Ionic liquids: polar, but weakly coordinating solvents for the first biphasic oligomerisation of ethene to higher α-olefins with cationic Ni complexes

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Ethylene oligomerisation in ionic liquids gives predominately alk-1-ene products with better reactivity and selectivity than in conventional solvents; turnover frequencies are correlated with polarity data obtained using solvatochromic dyes.

Ionic liquids are salts/salt mixtures with melting points below ambient temperature. The first use of ionic liquids in homogeneous catalysis was reported in 1990 for dimerisation[1] and polymerisation[2] reactions. Since then, a rapidly growing number of transition metal catalysed reactions have been described in various ionic liquids (for general reviews see ref. 3). Several papers describing the oligomerisation of ethylene and higher olefins in ionic liquids have been published.[1,4] However, all work described to date has used chloroaluminate ionic liquids, giving a high degree of isomerisation, and the formation of mainly internal olefins. For example, 9% of but-1-ene, but 91% of but-2-enes are obtained in the C_4-fraction from the reaction of ethylene with $[Ni(MeCN)_6][BF_4]_2$ in chloroaluminate ionic liquid at room temperature.[4c]

Higher α-olefins (HAOs) represent an important group of industrial chemicals. Depending on chain length, they are used as intermediates for plastics, plasticizers, lubricants and surfactants. HAOs can be obtained from ethylene via oligomerisation processes, such as those practised by BP Amoco (alkylaluminium catalyst) and Shell (SHOP, neutral nickel/phosphine catalyst). The latter is a biphasic process, the catalyst being dissolved in butane-1,4-diol, and the products forming a second layer easily removed by phase separation.

Besides the neutral nickel/phosphine compounds used in SHOP, cationic Ni complexes have attracted some attention as highly active catalysts for ethylene oligomerisation.[5] The positive charge means that they usually possess a more electrophilic Ni centre, often resulting in higher oligomerisation activity. To our knowledge, no example of biphasic ethylene oligomerisation to HAOs with cationic Ni complexes could be realised to date owing to the lack of a suitable solvent for the catalyst.

Here, we report the use of ionic liquids 1a–d as catalyst solvents in the biphasic oligomerisation of ethylene to higher α-olefins using the cationic Ni catalyst 2.[5a] Ionic liquids 1a–d were synthesised by reacting the appropriate chloride salt[6] with HPF_6, following a method described by Fuller et al.,[7] or purchased from Solvent Innovation GmbH, Cologne, Germany.[8] It was important that the liquids were completely free of water and chloride ions for 2 to exhibit good activity. The catalytic experiments were carried out under a constant pressure of ethylene in a 150 ml autoclave specially designed for biphasic ethylene oligomerisation (four paddles, stirrer with special gas inlet, baffles).

Catalyst 2 is found to be highly active in ionic liquid 1a, selectively forming HAOs via a biphasic reaction (Table 1, entry 1). The products separated as a clear and colorless organic

1a: R = butyl; A⁻ = $[PF_6]^-$
1b: R = hexyl; A⁻ = $[PF_6]^-$
1c: R = octyl; A⁻ = $[PF_6]^-$
1d: R = decyl; A⁻ = $[PF_6]^-$

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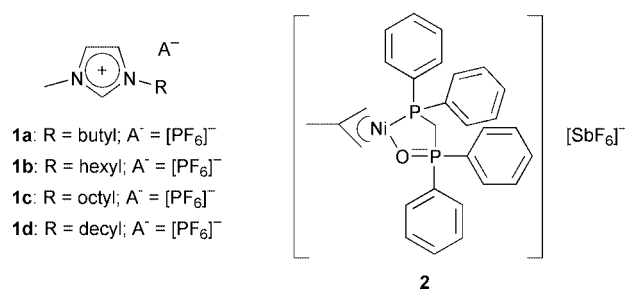
layer from the ionic catalyst solution after reaction (catalyst leaching being < 0.1% (detection limit)), with high selectivity for linear alk-1-enes. Previously, internal isomers have been the major components in reactions of this type.[4] The ionic catalyst solution was recyclable with little change in selectivity, although with somewhat lower activity (Table 1, entries 2 and 3). Since catalyst 2 is very sensitive to traces of water, the deactivation may be assigned to the practical problem of quantitative transfer back into the autoclave under completely inert conditions. In contrast, almost no ethylene conversion was observed in butane-1,4-diol, presumably due to catalyst deactivation (Table 1, entry 4). Butane-1,4-diol was chosen since this solvent is used successfully in biphasic reactions with neutral Ni complexes (e.g. SHOP). Following these observations, we decided to investigate the polarity and coordination properties of 1a in comparison to butane-1,4-diol.

