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How does the presence of impurities change the performance of catalytic systems in ionic liquids? A case study: the Michael addition of acetylacetone to methyl vinyl ketone

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The catalytic activity of several metal complexes in ionic liquids towards Michael addition of acetylacetone to methyl vinyl ketone is found to be strongly dependent on the presence of halogenide impurities of the solvent. The tested metal complexes are Ni(acac)$_2$·2H$_2$O, FeCl$_3$·6H$_2$O, Yb(TfO)$_3$ (TfO = triflate) and Co(acac)$_2$, and the ionic liquids used as solvents are [bmim]BF$_4$ and [bmim]PF$_6$ (bmim = 1-n-butyl-3-methylimidazolium). The rationalisation of the halogenide effect in terms of ligand exchange from the starting complex with the excess chloride of impure ionic liquids is demonstrated in the case of the cobalt based system where the formation of the poorly active CoCl$_4^{2-}$ species is detected by UV-Vis analysis.

Introduction

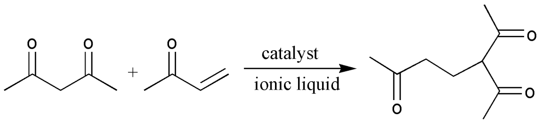
In recent years the attention paid by the scientific community towards the use of ionic liquids (hereafter referred to as ILs) as innovative solvents has been ever increasing.[1] The lack of volatility of ILs renders the catalytic systems made up of a transition metal complex or salt dissolved in an ionic liquid environmentally friendly. In fact, when distillation of products can be performed, the catalytic system becomes potentially recyclable without the drawback of the use of volatile solvents.

A salient point emerging from several recent studies concerns the purity of ILs.[1a] It has been claimed, for instance, that their physical properties can be affected by impurities such as water and halide ions, the commonest contaminants of ILs.[2] Already back in 1995 a detrimental effect of the chloride impurities has been invoked in order to account for lower activity of the catalytic system comprised of [Rh(nbd)(PPh$_3$)$_2$]PF$_6$ in ILs towards the hydrogenation of pent-l-ene.[3]

More recently the effect of halide on the catalysis of styrene/CO copolymerisation[4] and in the rhodium catalysed polymerisation of phenylacetylene[5] has been evaluated. In the latter case it has been shown that the presence of halide impurities in the IL rendered the addition of NEt$_3$ cocatalyst necessary in order to trigger the Rh(diene)(acac) based catalysis. The effect of impurities in ILs on biocatalytic systems has also been investigated.[6]

The amount of impurities in ILs is variable even when the same synthetic protocol is followed, and this may result in the lack of reproducibility of catalytic results.

To date no systematic study has been devoted to this topic, therefore we deemed it worthwhile to investigate the effect of impurities contained in 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF$_4$ in the following) when used as solvent in the metal catalysed Michael addition[7] of acetylacetone (Hacac) to methyl vinyl ketone (mvk), a model reaction already explored by us[8] from the activity and recyclability point of view (Fig. 1).



(1)

Fig. 1 Model reaction.

Results and discussion

The simplest and most widely used preparation method for [bmim]X (X = BF$_4^-$, PF$_6^-$) is the metathesis between [bmim]Cl and NaBF$_4$ in acetone followed by filtration and solvent evaporation.[9] The obtained IL contains variable amounts of chloride ions, the counter-cations of which being both [bmim]$^+$ and Na$^+$.

This has been ascertained by assessing the chloride percentage *via* potentiometric titration and the sodium content *via* atomic emission analyses (AES). Two different batches of [bmim]BF$_4$ gave, for instance, 0.62 ± 0.05% Cl together with 0.29 ± 0.01% Na and 1.21 ± 0.05% Cl together with 0.33 ± 0.01% Na. Moreover slow precipitation of NaCl, which is nearly insoluble in [bmim]BF$_4$, from the supersaturated IL results in a variability of the amount of impurities with time.

Carrying out Ni(acac)$_2$·2H$_2$O catalysed Michael addition in the two aforementioned batches of [bmim]BF$_4$, reaction completion was achieved after 5.0 h in the case of the IL containing 0.62% chloride (TOF of 18.8 h^{-1}, Table 1, entry 1) and after 9.0 h in the case of the IL containing 1.21% chloride (TOF of 10.8 h^{-1}, entry 2).

In order to obtain a batch of sodium- and chloride-free [bmim]BF$_4$, we used the protocol devised by Rogers,[2a] suitably modified. The analyses ascertained the absence of chloride as well as of sodium ions.

