

Ionic Liquids and Dense Carbon Dioxide: A Beneficial Biphasic System for Catalysis

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1. Introduction

Increasing ecological concerns alongside with economical considerations have triggered research into greener catalytic applications for quite some time. Green chemistry has become an important aspect in academia, but also industrial applications in bulk and fine chemistry raised requirements for more sustainable processes, as many legal framework conditions changed in the last decades, and cleaner, more efficient reactions often avoid costly reagents and process steps. One major aspect regarding greener reaction design concerns the avoidance of volatile organic solvents, as it is estimated that about 20 million tons of them are annually released to the atmosphere and contribute severely to air pollution.¹ Thus, extensive research was done during the past decade on investigating new solvents with peculiar properties,

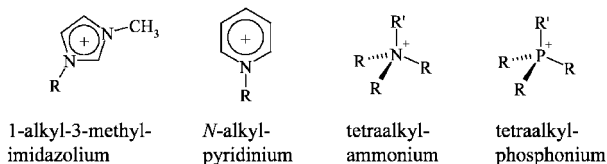
which not only offer a greener alternative to volatile organic solvents (e.g., by being less toxic or less volatile) but also

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Alfons Baiker, born in 1945, studied chemical engineering at ETH Zurich and earned his Ph.D. degree in 1974. After several postdoctoral stays at various universities, he finished his habilitation at Stanford University (California) and returned to ETH in 1980, where he started his own research group, focusing on heterogeneous catalysis and reaction engineering at the Department of Chemistry and Applied Biosciences. He moved up the ranks to become Full Professor in 1990. His research interests, documented in more than 830 publications in refereed journals and numerous patents, are centered on catalyst design and novel catalytic materials, mechanisms and kinetics of catalytic surface processes, asymmetric hydrogenation, selective oxidation, environmental catalysis, chiral surfaces, in situ spectroscopy, and the application of supercritical fluids and ionic liquids in catalysis. His goal is to further the scientific basis needed for developing environmentally benign chemical processes which make optimal use of raw materials and energy.

Cations



Anions

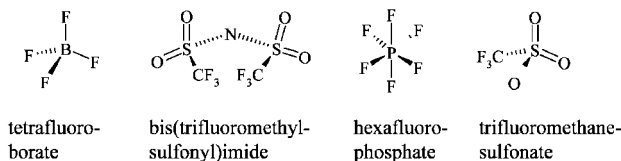


Figure 1. Some of the most commonly used IL cations and anions (halides excluded).

show some intrinsic advantages based on their chemical structure. One of these new reaction media are the exponentially growing substance class of ionic liquids (ILs), which have been known for almost a century but have only found considerable attention as promising solvents in the last two decades.² ILs are (at least partially organic) salts with a melting point below 100 °C and very low volatility due to their extremely low vapor pressures. Their structural diversity (the most important ions are depicted in Figure 1) allows tuning of their (solvent and other) properties and thus makes them highly promising candidates for tailored solvent applications, especially in biphasic reactions, as they are immiscible with numerous solvents. During the past decade, countless articles and several reviews and book sections have addressed the use of ILs in catalysis, offering to the interested reader a very suitable introduction to properties and applications thereof.^{1–12} A special consideration in the green context of using ILs needs the combination with subcritical and supercritical carbon dioxide (scCO₂), as numerous benefits

arise from combining these two peculiar solvents. Supercritical CO₂, due to its low critical pressure (73.75 bar) and temperature (31.0 °C) itself having received considerable attention as a green alternative to organic solvents and being nonflammable, nontoxic, and abundantly available, offers striking possibilities when combined with ILs. These benefits mainly arise from the fact that CO₂ is well soluble in ILs (much more than other common gases), while most ILs are virtually insoluble in CO₂, even at elevated pressures. This phenomenon allows designing very promising bi- and multiphasic reaction systems, where, for example, scCO₂ can be employed to efficiently extract reaction products out of the catalytically active IL phase, while leaving IL and (often poorly CO₂-soluble) catalyst behind. On the other hand, CO₂ can be employed as “carrier”, to bring reactants or gases into the IL phase, as it enhances the solubility of many gases and rather nonpolar substances in ILs. In this interplay of the two peculiar solvents scCO₂ and IL lies the greatest potential for green chemistry. ILs by themselves are not necessarily greener than conventional solvents,^{13,14} but in combination with CO₂ they offer intrinsic advantages in catalytic reactions compared to classical solvents, especially for separations. Some reviews published in the past decade already address this beneficial combination partially, e.g. by focusing on transition metal catalysis,¹⁵ phase behavior,¹⁶ more general supercritical fluid applications,³ gas-expanded liquids (including ionic liquids),¹⁷ separation phenomena,⁴ catalysis and ILs without CO₂,⁵ the partitioning behavior of the two phases,¹⁸ or the production of cyclic organic carbonates from CO₂ in ILs.¹⁹ As some of these reviews focus on a broader (or narrower) context, while others may be already somewhat outdated due to the fast research progress, we feel that it would be timely to summarize and discuss the progress made in the past decade on catalytic applications of combined IL/CO₂ systems. In this review, we give a broad overview on the numerous applications in bi- and multiphase catalysis, while addressing also fundamental properties of such IL/CO₂ systems. Not only is the focus set to pure solvent applications, but also the increasing possibilities of chemical CO₂-transformation in ILs are addressed (such as for the formation of cyclic carbonates), as this is a fast-growing field in a research world where sustainable carbon sources become increasingly attractive. Moreover, many ILs show, due to their chemical structure, a high affinity toward CO₂, e.g. by being able to form interactions via fluoro-substituents or amino-groups, which make them additionally interesting candidates for CO₂ activation or capturing processes. This review covers works of the past decade up to early 2010, with a more detailed focus on the very recent contributions not yet addressed in similar reviews^{3,6,15,17} and books.^{10–12}

2. Fundamental Properties of IL/CO₂ Biphasic Systems

2.1. Solubility Phenomena and Swelling

Whenever several (liquid, gaseous, or supercritical) phases are involved in a catalytic system, solubility phenomena play a crucial role. This is especially the case when a biphasic system such as IL/CO₂ is employed, where one phase (IL) is acting as the (stationary) catalytic phase, and the other phase (CO₂) takes part as carrier and/or extracting agent. The solubility of CO₂ in ILs should be sufficiently high in order to meet this requirement, while the solubility of IL in

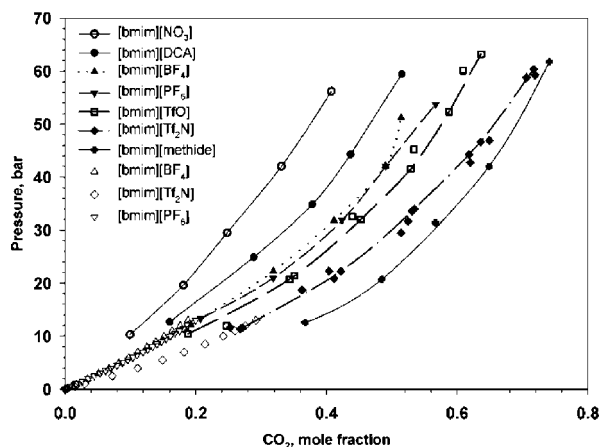


Figure 2. Effect of anion and pressure on the solubility of CO₂ in [BMIm]⁺ cation-based ILs at 40 °C. Reprinted with permission from ref 22. Copyright 2004 American Chemical Society.

CO₂ should be sufficiently low to avoid cross-contamination or catalyst loss, especially in continuous reaction mode. As shown in this section, this is the case for most IL/CO₂ systems. Apart from this, CO₂ dissolved in a (conventional) liquid phase tends to swell the liquid phase considerably, which in many catalytic reactions might cause dilution problems that hamper the reaction rate significantly. This effect is comparably low for ILs. In this section, fundamental properties of IL/CO₂ biphasic systems are summarized and discussed, which is a prerequisite for understanding such biphasic systems and important to be able to rationally design catalytic applications using ILs in combination with CO₂.

