Expanding the useful range of ionic liquids: melting point depression of organic salts with carbon dioxide for biphasic catalytic reactions

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Large and previously unreported melting point depressions (even exceeding ΔT_m of 100 °C) were observed for simple ammonium and phosphonium salts in the presence of compressed CO_2, bringing them well within the range of typical ionic liquids; possible applications include biphasic catalysis in IL/scCO_2 systems as demonstrated for rhodium complex catalyzed hydrogenation, hydroformylation, and hydroboration of 2-vinyl-naphthalene using a CO_2-induced molten sample of [NBu_4][BF_4] as a catalyst phase at temperatures in the range of 55–75 °C, *i.e.* 100 °C below the normal melting point of the organic salt.

Room temperature ionic liquids (ILs) are currently the subject of intense research focus due to their demonstrated potential as green solvents and advanced materials in a broad range of technical processes.[1–5] In particular, this includes their application as solvents for modern chemical synthesis and catalysis. In fact, the typical operating temperatures of organic synthesis have played an important role in defining ILs as "organic salts having melting points below 100 °C".[1–3,5] Consequently, reaching a low melting temperature has been the primary design principle for the molecular structure of ionic liquids. In practice, however, designing organic salts with particular properties and functions that are at the same time liquid below 100 °C or even near room-temperature is not a trivial task. The effective combinations of cations and anions that produce liquids under the present definition are small compared to the combinatorial possibilities. Therefore, a methodology or process to increase the range of possible ionic compounds for use as solvents for reactions and extractions would be highly useful. In the present communication, we demonstrate that pressurizing simple organic salts with CO_2 can lead to remarkably high melting point depressions (up to ΔT_m of 120 °C) allowing use of them as liquid phases in catalytic processes at temperatures far below their regular melting points (Fig. 1). This opens the possibility to consider typical "ionic liquid applications" for structures that had to be discarded previously owing to their high melting points.

It has long been known that organic compounds can undergo solid/liquid transitions below their normal melting points in the presence of compressed gases.[6] At a particular pressure of a gaseous component, the first temperature at which a solid partially melts represents a point on the solid–liquid–vapor equilibrium (*SLV*) line. The difference between this *SLV* temperature and the normal melting point (or the triple point) is called the melting point depression (ΔT_m). The melting point depression of organic molecular solids by application of compressed CO_2 is a well established phenomenon.[7–9] CO_2-induced melting has been used to carry out reactions in neutral organic substances that would otherwise be solid at the reaction temperature.[10,11] The CO_2-induced melting of high molecular weight poly(ethyleneglycol) has been exploited to utilize this medium for liquid/supercritical biphasic catalysis.[12–14] Melting point depressions were typically in the range of 20–25 °C in these systems. There have also been isolated reports on melting point depressions in the IL/CO_2 system. In our earlier study on Ni-catalyzed hydrovinylation in this system, we noticed that some of the low-melting salts showed a reduced viscosity or transition from a waxy solid to a liquid under CO_2-pressure.[15a,16] In an IR spectroscopic study attempting to understand the molecular interaction between ILs and scCO_2, Kazarian *et al.*[17] observed a reduction of the liquid-crystal transition temperature of long alkyl-chain imidazolium salts. However, so far no attempts have been made to explore this effect more systematically and to apply it to reactive systems. We therefore initially set out to study the melting point depression for a variety of organic salts with melting points above room temperature under operating conditions typical of the IL/scCO_2 system using 150 bar of CO_2 pressure (Table 1).

All solid samples were dried *in vacuo* (~0.1 mbar) for approximately 8 hours and stored under argon in Schlenk tubes prior to use. The melting points of the solids in the absence and presence of CO_2 were visually determined in a high-pressure view

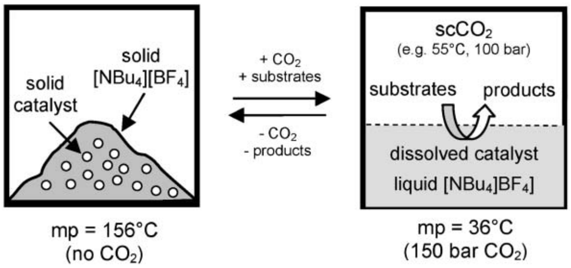

Fig. 1 CO_2-induced melting point depression to generate ionic liquids: schematic representation of catalytic processes carried out in an "ionic liquid"/scCO_2 biphasic mixture using CO_2-induced molten [NBu_4][BF_4] as catalyst phase at reaction temperatures 100 °C below its regular melting point.

