (3 × 30 cm^3), and dried under vacuum (0.01 mbar) at 50 °C to give 1-octyl-3-methylimidazolium bromide (23.47 g, 75%) as a colourless liquid. δ_H(300 MHz, CDCl$_3$) 0.21 (3H, t, ^3J 6.7, NC$_7$H$_{14}$C*H*$_3$), 0.55–0.78 (6H, m, C*H*$_2$), 1.30 (2H, quintet, ^3J 6.9 NCH$_2$C*H*$_2$), 3.52 (3H, s, NC*H*$_3$), 3.74 (2H, t, ^3J 7.4, NC*H*$_2$), 7.14 (1H, t, ^4J 1.7, NCHC*H*N), 7.25 (1H, t, ^4J 1.7, NC*H*CHN) and 9.59 (1H, s, NC*H*N).

1-Octyl-3-methylimidazolium bromide, [OctMim]Br. *N*-Methylimidazole (29 cm^3, 29.87 g, 0.364 mol), 1-bromooctane (69 cm^3, 77.14 g, 0.399 mol) and ethyl acetate (100 cm^3) were heated under reflux for 16 h in an atmosphere of argon. The biphasic system obtained was separated and the upper organic phase discharged. The bottom product phase was washed with ethyl acetate (3 × 100 cm^3), and dried under vacuum (0.01 mbar) at 50 °C to give 1-octyl-3-methylimidazolium bromide (87.16 g, 87%) as a colourless liquid. δ_H(400 MHz, CDCl$_3$) 0.65 (3H, t, ^3J 6.9, NC$_7$H$_{14}$C*H*$_3$), 0.99–1.16 (10H, m, C*H*$_2$), 1.71 (2H, quintet, ^3J 7.2 NCH$_2$C*H*$_2$), 3.93 (3H, s, NC*H*$_3$), 4.13 (2H, t, ^3J

7.4, NCH_2), 7.37 (1H, t, ^4J 1.8, NCHC*H*N), 7.56 (1H, t, ^4J 1.8, NC*H*CHN) and 9.97 (1H, s, NC*H*N)

1-Decyl-3-methylimidazolium bromide, [DecMim]Br. *N*-Methylimidazole (10 cm^3, 10.30 g, 0.125 mol), 1-bromodecane (29 cm^3, 77.14 g, 0.140 mol) and ethyl acetate (40 cm^3) were heated under reflux for 28 h in an atmosphere of argon. The biphasic system obtained was separated and the upper organic phase discharged. The bottom product phase was washed with ethylacetate (3 × 40 cm^3), and dried under vacuum (0.01 mbar) at 50 °C to give 1-decyl-3-methylimidazolium bromide (33.74 g, 89%) as a colourless viscous liquid. δ_H(300 MHz, $CDCl_3$) 0.69 (3H, t, ^3J 6.7, $NC_7H_{14}CH_3$), 0.99–1.22 (14H, m, CH_2), 1.75 (2H, quintet, ^3J 7.2 NCH_2CH_2), 3.97 (3H, s, NCH_3), 4.16 (2H, t, ^3J 7.4, NCH_2), 7.40 (1H, t, ^4J 1.8, NCHC*H*N), 7.59 (1H, t, ^4J 1.8, NC*H*CHN) and 10.08 (1H, s, NC*H*N)

1-Octyl-3-methylimidazolium chloride, [OctMim]Cl. *N*-Methylimidazole (40 cm^3, 41.2 g, 0.502 mol), 1-chlorooctane (103 cm^3, 89.52 g, 0.602 mol) and ethyl acetate (100 cm^3) were heated under reflux for 5 days in an atmosphere of argon. The biphasic system obtained was separated and the upper organic phase discharged. The bottom product phase was washed with ethyl acetate (3 × 50 cm^3), and dried under vacuum (0.01 mbar) at 50 °C to give 1-octyl-3-methylimidazolium chloride (63.0 g, 54%) as a pale yellow liquid. δ_H(300 MHz, $CDCl_3$) 0.69 (3H, t, ^3J 6.8, $NC_7H_{14}CH_3$), 1.12 (10H, m, CH_2), 1.75 (2H, quintet, ^3J 7.3 NCH_2CH_2), 3.97 (3H, s, NCH_3), 4.18 (2H, t, ^3J 7.7, NCH_2), 7.39 (1H, t, ^3J 1.7, NCHC*H*N), 7.63 (1H, t, ^3J 1.7, NC*H*CHN) and 10.42 (1H, s, NC*H*N).