2.1.1. CO₂ Solubility in ILs

The solubility of CO₂ in ILs under low and high pressure has been extensively studied in the past decade. Brennecke's group initiated the research using view cells to measure the solubility of CO₂ in numerous ILs.^{20–23} Over the years, the effects of pressure, temperature, anion, cation, and impurities have been discussed. Figure 2 illustrates the effect of the IL anion and the pressure on the solubility of CO₂ in [BMIm]⁺ cation-based ILs at 40 °C.

At lower pressures, the concentration of CO₂ in the liquid phase strongly increases with rising CO₂ pressure (typically up to 60–80 bar). At higher pressures, the increase of the solubility with the pressure is rather small when the pressure is higher than 100 bar (for temperatures < 80 °C). This strong difference between the low and high pressure regimes is rather unusual. At lower pressures, the addition of CO₂ is rather facile, as interactions between the IL anion and the CO₂ molecules (and hence the inclusion of CO₂) do not change significantly the conformational alignment of the IL. At higher pressures, the IL/CO₂ liquid phase is already saturated with CO₂, and the inclusion of CO₂ is thus much more difficult, as it requires changes in the structural alignment of the IL. The concentration of CO₂ in IL at high pressures is mainly controlled by the number of CO₂ molecules which are able to fit around the anion without disturbing significantly the structure of the IL,^{24–27} in other words, the cavities in the IL are already occupied by CO₂, and no further insertion of CO₂ is possible without a conformational rearrangement of the IL and the energetic expense going along with it. A more detailed discussion of such molecular interactions is given in section 2.5.

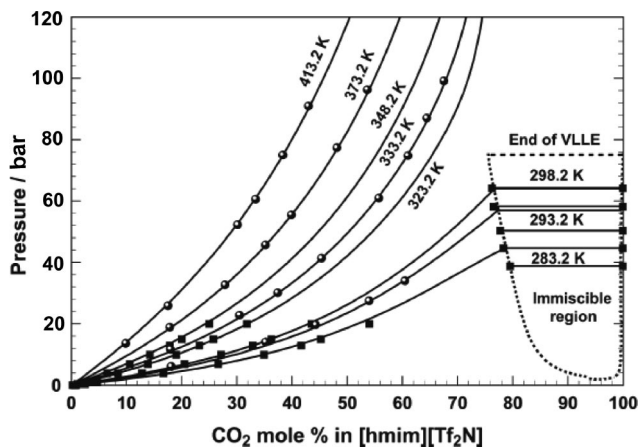


Figure 3. Solubility of CO₂ in [HMIm][Tf₂N] at different temperatures (lines represent EoS calculations; symbols represent experimental data). Reprinted with permission from ref 28. Copyright 2009 American Chemical Society.

In general, the solubility of CO₂ in ILs increases with increasing pressure and decreases with increasing temperature. The temperature effect on the solubility is depicted in Figure 3 for [HMIm][Tf₂N], as calculated and compared with experimental data by Yokozeki and Shiflett.²⁸ Compared to other gases, CO₂ has a high solubility in ILs such as [HMIm][Tf₂N], which led to promising investigations using ILs for gas separations and CO₂ capturing processes^{28–32} and later also to task-specifically tailored ILs for CO₂-capturing via covalent chemical bonding, as a very recent communication by Brennecke's group shows, in which the authors report for their anion-functionalized IL even higher CO₂-uptake capacities than those of aqueous amine absorbents.³³ Also very recently, Carvalho et al. reported an exceptionally high CO₂ solubility in the phosphonium-based ILs [THTDP][Tf₂N] and [THTDP]Cl, exceeding those of imidazolium-based ILs with the same anions in terms of maximum CO₂ solubility (on a molar fraction basis).³⁴ Based on their findings, the authors concluded that the ILs investigated in their study exhibit the highest CO₂ solubility observed so far in the absence of specific chemical interactions (as present in specially tailored ILs for CO₂ capturing, containing amine groups or similar substituents). Note that the high solubility of CO₂ in ILs is only true regarding the mol % solubility, and not the mass % solubility, which is generally rather low. Therefore, ILs with a high molecular weight (such as [THTDP][Tf₂N]) exhibit naturally a higher CO₂ solubility (on a molar fraction basis) than ILs with low molecular weight.¹⁷

The choice of the anion has a strong effect on the solubility of CO₂. ILs with nonfluorinated anions, such as [NO₃][−] and [DCA][−], lead to low CO₂ solubility, while the anions containing fluoroalkyl groups, [OTf][−], [Tf₂N][−], and [methide][−] lead to a high CO₂ solubility in ILs.²² The choice of the cation has a smaller effect on the solubility, as, for example, variations of the alkyl groups of imidazolium-based cations with [Tf₂N][−] anion have relatively little influence on the solubility of CO₂ in such ILs (the solubility increases only slightly with the alkyl chain length),²² as well as for the same imidazolium cations with [PF₆][−] and [BF₄][−] anions.²³ The substitution of a methyl group in C₂ (from [BMIm] to [BMMIm]) does not change much the solubility.²³ However, partially fluorinated alkyl chains on the imidazolium cation combined with a [Tf₂N][−] anion have led to an increase of the CO₂ solubility in such ILs.³⁵

Research on IL/CO₂ binary systems still remains motivated, as some specific constraints remain not completely understood. [HMIm][Tf₂N] is under particular attention, as it has been chosen by IUPAC as the reference IL (IUPAC Project 2002-005-1-100).^{36,37} In general, the solubility of CO₂ in ILs with a [Tf₂N][−] anion is fairly high, and Shiflett and Yokozeki even showed that, at subcritical temperatures, [HMIm][Tf₂N] can be saturated with CO₂ (at 79.5 and 76.2% CO₂ in the IL phase at 4 and 25 °C, respectively) and then a liquid–liquid equilibrium is possible between an IL liquid phase and a pure CO₂ liquid phase, as predicted by equation-of-state (EoS) models.³¹ Often there are large discrepancies of the CO₂ solubility in a specific IL from one publication to another, and mainly the amount of impurities (most often chloride and water) in ILs was considered to be responsible. Nevertheless, some variation in the results could not be completely explained by the initial amount of impurities in the IL.³¹ This is important, as, even for the apparently simple measurement of CO₂ solubility in IL binary systems, the results under high pressure are not always consistent; it is not trivial to measure such parameters exactly, as slow mass transfer can cause equilibria to take considerable time to be established in such highly viscous liquids. Thus, any surprising results must be taken carefully. As an example, an unexpected result has been presented by Hutchings et al. concerning the high solubility of the IL [THTDP]Cl in CO₂.³⁸ In these experiments a view cell was used to observe at which pressure and temperature the IL/CO₂ system was biphasic or monophasic. The authors observed a solubility of the IL in pure CO₂ of up to 7 mass %. Recently, Carvalho et al. tried to reproduce these data without any success.³⁹

Predictive models are under development to avoid in the future a large number of unnecessary experimental syntheses and analyses of ILs. As an example, an EoS model was employed to investigate the solubility of CO₂ in a series of ILs including [EMIm][Tf₂N], [HMIm][Tf₂N], and [DMIm][Tf₂N] at sub- and supercritical temperatures up to 250 bar.⁴⁰ The EoS model showed accurate prediction of solubility at lower pressures (below 100 bar), but limited correlation at higher pressures was found. At 70 °C, the model predicted a high solubility of [HMIm][Tf₂N] in the scCO₂ phase (0.13% at 170 bar) and a mixture critical point at ~400 bar, which are both far from reality. Hence, at present, EoS models are not yet able to predict accurately the equilibrium IL/CO₂ binary systems under high pressure.

Another modeling approach was taken by Ji and Adidharma, who used heterosegmented statistical associating fluid theory (SAFT) to represent the CO₂ solubility in a series of imidazolium-based [BF₄], [PF₆], and [Tf₂N] ILs for selected pressures up to 200 bar.⁴¹ The authors compared their model with various experimental data and found in most cases good agreement, especially in lower pressure regimes and temperatures between 10 and 142 °C.