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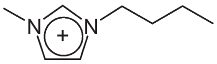
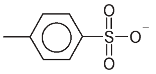
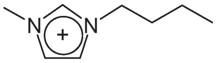
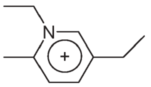
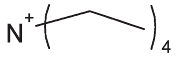
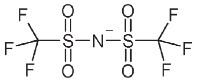
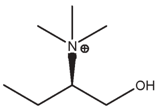
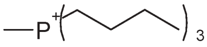
Table 1 Summary of melting point depression (ΔT_m) of organic ionic solids in CO_2

Entry	Organic salt	Cation	Anion	P_{SLV} [bar]	T_{SLV} [°C]	T_m [°C] *(lit.)*	*MPD* (ΔT_m)
1	[BMIM][OTos]			150	40–42	67 *(50.1)*[a]	26
2	[BMIM][CH_3SO_3]		$CH_3SO_3^-$	150	52	72 *(71)*[a]	20
3	[EMEPy][$EtSO_4$]		$CH_3CH_2SO_3^-$	150	48	68	20
4	[NBu_4][BF_4]		BF_4^-	150	36	156 *(159–162)*[b]	120
5	[$NHex_4$][Br]	$N^+\!\left(nC_6H_{13}\right)_4$	Br^-	150	27	99 *(97–100)*[b]	72
6	[NEt_4][BTA]			35	20	102	82
7	[AB][OTf]		$CF_3SO_3^-$	40	17	48	31
8	[TBMP][OTf]		$CF_3SO_3^-$	150	40	119	79

[a] Reference 18. [b] Reference 19.

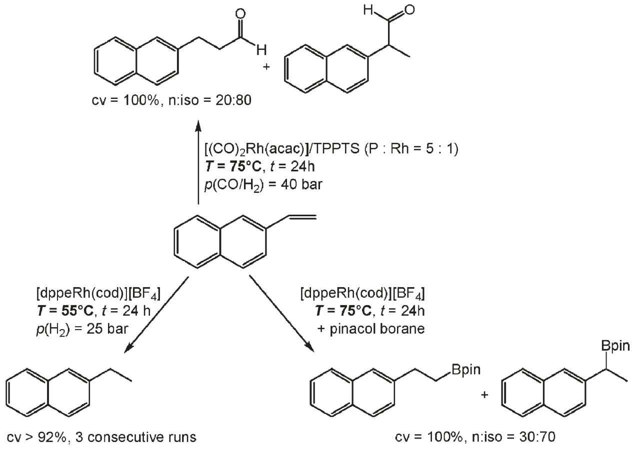
cell of 10 mL volume with a maximum operating pressure of 400 bar.† The so-called "first melting" method was used, where the solid sample is slowly heated at constant pressure and visually observed for the first signs of melting, *i.e.* loss of crystallinity and flow due to gravity. The method was verified by detection of the normal melting point of several of the compounds with the same technique.

First, we tested some imidazolium and pyridinium salts that would qualify as ionic liquids but with melting points significantly above room temperature. As seen in Table 1, entries 1–3, they experienced moderate melting point depressions in the range of 20–26 °C at 150 bar. In contrast, salts based on quaternary ammonium and phosphonium cations displayed much larger melting point depression with CO_2, reaching and surpassing ΔT_m of 80 °C in several cases (entries 4–8). Notably, the simple quaternary ammonium salt tetra-*n*-butyl-ammonium tetrafluoroborate [NBu_4][BF_4] with a normal melting point of 156 °C first encounters solid–liquid–vapor equilibrium at 36 °C at 150 bar of CO_2. This corresponds to a melting point depression of ΔT_m = 120 °C. After higher pressure, the temperature of melting decreases further, but less pronounced than in the lower pressure regime (ΔT_m = 129 °C at 335 bar). To our knowledge, such a dramatic decrease in the melting point of a simple solid organic compound with CO_2 is unprecedented in the literature

For [NEt_4][BTA] and the chiral IL [AB][OTf], the melting points in the presence of 150 bar CO_2 were too low to be determined with the setup used here (entries 6 and 7, respectively). In the phase equilibrium of a binary solid/gas mixture, the melting point depression is associated with the solid–liquid–vapor equilibrium line and is therefore pressure dependent. Indeed, reducing the CO_2 pressure brought the melting points into the experimentally accessible region also for these compounds. The simple tetraethylammonium based salt exhibited a remarkable ΔT_m = 82 °C at a CO_2 pressure of only 35 bar. This demonstrates that even gaseous CO_2 at low to moderate pressures can be used to generate ILs from organic salts and that it is possible to control the liquid range by adjusting the system pressure.