Solvatochromic dyes have been widely used to help quantify solute–solvent interactions.[9] Many different scales exist, but most probe only particular interactions of a given solvent. Defining the 'polarity' of ionic liquids is made difficult by the wide range of interactions possible within systems like 1a. The

Table 1 Comparison of ethylene oligomerisation in different solvents

Entry	Solvent (cycle)	TOF^a/ h^{-1}	$L(C_6)^b$ (%)	$S(\alpha)^c$ (%)	Oligomer distribution^d	C_n (max)^e
1	1a	12712	95	93	0.16	14
2	1a (2)	9889	94	92	0.16	14
3	1a (3)	7952	93	91	0.16	14
4	Butane-1,4-diol	< 10	—	—	—	—
5	CH_2Cl_2	1852	95	88	0.48	18
6	1b	5527	91	89	0.18	14
7	1c	2885	92	90	0.22	14
8	1d	2058	96	94	0.24	16

Conditions: T = 25 °C; t = 2 h; p(ethylene) = 50 bar; 0.05 mmol 2; 20 ml heptane, 10 ml ionic liquid (entries 1–3, 6–8); 20 ml organic solvent (entries 4, 5). ^{a} TOF = turnover frequency; mol feedstock converted per mol catalyst. ^{b} $L(C_6)$ = linear hexene selectivity in C_6-fraction of product. ^{c} Hex-1-ene selectivity in the linear hexene fraction of the product. ^{d} Schultz–Flory distribution calculated from α = mol C_{10}/mol C_8. ^{e} C_n (max) = maximum chain length of detected products.

few studies reported to date suggest that ionic liquids are low dielectric materials,[10] whose apparent 'polarity' depends on the probe molecule employed.[11]

One of the most widely quoted scales of solvent polarity is the E_T scale, based on the position of the charge transfer band of betaine dyes such as **3**.[9] This molecule displays an extremely large wavelength shift in its charge-transfer band between non-polar solvents (λ_{max} = 810 nm for Ph_2O) and polar solvents (λ_{max} = 453 nm for H_2O). The position of the CT band is most strongly influenced by specific interactions with the highly basic phenoxide oxygen atom.[12] When **3** is dissolved in **1a** (*ca.* 1 mM), which had been dried under vacuum at 70 °C for several hours, λ_{max} = 547 nm [$E_T(30)$ = 52.3 kcal mol^{-1}],† approximately the same as that obtained for butane-1,4-diol [$E_T(30)$ = 53.5 kcal mol^{-1}]. Karl–Fischer titration measurements indicated a water content of *ca.* 6.0×10^{-3} M in the dried **1a**. It was found that extended drying and different concentrations of **3** resulted in no further change in the value of $E_T(30)$. Clearly the residual water may have some influence on the recorded value of $E_T(30)$, given the similar concentrations of probe molecule and water, but it is likely that removal of all traces of water will be impossible in any synthetic applications. By way of contrast, for undried [bmim][PF_6] (water content *ca.* 0.15 M), λ_{max} = 541 nm [$E_T(30)$ = 52.9 kcal mol^{-1}]. With regard to this polarity scale, **1a** can be regarded as behaving similarly to alcohols, possibly as a result of specific interactions between the hydrogen atoms on the imidazolium ring and the phenoxide oxygen. Thus, these results give no explanation for the difference in ethylene oligomerisation activity between **1a** and butane-1,4-diol.