The NIST ILs database (ILThermo) is providing fundamental thermodynamic and transport properties of numerous pure ILs as well as the binary and ternary systems (including ILs/CO₂) and offers a very suitable and flexible tool for initial prediction and evaluation of such systems on a broad scale.⁴² Additionally, Vega et al. very recently published an elaborated review on the modelization of ILs and the solubility of gases therein, thoroughly discussing different models and creating perspectives for future applications.⁴³ With such resources, it is possible to evaluate and partially predict the

Table 1. Henry's Law Constants (bar) for Gases in [BMIm][PF₆]²¹

| gas | <i>T</i> = 25 °C | <i>T</i> = 50 °C |
|-------------------------------|--------------------|--------------------|
| CO ₂ | 53.4 ± 0.3 | 81.3 ± 0.5 |
| C ₂ H ₄ | 173 ± 17 | 221 ± 22 |
| CH ₄ | 1690 ± 180 | 1310 ± 290 |
| O ₂ | 8000 ± 5400 | 1550 ± 170 |
| H ₂ | undetected (>1500) | undetected (>1500) |

solubility behavior of CO₂ in ILs chosen for catalytic and other applications involving biphasic IL/CO₂ systems.

2.1.2. Henry's Law Constants of Gases in ILs

Of course not only the CO₂ solubility in ILs is crucial for such biphasic systems, but also the solubility of other gases (mostly reactants) needs to be taken into account. For lower pressures, the Henry's law constant is used to compare the solubility of gases in different ILs. The Henry's constant *H* corresponds to the slope in the linear relationship between gas concentration (mol/mol) in the liquid phase and equilibrium gas pressure, *p*_i = *H*_i*c*_i (a higher Henry's law constant means lower solubility). In practice, Henry's law constants are found by calculating the slope of the isotherm in the limit of low solute concentrations. Gases with large dipole moments, such as water, with quadrupole moments, such as CO₂, or with the ability to maintain specific interactions (e.g., hydrogen bonds) show a high solubility in ILs, while the solubilities of other, nonpolar gases correlate well with their polarizability.⁴⁴ Carbon dioxide is (on a mol % basis) highly soluble in ILs and more soluble than many other usual gases, as shown in Table 1.

While at higher pressures (>100 bar) the solubility is mainly attributed to molecular interactions and molecular organization of CO₂ molecules around the anions,^{24–27} Camper et al. showed that at lower pressures (<few bar) the regular solution theory is able to model the solubility of gases in ILs with empirical constants that depend only on the gas.⁴⁵ Regular solution theory is useful to predict the phase behavior of solutions without molecular polarity or specific interactions, which could indicate that, at lower pressures, specific molecular interactions (as hydrogen bonds) are not the driving force for the solubility of gases in ILs. However, a thorough study by Prasad and Senapati indicates that gas–IL anion interactions play a crucial role for the solubility of polar gases (such as SO₂) in ILs, while for apolar gases (such as N₂) regular solution assumptions apply.²⁵ For CO₂, the authors state that while it does not have an overall dipole, it is at least easily polarizable, and interactions with certain IL anions would lead to an induced dipole accompanied by a geometry distortion from linear to slightly bent. The authors calculated an approximate error of 2% for CO₂, if these molecular interactions are neglected and only regular solution theory is applied to describe the solubility of CO₂ in certain ILs with fluorinated anions.

Henry's law constants have been measured experimentally for many ILs, and a systematic analysis of hundreds of ILs was simulated as depicted in Figure 4 using COSMO-RS (conductor-like screening model for real solvents), which was designed for the inclusion of solvent effects in quantum chemical calculations. More details of such models are nicely explained by Klamt et al.⁴⁶ Experiments and model calculations found the same trend for the Henry's law constants of CO₂ in ILs with four anions [FEP][−] > [Tf₂N][−] > [PF₆][−] > [BF₄][−], while the cations have much smaller influence on the solubility of CO₂ in ILs.⁴⁷

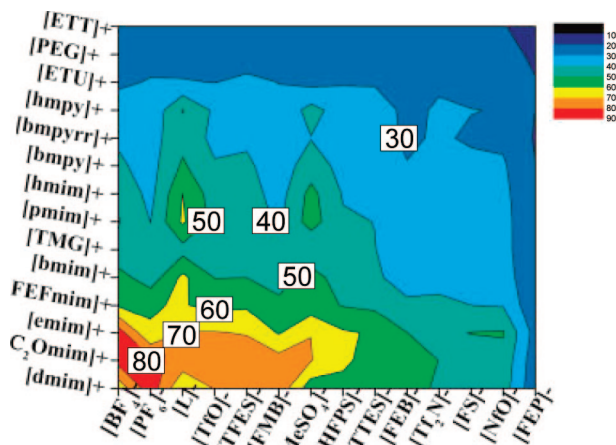


Figure 4. Henry's law constants of CO₂ (in bar) in 196 ionic liquids predicted by the COSMO-RS method at 298.15 K. Reprinted with permission from ref 47. Copyright 2008 American Institute of Chemical Engineers.

A similar approach using a refined COSMO-RS method (including chemical potential terms) to study more accurately the CO₂ solubility in various ILs for CO₂ storage applications was performed later by Maiti.⁴⁸ The results of this method are very consistent with experimental data for a wide range of temperatures and pressures and predict some interesting phenomena that are not yet experimentally verified. For example, the authors predicted based on their calculations that all-functionalized-guanidinium cation- and [BF₄][−] anion-based ILs should possess ca. 80% higher (molality scale) solubility for CO₂ than the best imidazolium-based ILs experimentally investigated so far.

COSMO-based thermodynamic models, such as that used by COSMOthermX (advanced software tool based on quantum chemistry calculations), allow the determination of gas solubilities in ILs and comparison of such a model with literature data obtained from the IUPAC database.⁴⁹ The authors explain that COSMOthermX is capable of qualitatively predicting gas solubilities in ILs. Some effects, such as the effect of the size of the alkyl chain on the cation in 1-alkyl-3-methylimidazolium ILs, can be fitted by the model, while for instance the effect of the addition of a methyl group in the C2 position of the imidazolium ring is wrongly predicting the increase of the CO₂ solubility in [HMIm][Tf₂N]. More importantly, the strong effect of the anion ([NO₃][−], [BF₄][−], [OTf][−], [PF₆][−], and [Tf₂N][−], with [BMIm]⁺) could be generally calculated. Such modelizations are not perfect but are able to give important inputs for a better understanding of the system and also to avoid unnecessary (screening) experiments. The potential number of ILs is tremendous, and thus testing all the properties of all ILs would be a preposterous task to complete. A more useful approach is to develop models to understand ILs and anticipate the correct experiments to perform. Many models are under development, and the dilemma is often the balance between the simplicity and the accuracy of the model. Unfortunately, simple models cannot be used to simulate IL/CO₂ binary systems, since these systems show in many cases a nontrivial behavior. One example is the discrepancy between a relatively high solubility of CO₂ in ILs under low pressure, the sharp pressure increase at a certain maximum CO₂ concentration, and the extremely poor solubility of ILs in CO₂. Details of modeling the CO₂ solubility in ILs have recently been summarized and discussed comprehensively by Vega et al.⁴³

2.1.3. Swelling (Volume Changes)

There is almost no volume expansion when CO₂ is added to ILs (with 10 mol % of CO₂ in IL), which is in contrast to the case of most conventional solvents.²³ Regarding an equimolar dissolution of CO₂, only very few solvents (such as water) are expanding less than ILs, and some liquid polymers or crude oil mixtures exhibit the same (low) swelling behavior. Most of the classical solvents expand much more. A thorough discussion of this, and a classification of the swelling behavior of solvents, can be found in the comprehensive review on gas-expanded liquids by Jessop and Subramaniam.¹⁷ The strong difference in behavior between IL/CO₂ and conventional liquid/CO₂ has been nicely shown by comparing the solubility of CO₂ in [BMIm][PF₆] and in 1-methylimidazole. At 85 bar, the IL expands only by 18% (0.69 mol fraction CO₂) while 1-methylimidazole shows a volume increase of 103%.²⁰ CO₂ molecules in ILs are mainly localized in cavities of larger size than those spontaneously forming in the neat IL,⁵⁰ which explains why ILs are not swelling while CO₂ is being dissolved in them. And after that, when the void spaces are filled with CO₂, even under high pressure, almost no more CO₂ can dissolve in the IL.²⁰

2.1.4. Solubility in Ternary Systems

While IL/CO₂ binary systems are intensively studied to measure fundamental parameters, the case of ternary (or more component) systems are studied with parsimony. To be able to understand how IL/CO₂ binary systems should be used in catalytic processes, it is crucial to anticipate the effects of other chemicals, which of course cannot be neglected in their role as, for example, reactants and are often present in significant concentrations.