The ability to melt organic ionic compounds under CO_2 pressure opens the door to a larger number of applications and increases the number of structures and functional groups to be considered for use in ionic liquids. To demonstrate the potential of this approach, we have performed a series of catalytic reactions in a biphasic ionic liquid/scCO_2 system using [NBu_4][BF_4] to form a liquid catalyst phase (*cf.* Fig. 1). [NBu_4][BF_4] was chosen as a prototypical catalyst phase with a weakly coordinating anion. Scheme 1 lists the results of batch reactions of this biphasic system with 2-vinyl-naphthalene as the common substrate for hydrogenation, hydroformylation, and hydroboration. The reaction temperatures for some of the reaction were kept a full 100 °C below the normal melting point of the ionic solid. Visual inspection of the reaction mixtures in window-equipped high pressure reactors confirmed the presence of an ionic liquid/scCO_2 with the catalyst in the liquid phase as observed for related systems with standard ionic liquids.[15]

The well-known cationic rhodium phosphine complex [(cod)Rh(dppe)][BF_4] (cod = 1,5-cyclooctadiene, dppe = 1,2-bis(diphenylphosphino)ethane) was employed for the hydrogenation and hydroboration reactions. Quantitative hydrogenation was achieved at 55 °C and 125 bar with 25 bar of H_2 using 0.2 mol-% catalyst. The hydroboration had a somewhat lower conversion at 79% with a chemoselectivity to the borate of 100% and ratio of the linear (*n*) to the branched (*iso*) product of 30 : 70. The *in situ*



Scheme 1 Prototypical catalytic reactions carried out in molten $[NBu_4][BF_4]/scCO_2$ using the setup depicted in Fig. 1.

generated neutral hydroformylation catalyst of type $[HRh(CO)(PAr_3)_3]$ was solubilized in the liquid salt by using the ionic ligand $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS), leading to a 98% yield of aldehyde with the typical *n*/*iso* ratio of *ca.* 20 : 80. All these reactions were carried out under a standard set of benchmark conditions and remain un-optimized as to temperature, pressure, and catalytic system. Nevertheless, they adequately illustrate the range of catalytic transformations possible in this biphasic system using what would normally be an overlooked salt as an ionic liquid.

Finally, the possibility of catalyst recycling was briefly examined using the hydrogenation of 2-vinyl-naphthalene as test reaction. After a standard reaction time of 1 hour (two hours in the first run), the reactor content was extracted for 2.5 hours with CO_2 at 55 °C and 200 bar with approximate flow rates of 200 liter per hour (standard temperature and pressure). The CO_2 stream was passed through two cold traps held in dry ice/acetone to condense out the products. After the extraction step the reactor was depressurized leaving the re-solidified salt with the catalyst trapped within the matrix in the reactor. Conversions of 93–98% were achieved in the first three runs (0.25 mol-% catalyst at 55 °C and 125 bar with 25 bar of H_2) corresponding to an average turnover frequency of *ca.* 400 h^{-1} in each run. The conversion dropped markedly in the next two runs (run 4: 80%, run 5: 62%), indicating a certain loss of catalyst activity which may be attributed to accidental introduction of traces of oxygen or catalyst loss during this non-optimized procedure.

In conclusion, we have shown here that compressed carbon dioxide has the potential to control the transition between organic ionic solids and "ionic liquids" by inducing significant melting point depressions, some of which are the largest known to us in the literature. Lowering of melting points reaching ΔT_m = 120 °C were observed for simple ammonium and phosphonium salts, bringing them well within the definition of ionic liquids as characterized by melting points below 100 °C and even below room temperature. Rhodium complex catalyzed hydrogenation, hydroformylation, and hydroboration of 2-vinyl-naphthalene were performed using a CO_2-induced molten sample of $[NBu_4][BF_4]$ as liquid catalyst phase at temperatures in the range of 50–70 °C, *i.e.* 100 °C below its normal melting point. High rates and selectivities were observed and catalyst recycling was demonstrated for prototypical examples. This methodology has the potential to greatly expand the numbers of compounds and structures that can be employed as ionic liquids in reactive systems and other applications.

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Notes and references

† **Experimental note**: A small sample of the organic salt (approx. 200 mg) was transferred under argon to a small vial and put inside the autoclave (*V* = 10 mL). The solid was pressurized with CO_2 to induce melting and was purified by dynamic extraction with supercritical CO_2 (40 °C, 250 bar) to remove any trace volatile impurities. The sample was vented and re-solidified on the bottom of the vial to form a thin crystalline film. The autoclave was pressurized with CO_2 to the desired pressure and the temperature was raised slowly (0.5 °C/minute) until the film both became clear and began to flow with gravity. This was repeated until better than 1 °C reproducibility was achieved.

For the catalytic reactions, approximately 2 grams of the ionic salt, $[NBu_4][BF_4]$, 100 mg of 1-vinyl-naphthalene (1VN), and a 500 : 1 ratio of 1VN to Rh were added to a 10 mL autoclave. CO_2 was added until the total pressure was constant at 150 bar. For the hydroformylation reaction, CO_2 was used to induce melting of the ionic salt, and allow complexation of the Rh precursor and ligand for 4 hours. The mixture was vented and the reactants, synthesis gas, and CO_2 were added to initiate the reaction. All reactions were extracted with either with $scCO_2$ or a 5-fold excess of hexane and analyzed with GC-MS. Product recovery was found to be > 97% in selected examples.

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