1-Octyl-3-methylimidazolium trifluoroacetate, [OctMim]TfA. 1-Octyl-3-methylimidazolium chloride (7.48 g, 0.032 mol) in solution in water (25 cm^3) was added to a suspension of silver trifluoroacetate (7.42 g, 0.034 mol) in water (25 cm^3) and the mixture was stirrer overnight. The silver chloride precipitate was removed by filtration and the aqueous phase was extracted with dichloromethane (4 × 25 cm^3). The organic phases were combined and washed with small portions of water (10 cm^3) until silver nitrate test on the washings gave no precipitate. The solvent was evaporated, and further drying under vacuum (0.01 mbar) gave 1-octyl-3-methylimidazolium trifluoroacetate (3.2 g, 31%) as a colourless liquid. δ_H(400 MHz, $CDCl_3$) 0.81 (3H, t, ^3J 6.9, $NC_7H_{14}CH_3$), 1.27 (10H, m, CH_2), 1.88 (2H, quintet, ^3J 7.2 NCH_2CH_2), 4.04 (3H, s, NCH_3), 4.24 (2H, t, ^3J 7.4, NCH_2), 7.27 (1H, t, ^4J 1.7, NCHC*H*N), 7.33 (1H, t, ^4J 1.7, NC*H*CHN) and 10.36 (1H, s, NC*H*N).

***N*-Octylpyridinium bromide, [OctPyr]Br.** Pyridine (10 cm^3, 9.78 g, 0.124 mol), 1-bromooctane (24 cm^3, 26.83 g, 0.139 mol) and ethyl acetate (30 cm^3) were stirred under reflux for 14 h in an atmosphere of argon. The biphasic system obtained was separated and the upper organic phase discharged. The bottom product phase was washed with ethyl acetate (3 × 30 cm^3), and dried under vacuum (0.01 mbar) at 50 °C to give *N*-octylpyridinium bromide (26.1 g, 77%) as a colourless liquid. δ_H(300 MHz, $CDCl_3$) 0.66 (3H, t, ^3J 6.8, $NC_7H_{14}CH_3$), 0.96–1.26 (10H, m, CH_2), 1.89 (2H, quintet, ^3J 7.3 NCH_2CH_2), 4.83 (2H, t, ^3J 7.5, NCH_2), 8.04 (2H, t, ^3J 7.2, C*H*CHC*H*), 8.42 (1H, tt, ^3J 7.8, ^4J 1.2, CHC*H*CH) and 9.46 (2H, dd, ^3J 6.7, ^4J 1.2, C*H*NC*H*).

***N*-Octyl-*N*,*N*,*N*-triethylammonium bromide,[OctNEt$_3$]Br.** Triethylamine (12 cm^3, 8.71 g, 0.086 mol), 1-bromooctane (12 cm^3, 13.41 g, 0.069 mol) and acetonitrile (25 cm^3) were heated under reflux for 18 h in an atmosphere of argon. The mixture obtained was cooled to 0 °C and ethyl acetate was added in portions until precipitation of a white solid. The cold suspension was filtered, the solid collected, washed with ethyl acetate (3 × 30 cm^3) and dried under vacuum (0.01 mbar) to give *N*-octyl-*N*,*N*,*N*-triethylammonium bromide (15.12 g, 74%) as a white solid. δ_H(300MHz; $CDCl_3$) 0.87 (3H, t, ^3J 6.8, $NC_7H_{14}CH_3$), 1.21–1.44 (19H, m, CH_2 and NCH_2CH_3), 1.70 (2H, quintet, ^3J 7.1, NCH2C*H*2), 3.24–32.27 (2H, m, $NCH_2C_7H_{15}$) and 3.52 (6H, q, ^3J 7.3, NCH_2CH_3); *m*/*z* (ESI) 214 (M+, 100%).

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