2.1.4.1. CO₂ Solubility in the IL Phase of Ternary Systems. For many catalytic reactions, water might be necessary (especially in enzymatic reactions), and in any case, ILs are often extremely hygroscopic; thus, many applications are performed in the presence of a significant concentration of water. Water does not show any strong influence on the solubility of CO₂ in [BMIm][PF₆] while it is considered an impurity for the calculation of the CO₂ solubility with a mass fraction of water up to 1.6%.⁵¹ In the case of [BMIm][BF₄], the solubility of CO₂ in IL was not perturbed by a high concentration of water (50 mol %). Moreover, *in situ* infrared spectroscopy also showed that the presence of water does not strongly decrease the molecular interaction between the anion and CO₂,⁵² while at subcritical temperature, similarly, the presence of water does not appear to have any strong effect on the solubility of CO₂ in [BMIm][Tf₂N] at 25 °C.²² However, a phenomenon was observed when working with a high water concentration in some ILs at subcritical temperature; CO₂ can induce a phase separation of ILs (e.g., [BMIm][BF₄], [BMIm][PF₆], [PMMIm][Tf₂N], and others) and water.⁵³

Later, the three-phase region of the [BMIm][BF₄]/water/CO₂ ternary system (with two liquid phases, including an IL rich phase and a water rich phase) was studied in more detail, and the solubility of CO₂ in the IL rich phase appeared to be smaller than that in the wet ILs.⁵⁴ As CO₂ is less soluble in water than in ILs, this result could be expected, especially when noticing that the mole fraction of water in the IL-rich phase is still over 65%, even under a pressure of 160 bar of CO₂.

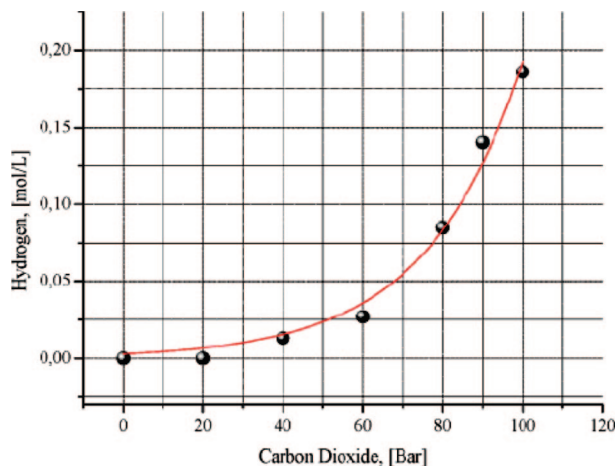


Figure 5. Solubility of hydrogen in [EMIm][Tf₂N] at a constant partial pressure $p(\text{H}_2) = 30$ bar as a function of the added CO₂ pressure as determined by high-pressure ¹H NMR spectroscopy ($T = 297 \pm 2$ K; concentrations below the estimated detection limit of 0.01 mol L⁻¹ were set to zero). Reprinted with permission from ref 58. Copyright 2004 American Chemical Society.

Similar to the water case, using a high concentration of an organic cosolvent (e.g., methanol), a phase separation of IL–methanol by CO₂ is observable due to the decrease of the solvent strength of methanol while CO₂ is dissolved in it, and then the IL is not fully soluble in the methanol phase anymore. With a higher concentration of IL (50 mol %), it is not possible anymore to observe the liquid/liquid-phase separation by addition of CO₂.⁵⁵ For catalytic applications, the effect of a smaller concentration of organic molecules dissolved initially in IL could also be interesting. Kühne et al. investigated the effect of 10–50 mol % of 1-(4-isobutylphenyl)ethanol, 1-phenylethanol, or 4-isobutylacetophenone in [BMIm][BF₄] under CO₂ pressure.⁵⁶ The solubility of CO₂ in the liquid phase ([BMIm][BF₄] + solute) is higher for the ketone than for an alcohol, which could be explained by specific interactions between solute and anion. Adding an alkyl group to the solute is increasing the CO₂ solubility, which could be related to the increase of free space (and apolar groups) available for the CO₂ molecules around the IL.

2.1.4.2. Enhanced Solubility of a Ternary Component in the IL Phase. While the understanding of the solubility of CO₂ in ILs is necessary for the understanding of catalytic reactions using IL/CO₂ binary systems, the solubility of reactants in ILs is crucial in the design of such reactions. As depicted in Table 1, the solubilities of H₂ and O₂ are fairly low in many ILs, and the low concentration of gases such as hydrogen could be a limitation for catalytic applications using ILs. For example, H₂ shows a solubility of 0.0777 mol kg⁻¹ in [BMIm][PF₆] at 40 °C and 90 bar.⁵⁷ The addition of CO₂ to an IL–H₂ mixture strongly improves the solubility of H₂ in the IL phase, as shown in Figure 5.⁵⁸ The possibility to increase the concentration of H₂ (or other poorly soluble gases) in ILs by adding CO₂ to the system is clearly a strong advantage compared to the use of solely H₂ under higher pressure.

Also, the solubilities of oxygen and methane were investigated in [HMIm][Tf₂N] at 25 °C, and the experiments clearly show the positive effect of mixing O₂ or methane with CO₂ to improve their concentration in the IL phase.⁵⁹ The effect cannot be predicted by a regular solution theory model and indicates that ILs are not behaving in the same

way as usual organic solvents. More experiments and modeling are necessary to fully understand these mixed gases systems, as this phenomenon is particularly useful and crucial for catalytic applications but could also be disadvantageous for the potential application of ILs in the field of gas separation.

2.1.4.3. IL Solubility in the CO₂ Phase. One of the key properties of ILs is their negligible vapor pressure. Likewise, ILs are practically insoluble in pure scCO₂ under mild conditions,⁶⁰ which makes these binary systems ideal for extraction/separation processes of nonvolatile molecules. Thus, the problem is to know if any cosolvent can make ILs soluble in the CO₂ phase, which could contaminate the extracted products. Only few works have been performed so far to answer that question.

The first communication showing the dramatic increase of the solubility of ILs in the CO₂ phase while adding a cosolvent was focusing on [BMIm][PF₆]/CO₂ in combination with usual solvents (including ethanol, acetone, and *n*-hexane).⁶¹ In order to analyze the solubility of the IL in the supercritical phase, CO₂ with the cosolvent was slowly flown over the IL at constant concentration of the cosolvent, pressure, and temperature. The IL was precipitated in a trap after depressurization and analyzed by gravimetric techniques and UV/vis spectroscopy. With this experiment, Wu et al. reported a solubility of the IL in the supercritical phase in the case of ethanol and acetone at a pressure of 120–150 bar, a temperature of 40–55 °C, and a cosolvent concentration of 15–30 mol %. *n*-Hexane did not show any strong enhancement of the IL solubility in the sc phase under these conditions, but in the case of ethanol and acetone as cosolvent these experiments detected IL in the sc phase (on the scale of 10⁻⁴ mol/mol). The authors then concluded that the cosolvent effect was strong when the polarity of the cosolvent was high. Later, the same group continued the work by studying also the [BMIm][BF₄]/CO₂/ethanol ternary system, as well as some quaternary systems containing [BMIm][PF₆]/CO₂ with two cosolvents (ethanol, acetone, *n*-hexane).⁶² [BMIm][BF₄] appeared to be much more soluble in the sc phase than [BMIm][PF₆], in the case of CO₂/ethanol, showing an impressive solubility of 0.86 mol % at 40 °C, 150 bar, and 30 mol % of ethanol as cosolvent. [BF₄]⁻ is known to interact strongly with CO₂, which could explain why [BMIm][BF₄] would be more soluble than [BMIm][PF₆]. Later, the same authors analyzed more precisely the phase behavior of [BMIm][PF₆]/CO₂/acetone at 40 °C under similar conditions.⁶³ As for other systems, CO₂ can induce a phase separation between IL and acetone and create a liquid/liquid/scCO₂ three phase system. But more intriguing, under 150 bar of CO₂, forming a two phase system, the solubility of [BMIm][PF₆] was measured up to 2.5 mol % in the top phase. The increase in pressure from 70 to 150 bar only increased the solubility of IL in the top phase from 1.9 to 2.5 mol %. This high solubility of several ILs in the sc phase is surprising, but the authors explain it by the high acetone concentration in the top phase (more than 30 mol %) and by the fact that the top phase is not supercritical or vapor, but rather a liquid phase with acetone exhibiting a strong cosolvent effect. It should also be noted that both phases of the system have comparable composition (60/33.5/6.5 and 56/31.9/2.5 mol % of CO₂/acetone/[BMIm][PF₆] for the bottom phase and top phase, respectively, at 150 bar and 40 °C).