Table 1 Ni(acac)$_2$·2H$_2$O catalysis of the reaction (1)[a]

Entry	Solvent	Cl (%)	Na (%)	TOF/h^{-1}
1[b]	[bmim]BF$_4$	0.62	0.29	18.8
2	[bmim]BF$_4$	1.21	0.33	10.8
3	[bmim]BF$_4$	0.00	0.00	46.0
4	[bmim]BF$_4$	1.21[c]	0.00	10.1
5	[bmim]PF$_6$	0.00	0.00	48.0

[a] 0.025 mmol Ni(acac)$_2$·2H$_2$O, 2.0 g ionic liquid, Hacac/cat = 100 mol mol^{-1}, mvk/Hacac = 1.2, T = 85 °C. [b] From ref. 8. [c] Deriving from [bmim]Cl deliberately added to [bmim]BF$_4$.

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In the following we will refer to [bmim]BF_4 and [bmim]PF_6 as halogenide- and sodium-free solvents, specifying, when needed, the amount of impurities present.

Carrying out reaction (1) in [bmim]BF_4 resulted in a much higher average TOF (46.0 h^{-1}, entry 3): the reaction was in fact complete after 2.0 h.

This finding supports the hypothesis that chloride impurities might exert a detrimental effect on the activity towards the Michael addition of the catalytic system comprised of Ni(acac)$_2$·$2H_2O$ in [bmim]BF_4. Reaction (1) was also carried out in the (chloride-free) [bmim]BF_4 to which a known amount of chloride was deliberately added as [bmim]Cl, so to obtain the same Cl% of the IL used in entry 2. As expected, the observed drop in activity brought the TOF to a value (10.1 h^{-1}, entry 4) comparable with that reported in entry 2. This proves the above-mentioned hypothesis on the chloride effect.

As a confirmation, reaction (1) was eventually carried out in [bmim]PF_6 which can be obtained free from impurities because of its scarce water miscibility which enables the easy washing out of chloride ions.[2a] In [bmim]PF_6 (entry 5) the reaction course is the same as that reported in entry 3.

The effect of the halide in reaction (1) can be explained by admitting a ligand exchange between the acetylacetonate and the chloride (present in strong molar excess with respect to the metal) giving rise to less active chloronickelate species. The ligand exchange also has an effect on the solubility of the catalyst: in chloride-free IL (both [bmim]BF_4 and [bmim]PF_6) Ni(acac)$_2$·$2H_2O$ is only sparingly soluble and in the reaction mixtures most of it is present as a solid.

When an excess of chloride is contained in the IL, the reaction mixtures are homogeneous probably because of the good solubility of the formed anionic chloronickelate species in IL.

As to the influence of water, another common impurity in ILs, it has been ascertained that it has no effect on the catalysis of the Michael addition. On carrying out reaction (1) in water-free or water-containing ILs no difference in performance was noticed for all catalytic systems dealt with in this paper. Concerning the possible contamination of fluoride ions resulting from PF_6^- and BF_4^- decomposition, we did not undertake this analysis in the ILs used because, according to recent studies,[1a] the hydrolysis of the inorganic anion may occur only in the presence of water impurities, which were eliminated by azeotropic distillation prior to use.

The "halide effect" discovered for nickel(II) catalysis sheds light on the behaviour of Fe(III) and Yb(III) catalysis of reaction (1), previously studied by us.[8] We have reported that low catalytic activity was shown both by $FeCl_3$·$6H_2O$ and Yb(TfO)$_3$ in reaction (1) carried out at room temperature in [bmim]BF_4 containing 0.62% Cl (entries 1 and 5 of Table 2).

In order to verify a possible halogenide effect in the Fe(III) and Yb(III) catalyses, we have carried out reaction (1) with both catalysts in chloride-free [bmim]BF_4 and [bmim]PF_6. In Fe(III) and Yb(III) catalyses the reaction mixtures were in all cases homogeneous. Results shown in Table 2 indicate that in these conditions both catalysts exhibit high activity, turn over frequencies being higher than 29 h^{-1} at room temperature (entries 2, 4, 6 and 8). It is worth noting that in the case of Fe(III) catalysis a remarkable solvent effect can be evidenced: the TOF more than doubled passing from [bmim]BF_4 to [bmim]PF_6.