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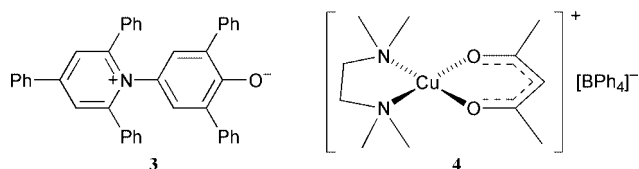
Since catalyst activity is most likely to be affected by the solvent basicity, we decided to probe this parameter using **4**, a complex whose d–d absorption band shifts to longer wavelengths as the degree of solvent coordination at the copper atom increases. A relationship has been reported between λ_{max} and the Gutmann donor number of the solvent, allowing **4** to be used as a measure of solvent and anionic basicity.[13]

When **4** is dissolved in dried **1a** ([**4**] = 10–50 mM), λ_{max} = 516.5 nm, while λ_{max} = 598.0 nm for butane-1,4-diol indicating much stronger coordination of the latter to the Cu(II) centre. The same probe in undried **1a** (water content *ca.* 0.15 M) gave a λ_{max} value of 535 nm, suggesting that the presence of water has a more significant effect than is the case for probe **3**. Thus, we conclude that the beneficial properties of **1a** with regard to the ethylene oligomerisation with catalyst **2** can be explained, at least in part, by a unique combination of high polarity and low coordination power displayed by this ionic liquid.

Our data suggested that the coordination strength of **1a** is only slightly higher than that of CH_2Cl_2. Consequently, we applied this solvent to the ethylene oligomerisation reaction with catalyst **2**. In CH_2Cl_2, the reaction is monophasic, thus preventing simple product recovery by phase separation (Table 1, entry 5). More importantly, a comparison with entry 1 reveals a much higher activity of **2** in the ionic liquid. Bearing in mind the similar λ_{max} values, this result seems to be somewhat surprising at first.

Therefore, a comparison of **1a** with other [PF_6]$^-$-based ionic liquids **1b–d** was carried out. As expected, measurements with **3** reveal a slight decrease in polarity on increasing alkyl chain length at the imidazolium cation [λ_{max} = 557 nm, $E_T(30)$ = 51.3 kcal mol^{-1} for dried **1c**]. In contrast, **4** displays effectively identical λ_{max}-values for the series **1a–d** (λ_{max} = 516.5 nm for dried **1c**), indicating that the strength of interaction at the metal centre is purely anion dependent. All ethylene oligomerisation

experiments with catalyst **2** in **1b–d** showed enhanced activity compared to the reaction in CH_2Cl_2, but decreasing activity was observed with increasing alkyl chain length at the imidazolium cation. We suggest that weak coordination of the solvent to **2** is a prerequisite for catalytic activity, but is clearly not the only factor to explain the special usefulness of **1a** in this reaction. The greater reactivity may be explained by inhibition of the cationic Ni catalyst **2** by the oligomers formed. This would explain why the oligomerisation activity is reduced by both a monophasic reaction (*e.g.* CH_2Cl_2) and increasing solubility of the products in the catalyst solvent (*e.g.* **1b–d**).

Remarkably, the oligomer distribution also shows a strong solvent dependence. The lower α-value of the Schulz–Flory distribution shows that the yield of low molecular weight HAOs is much higher for biphasic reactions in **1a–d** than for the reaction in CH_2Cl_2. This observation may be explained by the lower ethylene solubility (25 °C/50 bar) in *e.g.* **1a** (0.110 g ethylene/g **1a**) and **1c** (0.183 g ethylene/g **1c**) compared with CH_2Cl_2 (0.651 g ethylene/g CH_2Cl_2).[14] Since the rate of insertion (k_{ins}) is dependent on the ethylene concentration, while the rate of elimination (k_{elim}) is not, a solvent with lower ethylene solubility shifts the ratio k_{ins}/k_{elim} to lower values since it decreases the relative ethylene concentration at the catalyst.

In conclusion, we believe that our results are of general importance, since many cationic transition metal complexes are excellent catalysts, but are often poorly soluble in non-polar solvents, thus requiring a compromise between the solvation and coordination properties of a solvent. Our investigations clearly show that hexafluorophosphate ionic liquids are very interesting solvents for these applications. We propose to pursue these investigations, and will report our findings in due course.

Notes and references

† Molar transition energy $E_T(30)$/kcal mol^{-1} = 28591/(λ_{max}/nm).

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