Aki et al. also worked on similar systems, including [BMIm][PF₆]/CO₂ with cosolvents (methanol, acetonitrile, or acetophenone).⁶⁴ To measure the composition of the individual phases under high pressure, a view cell with three sampling valves was employed, and the quantification of different components in the sample was obtained by UV/vis spectroscopy for the IL and by GC for the others components. However, many disagreements appeared between this work⁶⁴ and other reports.^{61–63} First, no IL was detected in the sc phase, even under similar conditions to those for the case studied previously by Wu et al.^{61–63} Some of the differences between the results of these works could be explained by impurities (most probably water) or possible reactions between PF₆[−] and water, such as hydrolysis.

It is difficult to quantify the concentration of an IL in a sc phase, and very few works published so far show only low solubility of ILs in scCO₂ with or without cosolvent. It has been possible to reproduce neither the data from Hutchings et al. presenting a high solubility of [THTDP]Cl in CO₂³⁸ nor the solubility of ILs in the sc phase even with cosolvents.^{61–63} For catalytic applications so far, a possibly too high solubility of ILs in the supercritical phase did not occur neither in repeated batch nor in continuous flow systems. Thus, it can be concluded that in IL/scCO₂ biphasic systems the dissolution of IL in the CO₂ phase is not a major problem that has to be dealt with; due to their ionic character, ILs seem to have an intrinsic insolubility in scCO₂ and thus are perfect candidates as a stationary phase for biphasic continuous reactions or corresponding extraction purposes.

2.1.4.4. Equilibrium between the Liquid Phases. As already introduced earlier, an increasing concentration of CO₂ in ILs can produce a phase separation and create a vapor–liquid–liquid equilibrium (VLLE). Some examples of already measured VLLE can be found in the literature for water with many ILs,⁵³ for usual organic solvents,^{55,65–68} and other organic compounds.^{69–73}

The distribution of selected model solute compounds between various ILs and CO₂ was studied for a range of conditions (*p*, *T*) by Planeta, Roth, et al. during the past few years.^{74–78} The authors developed a special technique for determining the infinite-dilution solute partition coefficients for a wide range of temperatures (40–80 °C) and pressures (normally 80–233 bar) using capillary column chromatography with scCO₂ as mobile phase and the IL of interest as stationary liquid phase.⁷⁷ While extending their studies, they were able to correlate the partition coefficients in terms of linear solvation energy relationships (LSERs) and thus provide a starting point for general conclusions.⁷⁸ Among the investigated ILs, mostly imidazolium-based species were in focus, including [BMIm][PF₆],⁷⁷ [BMIm][BF₄],⁷⁸ [BMIm][Tf₂N],⁷⁴ and [BMIm][MeSO₄],⁷⁶ which all showed a similar partitioning behavior for most of the 18 model solute compounds tested. In many cases, the authors found a strong dependence of the partitioning coefficient on the density of CO₂, which allows a certain tunability of the partitioning behavior. This effect on the partitioning coefficient changed it up to 1 order of magnitude, as in the example of [BMIm][Tf₂N].⁷⁴ For the only non-imidazolium-based IL tested, [THTDP]Cl, the partitioning behavior was considerably different, e.g., leading to a strong sensitivity on hydrogen bond formations with solutes capable of that.⁷⁵ Nevertheless, the possibility to change the partitioning coefficient of IL/CO₂ systems by adjusting the density of CO₂ (which is dependent on the pressure and temperature)

offers great potential to influence reaction equilibria (e.g., by removing products) and, thus, may improve certain catalytic applications significantly.

2.2. Melting Point Depression

Unfortunately, not all ILs are liquid at room temperature. For a specific application, only a limited number of ILs may be actual liquids and therefore used as solvents. When pressurized CO₂ is added to ILs, it induces a melting point depression (MPD), which increases the number of potential ILs suitable for a particular experiment. The first example of this effect was reported by Kazarian et al., who investigated [HDMIm][PF₆] using ATR-FTIR spectroscopy to observe the liquid (at 50 °C and 50 bar of CO₂) and solid (at 50 °C without CO₂) phase under high pressure.⁷⁹ Later many ILs have been tested by Scurto and Leitner, who also showed the potential of this phenomenon in catalytic applications with [NBu₄][BF₄] as liquid solvent. The melting point of [NBu₄][BF₄] is 156 °C without CO₂, while the solid–liquid transition temperature decreases to 36 °C under 150 bar of CO₂.⁸⁰ Recently, Cimpanu et al. from Leitner's group employed the CO₂-induced melting point depression to synthesize catalytically active Rh nanoparticles in ammonium-based ILs without the use of additional solvents.⁸¹ CO₂ was not only used as liquefier agent to induce MPD but was also able to extract the precursor ligands from the remaining IL/nanoparticle suspension. Furthermore, it increased the H₂ concentration in the IL, which was important for the hydrogenation test reaction (see section 2.1.4.2).

Alas, not all ILs show such a strong decrease of the melting point. While some salts based on quaternary ammonium and phosphonium cations show a strong decrease of the melting point (by ~80 °C), imidazolium and pyridinium salts have a much lower depression of approximately 20 °C. So the utility of a normally solid tetraethylammonium based salt should be reconsidered, as it becomes a RTIL (room temperature IL) with only 35 bar of CO₂. Even in cases where mixed gases (CO₂ + CO/H₂ or H₂) are required for a catalytic process, a MPD of the IL was observed. The authors applied this phenomenon in hydrogenation reactions of vinyl-naphthalene at 55 or 75 °C. More recently, this systematic analysis was continued to obtain the melting point depression of a large number of ILs induced by CO₂.⁸² The authors explained the melting point depression phenomenon by the very low melting temperature and negative deviations to Raoult's law of CO₂. Some examples of the melting point depression for tetrabutylammonium and phosphonium compounds and quaternary ammonium bromide are given in Table 2. The main trends observed are that [Tf₂N][−] anions give a high MPD, asymmetric ammonium cations have lower melting points with CO₂ pressure than the symmetric ones, and straight chain alkyl groups have a lower decrease of the melting point due to CO₂ than similar branched salts. In the case of ILs with imidazolium and pyridinium cations, the anion has a more prominent effect than the cation on the melting point depression of the ILs. Melting point depressions of some imidazolium-based ILs are also listed in Table 2. A very recent publication by Serbanovic et al. nicely summarizes the current knowledge about CO₂-induced melting point depressions in ILs.⁸³ The authors concluded that the most probable determining factor for the melting point depression is the dissolution of CO₂ in the lattice structure of the solid, which induces a disruption of the crystal structure. Furthermore, they found that the nature of