The catalyses carried out in [bmim]BF_4 with 0.62% added chloride (entries 3 and 7) gave results comparable to those reported in entries 1 and 5 thus evidencing a strong inhibiting effect of the chloride impurities.

Given that dioxygenato Co(II) complexes are active catalysts for the title reaction,[10] we decided to investigate its behaviour in ILs. When reaction (1) was carried out under Co(acac)$_2$ catalysis in [bmim]BF_4, the catalytic system was pink in colour and heterogeneous, due to the incomplete solubilisation of Co(acac)$_2$ in [bmim]BF_4. In this case satisfactory activity was obtained as evidenced by a TOF of 184 h^{-1} (entry 1 of Table 3).

Table 2 $FeCl_3$·$6H_2O$ and Yb(TfO)$_3$ catalysis of reaction (1)[a]

Entry	Solvent	Catalyst	% Cl in IL	TOF/h^{-1}
1[b]	[bmim]BF_4	$FeCl_3$·$6H_2O$	0.62	0.1
2	[bmim]BF_4	$FeCl_3$·$6H_2O$	0.00	29.3
3	[bmim]BF_4	$FeCl_3$·$6H_2O$	0.62[c]	0.1
4	[bmim]PF_6	$FeCl_3$·$6H_2O$	0.00	63.3
5[b]	[bmim]BF_4	Yb(TfO)$_3$	0.62	1.0
6	[bmim]BF_4	Yb(TfO)$_3$	0.00	120
7	[bmim]BF_4	Yb(TfO)$_3$	0.62[c]	0.4
8	[bmim]PF_6	Yb(TfO)$_3$	0.00	188

[a] 0.025 mmol catalyst, 2.0 g ionic liquid, Hacac/cat = 100 mol mol^{-1}, mvk/Hacac = 1.2, T = 25 °C. [b] Ref. 8. [c] Deriving from [bmim]Cl deliberately added to [bmim]BF_4.

Table 3 Co(acac)$_2$ catalysis of reaction (1)[a]

Entry	Additive	TOF/h^{-1}
1	—	184
2[b]	[bmim]Cl	43
3[c]	NaCl	3.5
4[d]	—	0.3

[a] 0.025 mmol catalyst, 2.0 g [bmim]BF_4, Hacac/cat = 100 mol mol^{-1}, mvk/Hacac = 1.2, T = 85 °C. [b] 119.2 mg of [bmim]Cl added to the reaction mixture. [c] 39.9 mg of NaCl added to the reaction mixture. [d] Catalyst: $[bmim]_2CoCl_4$.

Carrying out the reaction in the presence of 1.21% Cl as [bmim]Cl resulted in a drop in catalytic activity, the relevant TOF being 43 h^{-1} (entry 2). In this case the catalytic system was blue in colour and homogeneous. When the chloride was added as NaCl (entry 3) a suspension was obtained, due to the scarce solubility of NaCl in [bmim]BF_4 and the resulting catalytic system was blue in colour and nearly inactive for reaction (1) (TOF = 3.5 h^{-1}).

In order to gain an insight into the cooperative influence of the ionic impurities of the IL we have recorded absorption spectra of the cobalt based catalytic systems used in entries 1–3 of Table 2 (Fig. 2).

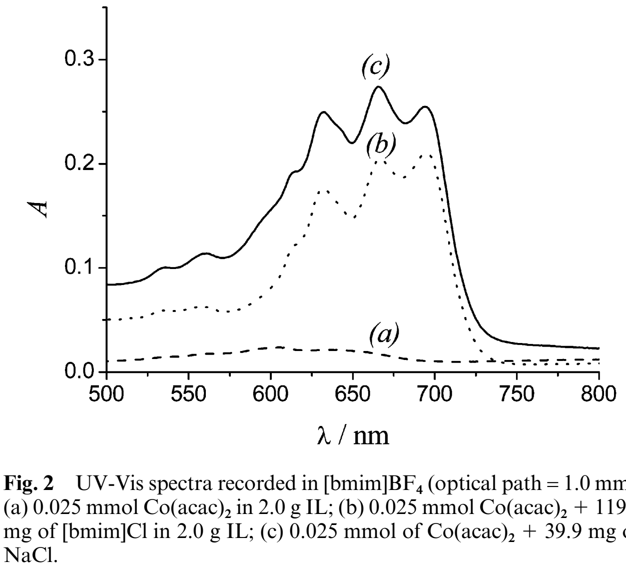

Fig. 2 UV-Vis spectra recorded in [bmim]BF_4 (optical path = 1.0 mm). (a) 0.025 mmol Co(acac)$_2$ in 2.0 g IL; (b) 0.025 mmol Co(acac)$_2$ + 119.2 mg of [bmim]Cl in 2.0 g IL; (c) 0.025 mmol of Co(acac)$_2$ + 39.9 mg of NaCl.

Analysis of the spectra obtained in the presence and absence of chloride ions [curves (b) and (c) *versus* (a)] shows, in the cases of (b) and (c) the formation of new absorption bands characteristic for tetrahedral cobalt(II) species. Such a Co(II) species has been identified as $CoCl_4^{2-}$, by comparison of spectra (b)

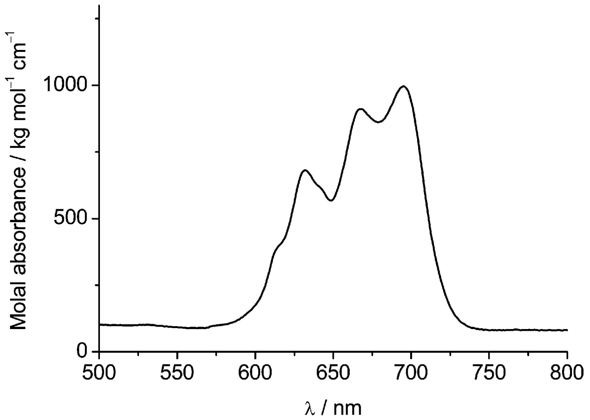

Fig. 3 UV-Vis spectrum of $[bmim]_2CoCl_4$ (1.0×10^{-3} mol kg^{-1}) in $[bmim]BF_4$.

and (c) with that of $[bmim]_2CoCl_4$ in $[bmim]BF_4$ (Fig. 3). The formation of $CoCl_4^{2-}$ can occur *via* equilibrium (2).

$$Co(acac)_2 + 4Cl^- \rightleftarrows CoCl_4^{2-} + 2acac^- \qquad (2)$$

As expected, catalysis carried out using $[bmim]_2CoCl_4$ as cobalt(II) source was nearly ineffective (entry 4, Table 3). The remarkable difference in catalytic activity observed on passing from [bmim]Cl to NaCl as chloride source (entry 2 *vs.* entry 3, Table 3) clearly points out the influence of the cations present in the system on the catalysis.

It is apparent from visible spectra that the amount of $CoCl_4^{2-}$ is dependent on the source of the chloride ions. Comparison of spectrum (b) with (c) shows, in fact, that, starting from the same number of moles of $Co(acac)_2$, and notwithstanding the low solubility of NaCl in $[bmim]BF_4$, a higher amount of $CoCl_4^{2-}$ forms when NaCl is added to the IL. The very low catalytic activity of $CoCl_4^{2-}$ explains the results of entries 2 and 3.

Concerning why the counter-cation of the chloride influences the amount of formed $CoCl_4^{2-}$, a possible explanation could be the different behaviour of NaCl with respect to [bmim]Cl in IL. It is known that the 1-alkyl-3-methylimidazolium cation forms strong hydrogen bonds with halide ions using all three ring protons.[11] If [bmim]Cl dissolved in $[bmim]BF_4$ exists prevalently in a quasi-molecular form, the chlorides supplied by [bmim]Cl are much less prone to exchange with acetylacetonates with respect to the case in which they come from NaCl. As a consequence, when the chloride is present as NaCl, reaction (2) is shifted to the right, explaining the observed increase of $CoCl_4^{2-}$.

In conclusion, we have demonstrated that the presence of halide impurities in ILs plays an important role in the Ni(II), Fe(III), Yb(III) and Co(II) catalysed Michael additions. In the cases of Ni(II), Fe(III) and Yb(III) the halide impurities have a detrimental effect of the catalytic activity which, for Fe(III) and Yb(III), completely inhibits the reaction. For Co(II) a cooperative effect of the counter-cation has been found.

The results reported in this study point out the desirability of future investigations on IL based catalytic systems being supported by precise specification of the amount of impurities in the solvent to warrant the reproducibility of results.

Experimental

General comments

All manipulations have been carried out under an inert atmosphere (nitrogen) using standard Schlenk techniques. $Ni(acac)_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $Yb(TfO)_3$ and $Co(acac)_2$ have been purchased from Aldrich and used as received.