Table 2. Melting Point Depression (MPD) Observed under CO₂ Pressure for Various ILs^a

| compound | <i>T_m</i> (°C) | pCO ₂ (bar) | MPD (°C) | ref |
|---|---------------------------|------------------------|----------|-----|
| [PBu ₄][Br] | 103.5 | 150 | 42.4 | 82 |
| [NBu ₄][Br] | 102–105 | 150 | 23.3 | 82 |
| [NBu ₄][Tosyl] | 71.5 | 150 | 33.8 | 82 |
| [NBu ₄][BF ₄] | 156 | 150 | 119.8 | 82 |
| [NBu ₄][PF ₆] | 244–246 | 150 | <i>b</i> | 82 |
| [NBu ₄][TfPF ₃] | 54 | 34.8 | 36.7 | 82 |
| [NPr ₄][Br] | 100–101 | 150 | 18.8 | 82 |
| [NHex ₄][Br] | 99 | 150 | 71.2 | 82 |
| [NHep ₄][Br] | 90 | 150 | 40.2 | 82 |
| [NOct ₄][Br] | 97.5 | 150 | 37.6 | 82 |
| [MTOA][Br] | 57.2 | 40 | 38.2 | 82 |
| [BDMMA][Br] | 48.52 | 50 | 23 | 82 |
| [EMIm][PF ₆] | 60 | 147 | 35 | 83 |
| [BMIm][Cl] | 69 | 150 | 10.2 | 83 |
| [BMIm][OTf] | 64 | 150 | 34 | 83 |
| [BMIm][Tosyl] | 67 | 150 | 25.8 | 83 |
| [BzIm][Tosyl] | 105 | 160 | 13 | 83 |
| [BzIm][OTf] | 73 | 170 | 20 | 83 |

^a The values given for MPD are the difference from the melting point under ambient conditions (*T_m*) compared to the melting point at a given CO₂ pressure (pCO₂).^{82,83} ^b Beyond upper limit of equipment used in that study.

the anion and its interaction with the carbon dioxide molecule seems to have a crucial influence on melting behavior, while the cation either hinders or facilitates that interaction. For catalytic applications, this melting point depression effect might have considerable consequences, as it broadens the range of available ILs to be used as solvents.

Nevertheless, a limitation of MPD by dissolving CO₂ in ILs is the low diffusion of CO₂ in ILs (under liquid and solid states) and then the probable long time necessary to melt ILs using this method.

2.3. Viscosity

In most catalytic applications the mass transport properties of the reaction medium, such as viscosity, are essential, and some ILs are known to be extremely viscous.⁸⁴ It is thus necessary to measure the effect of CO₂ on the viscosity of ILs.

The effect of dissolved CO₂ on the viscosity of ILs was measured first by Liu using a falling-ball viscometer with [BMIm][PF₆]/methanol mixtures.⁶⁸ With this first quantitative measurement it was already pointed out that using CO₂ would be an attractive way to reduce the viscosity of ILs in many applications. Adding 9.3 bar of CO₂ is enough to decrease the viscosity of [BMIm][PF₆] from 92.3 to 50.8 cP at 40 °C. Later, another group found slightly different results, but with similar trends.⁸⁵ Overall, a fast decrease of the IL viscosity is generally observed when adding CO₂. Furthermore, while the viscosity depends strongly on the temperature for pure ILs, for IL/CO₂ biphasic systems (pressure > 50 bar) the viscosity is only marginally sensitive to temperature and pressure.⁶⁸

To determine the viscosity of ILs under high pressures of CO₂, Laurenczy and Dyson simply watched the descent of a small stainless-steel ball (analogous to the falling-ball viscometer) in ILs using a NMR sapphire tube. The viscosity of two ILs dropped to around 22 cP at 55 bar and 25 °C (under subcritical conditions), while the viscosities were 381 and 54 cP without CO₂ for [BMIm][PF₆] and [BMIm][Tf₂N], respectively.⁸⁶

More recently, the viscosity of IL/CO₂ mixtures ([RMIm][Tf₂N], with the alkyl chain corresponding to R = ethyl,

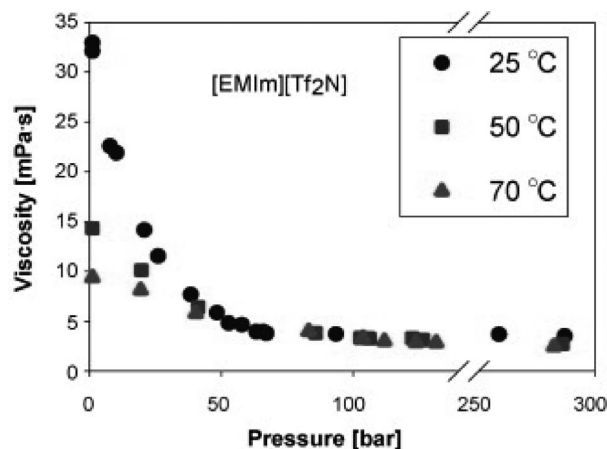


Figure 6. Viscosity of [EMIm][Tf₂N] with CO₂ pressure at 25, 50, and 70 °C. Reprinted with permission from ref 87. Copyright 2009 Elsevier Ltd.

n-hexyl, and *n*-decyl) at 25, 50, and 70 °C and up to high pressure (287 bar) was investigated.⁸⁷ As observed previously, the pressure and temperature had only a small effect under a CO₂ pressure higher than 50 bar. Moreover, at lower pressure (below 50 bar) the viscosity increased with the size of the alkyl chain of the imidazolium cation. The effect of CO₂ on the viscosity is illustrated in Figure 6 for [EMIm][Tf₂N] at several temperatures.

So far, only a few works have been published on the viscosity of ILs under high pressure of CO₂. It appears, as for the solubility of CO₂ in ILs, that for pressures higher than 50–60 bar the variation is minor. Nevertheless, it must be noted that only few ILs have yet been investigated under this point of view, and no work has been done on ILs which are solid without CO₂. Thus, it can be assumed that the decrease in viscosity caused by CO₂ is a general phenomenon in ILs, but further specific investigations are necessary to clarify the reasons for this behavior.

2.4. Diffusion Coefficient

As for viscosity, the analysis of diffusion phenomena (e.g., by means of the diffusion coefficients) is crucial to provide an insight on the mass transport properties in ILs. A lag-time technique can be used to determine the gas diffusivities through an IL film. Diffusion coefficients of CO₂ and other gases in many ILs ([DESMIm][OTf], [EMIm][Tf₂N], [EMIm]-[BETI], [BMIm][PF₆], [EMIm][OTf], [THTDP]Cl) were measured at low pressure, and the diffusion of CO₂ appeared to be on the scale of 10⁻¹⁰ m² s⁻¹, which is 1 or 2 orders of magnitude smaller than in usual organic solvents.^{88,89} The diffusion of molecules inside an IL phase can hence be a limiting factor in many applications. Similar trends are found, and as expected, the diffusion of CO₂ in IL increases with decreasing viscosity. Later, further ILs (with phosphonium-based cations) were tested. The gas diffusivity appears to be inversely proportional to the viscosity, with an average power of 0.35 and 0.6 for the phosphonium-based and imidazolium-based ILs, respectively, which indicates that the viscosity–diffusivity relationship varies for different classes of ILs, and viscosity cannot be used to compare the diffusivity of CO₂ in different ILs.⁹⁰ Diffusivity was found to be mainly dependent on IL and solute molar volumes and the viscosity. The authors also mention that the free volume could be a measure for diffusivity in ILs. Hou and Baltus presented an extensive study on solubility and diffusivity