The syntheses of 1-n-butyl-3-methylimidazolium hexafluorophosphate {$[bmim]PF_6$} was carried out following Roger's protocol[2a] whereas 1-n-butyl-3-methylimidazolium tetrafluoroborate {$[bmim]BF_4$} has been synthesised according to Dullius' procedure[9] (ILs of entries 1 and 2 of Table 1; entries 1 and 5 of Table 2) or by a modified Roger's protocol: $NaBF_4$ was used instead of HBF_4 and subsequent washings of the ionic liquid with a biphasic 1 : 1 mixture of water–dichloromethane warranted the elimination of sodium and chloride impurities. The chloride-free ILs were submitted to azeotropic distillation with toluene on Na_2SO_4 in order to remove water. Distillation was prolonged until the absence of water was ascertained by ^{1}H-NMR. The weight percentages of sodium and chlorine were determined by atomic emission spectroscopy (Na) and potentiometric titration (Cl) on water–IL mixtures. Co analysis was performed by AA. The atomic emission and atomic absorption analyses were performed with a Perkin-Elmer 3110 instrument. The potentiometric titrations (AgCl electrode) were carried out on a Metrohm 716 DMS Titrino instrument. Elemental analyses (C, H, N) were carried out using a Carlo Erba model EA 1108 instrument. Visible spectra were recorded with a Kontron Uvikon 942 instrument. Infrared spectra were recorded with a Bruker Vector 22 spectrometer. Gas chromatographic analyses were carried out on a HP 5890 instrument equipped with a HP-5 phenyl-methyl siloxane 30.0 m × 320 μm × 0.25 μm capillary column (carrier: nitrogen; injector temperature 280 °C, FID temperature 280 °C). The visible spectra reported as curves (a) and (c) in Fig. 2 refer to the solutions obtained by centrifuging the heterogeneous mixtures prepared using the components reported in the caption of Fig. 2.

Synthesis of $[bmim]_2CoCl_4$

The procedure proposed by Gill and Taylor for similar compounds[12] has been followed. Solutions of 1.31 g of $CoCl_2 \cdot 6H_2O$ (5.51 mmol) and 1.95 g of [bmim]Cl (11.2 mmol) in 15 cm^3 of absolute ethanol were boiled for five minutes. On cooling down to room temperature a biphasic system was obtained and evaporation of ethanol followed by washing with CH_2Cl_2 (3 × 10 cm^3) yielded pure $[bmim]_2CoCl_4$ as a thick blue liquid (1.90 g, 72%). (Found: C, 39.93; H, 6.37; N, 11.58; Cl, 29.55; Co, 12.15. $C_{16}H_{30}N_4Cl_4Co$ requires C, 40.10; H, 6.31; N, 11.69; Cl, 29.59, Co, 12.30%); IR (neat): ν_{max}/cm^{-1} 3149s, 3085s, 2964s, 2936s, 2876m, 1568s, 1451m, 1380w, 1334w, 1159vs, 838s, 750s, 650s, 614s, 301vs. UV-Vis ($[bmim]BF_4$, 1.0×10^{-3} mol kg^{-1}): λ_{max}/nm (ε/kg mol^{-1} cm^{-1}), 612 (sh), 632 (681), 668 (912), 695 (995).

Catalytic runs

A typical Michael addition was carried out as follows: in a 10 ml Schlenk tube, a mixture of 0.025 mmol of catalyst, 2.50 mmol of Hacac, 3.00 mmol of mvk and the additive (when present) in 2.0 g of ionic liquid was vigorously stirred at the desired temperature. Conversions were calculated by GLC analyses.

Turnover frequencies (TOFs) are quoted as the number of moles of substrate converted per mole of catalyst per hour and are averaged on at least two replicates. Their reproducibility (same batch of IL and same conditions) was in all cases within 4%. In the case of i) $Ni(acac)_2 \cdot 2H_2O$ catalysis (Table 1) ii) $FeCl_3 \cdot 6H_2O$ and $Yb(TfO)_3$ catalyses carried out in chloride-free IL (entries 2, 4, 6 and 8 of Table 2) and iii) $Co(acac)_2$ catalyses carried out in chloride-free or [bmim]Cl-containing IL (entries 1 and 2 of Table 3) the TOFs were calculated at the end of the reaction (conversion > 95%). In all other cases the reactions did not reach completion and the relevant TOFs were calculated at a fixed reaction time of 24 h.

Acknowledgements

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