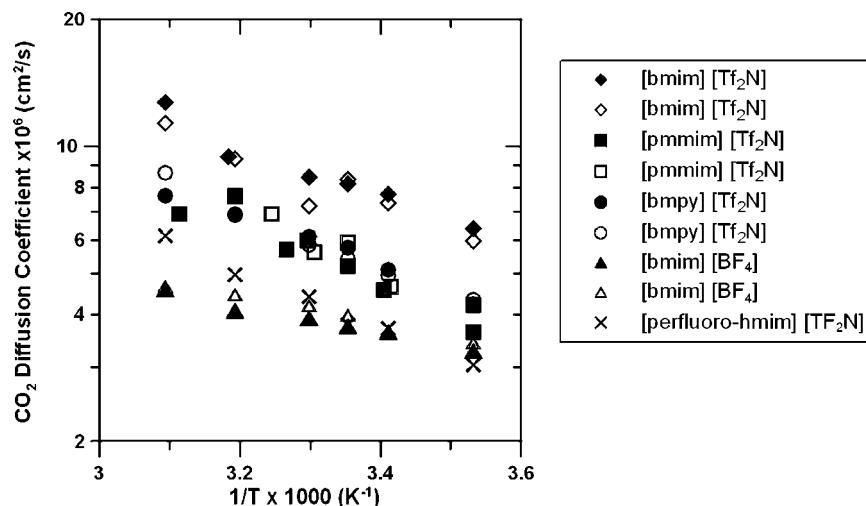


Figure 7. Semilogarithmic plot of D_{CO_2} vs $1/T$. Different symbols with the same ionic liquid represent results from different ionic liquid samples with different film thicknesses. Reprinted with permission from ref 91. Copyright 2007 American Chemical Society.

on five ILs (four different cations with $[\text{Tf}_2\text{N}]^-$ and $[\text{BMIm}][\text{BF}_4]$) at low pressure for temperatures between 10 and 50 °C using the transient thin liquid film method.⁹¹ The evolution of the diffusion coefficient of CO_2 in the five ILs with the temperature is shown Figure 7.

Trying to develop a model to fit the diffusion of CO_2 in ILs, the authors included as the main parameters the viscosity, the mass, and the density of the IL, as well as the temperature. At higher pressure, Shiflett and Yokozeki measured the diffusivities of CO_2 in $[\text{BMIm}][\text{PF}_6]$ and $[\text{BMIm}][\text{BF}_4]$ for pressures up to 20 bar using a gravimetric microbalance.³⁰ Within this range of pressure, the diffusion tends to increase with pressure; nevertheless, the increase of temperature by 10 °C has a bigger impact on the diffusion of CO_2 in IL. More recently, ATR-FTIR spectroscopy also showed the possibility to measure the diffusion of CO_2 in ILs by following the evolution of the concentration of CO_2 in the IL phase after changing the pressure.⁹² The advantage of this method is that not only CO_2 in the IL phase but also several solutes can be followed simultaneously. The diffusion of CO_2 under high pressure (100 bar) was found to be much faster than that at lower pressure (20 bar).⁹³ This finding is supported by an investigation using molecular dynamics simulations, where Bhargava et al. showed that the diffusion coefficient of CO_2 in $[\text{BMIm}][\text{PF}_6]$ should increase from 2 to $14.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in this pressure range.⁹⁴

Despite the lack of data available in the literature, high pressure CO_2 is undoubtedly able to decrease viscosity and improve the diffusion of molecules inside ILs. Many processes, including catalytic applications, can thus be improved significantly by adding CO_2 under moderate or high pressure. However, as not only the viscosity is affected by the CO_2 pressure, but also other effects (such as the partitioning behavior between the two phases) have to be taken into account, it is not necessarily beneficial for every reaction in ILs to be performed under CO_2 pressure.

Similar to mass transport phenomena, it is important to know for catalytic applications about the thermal conductivity of such biphasic systems. The thermal conductivity plays an important role in reactions where considerable heat evolves or is consumed. Isothermal conditions can only be reached in systems where heat transfer is sufficiently fast, which is particularly important for oxidation and hydrogenation reactions. Tomida et al. investigated the thermal

conductivities of imidazolium-based IL/ CO_2 mixtures using a transient short-hot-wire cell.⁹⁵ They found, on one hand, that impurities had only a very small impact on the thermal conductivity, while they may have a crucial influence on the viscosity. For instance, the Cl^- content of $[\text{BMIm}][\text{BF}_4]$ of 421 ppm compared with a sample with 4580 ppm showed only a difference of 1.2% in thermal conductivity. Likewise, for $[\text{BMIm}][\text{BF}_4]/\text{CO}_2$ and $[\text{BMIm}][\text{PF}_6]/\text{CO}_2$ binary systems, as measured by the authors for temperatures between 21 and 61 °C and CO_2 pressures up to 200 bar, the differences in thermal conductivity were insignificant. Thus, it can be assumed that the thermal conductivity in IL/ CO_2 biphasic systems should not be significantly different compared to that in monophasic IL systems.

2.5. Molecular Interactions between CO_2 and ILs

Due to their structural diversity, ILs have many possibilities for specific interactions on a molecular level, including Coulomb interactions and hydrogen bonds. A comprehensive review on the possibilities of ILs to interact on a molecular level and the possibilities thereof was recently published by Weingärtner.⁹⁶ As mentioned before, many ILs are able to interact relatively strongly with CO_2 , especially when their anions are fluorinated or when CO_2 -philic groups (such as amines) are present in their structure. IR and Raman spectroscopy are particularly sensitive to molecular interactions and thus offer a suitable tool to investigate such phenomena. Kazarian et al. first used ATR-FTIR spectroscopy to analyze the interaction of CO_2 and ILs ($[\text{BMIm}][\text{PF}_6]$ and $[\text{BMIm}][\text{BF}_4]$) at 68 bar and 40 °C in the IL phase.²⁴ The careful observation of the IL spectra with and without CO_2 provided information on the molecular organization and interactions, and the authors showed that CO_2 mainly interacts with the anion, while the CO_2 bending mode shape can indicate the strength of the interaction between anion and CO_2 . Comparison between IR spectra of different ILs demonstrates that $[\text{BF}_4]^-$ is a stronger Lewis base in its interaction with CO_2 than $[\text{PF}_6]^-$. This finding was applied later by our group for investigating the IL-catalyzed cycloaddition reaction of CO_2 with epoxides²⁶ (*vide infra*). Later, changes in the structure of the ILs (e.g., $[\text{BMIm}][\text{PF}_6]$) while CO_2 was dissolved in them were also investigated using Raman spectroscopy; there, only the change on the

gauche/trans configuration of the butyl chain in the cation could be detected, which shows that CO₂ dissolved in such ILs does not change much their conformational structure.⁹² This result is confirmed by Shi and Maginn, who investigated the solubility of water and CO₂ in [HMIm][Tf₂N] by atomistic Monte Carlo simulations.⁹⁷ They found that CO₂ does not perturb the IL conformation until very high CO₂ concentrations are reached. Furthermore, the authors were able to calculate isotherms, Henry's law constants, and partial molar enthalpies of absorption which are in very good agreement with available experimental data. At the highest CO₂ concentrations, they report slight conformational changes, including a small stretching of the cation's alkyl chain and a minor increase in cation–anion distance.

Lu and Liotta from Eckert's group used a solvatochromic indicator (*N,N*-dimethyl-4-nitroaniline) to spectroscopically investigate the Kamlet–Taft dipolarity/polarizability parameter (π^*) as well as the microviscosity and local dielectric property of [BMIm][PF₆] under a range of temperature and CO₂ pressure.⁹⁸ The authors found that the dipolarity/polarizability of [BMIm][PF₆] undergo only minimal reduction at a constant temperature in the presence of CO₂ over a wide pressure range. The same finding was concluded for the local dielectric constant of [BMIm][PF₆]/CO₂ around the probe molecule. Only for the microviscosity of [BMIm][PF₆]/CO₂ they found a significant decrease by a factor of 6.5 when increasing the CO₂ (partial) pressure from 0 to 68 bar at 35 °C. The authors concluded that addition of CO₂ is not influencing significantly the polarity of [BMIm][PF₆] due to a preferential solvation effect of the IL with a polar solute.

Molecular simulations have also been used to analyze the interactions of CO₂ with ILs. The molecular dynamic simulations of [BMIm][PF₆] and [BMMIm][PF₆] with 10 mol % of CO₂ (5–6 bar at 25 °C) confirmed that CO₂ is mainly interacting with the anion,²³ thus supporting the results obtained by spectroscopy. Under supercritical conditions, the analysis of the simulated [BMIm][PF₆]/CO₂ system (45 °C and 200 bar) also described similar organization of CO₂ in ILs.⁵⁰ More recently, *ab initio* molecular dynamic simulations made it possible to observe the Lewis acid–base interaction of the fluorine atoms donating a partial electronic charge to the carbon atom of CO₂.⁹⁹ The interactions between CO₂ and 14 common anions of room temperature ILs were subsequently calculated using DFT by Bhargava and Balasubramanian.¹⁰⁰ Their results agree well with infrared spectroscopy conclusions (showing a distortion of the CO₂ molecule away from linearity). Furthermore, the binding energy of CO₂ interacting with fluorinated anions is inversely correlated with the solubility of CO₂ in the ILs. For a more thorough understanding of this topic, Maginn recently reviewed the current status of molecular simulations of ILs, including the dissolution of solutes therein, and summarized the main problems and potential these simulations are facing.¹⁰¹

An interesting improvement nowadays in such calculations is to include a third (or more) component(s) in the IL/CO₂ system. For instance, gas mixtures in ILs were studied by Monte Carlo simulations with generally good results.²⁷ However, it was found that the addition of CO₂ would not lead to any enhancement of the solubility of O₂ in [HMIm][Tf₂N]. This is in contradiction with the experimental results reported by Brennecke's group.⁵⁹ Another interesting example is the adsorption of CO₂ on the TiO₂ rutile surface in [BMIm][PF₆] reported by Yan et al.¹⁰² They found by MD simulations that CO₂ would rather adsorb on the rutile

(110) surface than disperse in the surrounding bulk [BMIm][PF₆]. Similarly, Sieffert and Wipff analyzed the [BMIm][PF₆]/hexene interface with molecular dynamic simulations and the diffusion of rhodium complexes as well as the effect of CO₂ molecules at this interface.¹⁰³ These examples demonstrate the advantage of MD simulations to understand at a molecular level complicated systems such as catalytic reactions in ILs. However, as discrepancies with experiments and unexpected results may occur, it is (if possible) still necessary to support these calculations with experimental work (such as spectroscopy). Too shallow models or neglected parameters (e.g., impurities) may otherwise hamper the usefulness of such simulations and lead to wrong conclusions. Apart from aiming at understanding a specific system, simulations can also be used for screening purposes.

In fact, on binary IL/CO₂ systems, simulations are now able to be used for screening and to test hundreds of anion–cation combinations and thus anticipate good candidates for given tasks. For instance, [HMIm][FEP] was predicted to be a good IL for absorption of CO₂.^{47,104}

There is still a need for both experimental data and simulations describing molecular interactions between several gases (including CO₂) dissolved in ILs, the cosolvent effect on both liquid and gas phases, molecular organization at the interface, and the structure of the fluids on a solid surface, only to mention a few, to be able to design better catalytic systems. However, as the many excellent works published in the last years show, simulations are increasingly able to support and even replace experimental works in this field, which will even more be the case in the future.

2.6. Acid–Base Properties

For many catalytic reactions, the acid–base properties of the reaction medium play an important role, e.g. by tremendously influencing the product selectivity. Some reactions, such as esterifications or aldol reactions, are even catalyzed by proton transfer. Hence, the Brønsted (and/or Lewis) acid properties of ILs were subject to many investigations and are (among other solvent properties) summarized in several recent review articles.^{5,105–108} It is however not trivial to describe and quantify Brønsted acidity for ILs, as most of the common approaches use water-based definitions and scales, including the well-known pH and aqueous pK_a. More general ways of quantification use, for instance, gas phase proton affinities. A thorough discussion on the acidity of ILs and the underlining definitions can be found in a review by Johnson et al.,¹⁰⁷ while another recently published review focuses on basic ILs and their applications.¹⁰⁸ Not surprisingly, impurities such as water, halides, and IL precursor species may change the acid–base properties of ILs considerably.⁵ This has to be taken into account when using ILs for reactions which are strongly influenced by the acidity of the reaction medium. Commonly used ILs have by themselves some acid–base properties, as most anions such as [OTf][–] and also halides are conjugated bases of strong acids. But also the cations can exhibit some intrinsic Brønsted acidity. For example, dialkylimidazolium cations have a removable proton (on the carbon between the two nitrogen atoms) which can act as a very weak acid, yielding isolable basic carbenes.¹⁰⁷ The generation and application of such imidazolium-based carbenes was recently reviewed by Zhang and Chan.¹⁰⁹

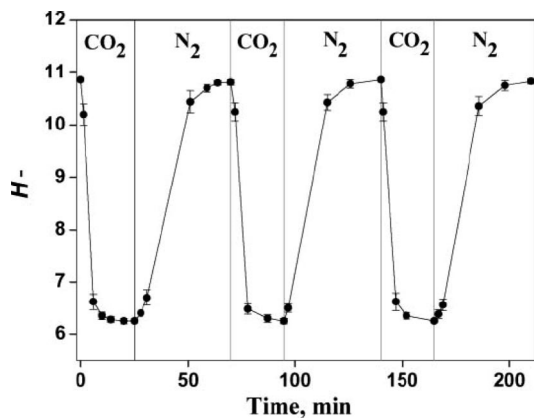


Figure 8. Hammet function (H_-) value of choline chloride/urea as a function of time during three cycles of treatment with CO_2 at 25 °C followed by N_2 at 60 °C. Reprinted with permission from ref 108. Copyright 2008 Royal Society of Chemistry.

Apart from the intrinsic acid–base properties present in ILs, there are especially designed protic (Brønsted acidic) ILs, which due to carbonic acid functions or added halide acids and/or polynuclear metallic anions (such as chloroaluminates) sometimes exhibit high acidity.⁵ In a similar approach, also ILs with basic functions (e.g., amino groups) are available, yet in a lesser extent. However, by using such amino-functionalized ILs in combination with CO_2 , new possibilities arise in connection with their acid–base properties. CO_2 itself exhibits considerable Lewis acidity and readily forms carbonic acid in water and alkylcarbonic acids with alcohols as a function of pressure,¹⁷ as well as Lewis acid–base adducts (and ionic species such as carbamates) with amines.¹¹⁰ Hence, the addition of CO_2 can lower the basicity of such basic ILs, while this effect is completely reversible when the CO_2 is removed by bubbling N_2 through the IL. The thus obtained switchable basicity has high potential for certain reactions, e.g. by influencing the solubility of a product, which ideally separates from the reaction mixture.¹¹¹ The efficiently working switchable basicity of an IL is depicted in Figure 8, showing the Hammet function (H_-) changes for the binary IL choline chloride/urea. With more common ILs, however, the CO_2 -induced change in acidity/basicity seems much less prominent, as for instance Kamlet–Taft parameter measurements on $[\text{BMIm}][\text{PF}_6]$, $[\text{BMIm}][\text{Tf}_2\text{N}]$, and other ILs indicate.¹¹² On the other hand, as mentioned before, specific Lewis acid/base interactions between CO_2 and, e.g., fluorinated IL anions lead to high solubilities of CO_2 in those ILs. This effect is, however, not completely explainable with traditional (aqueous) acid/base definitions and trends.¹¹³ In general, it seems assumable that common ILs without acidic or basic functionalities are not greatly influenced by CO_2 -addition in their acidity/basicity. ILs with basic functions, however, can have significant Lewis acid/base interactions with CO_2 and thus can be employed for switchable basicity solvents and/or CO_2 absorption. For applications where a high acidity is desirable, CO_2 is not offering significant contributions. In these cases, it is more viable to use tailored ILs with acidic functionalities (either on the IL itself or by addition of suitable acid species).

3. Applications in Catalysis

3.1. Extractions from ILs Using CO_2

Using ILs as solvents for chemical reactions leads to the same challenges concerning product recovery as encountered in classical solvent applications. Extractions with water work only for hydrophilic products, and under the condition that the IL is not miscible with water. This is of course not always the case, and partial solubility of some ILs in water adds to this problem. The same problems of cross-contamination occur in many cases when using organic solvents. Distillation, another commonly used technique for product separation, has the disadvantage of high energy and technical requirements and is only suitable for rather volatile and/or thermally stable products. Regarding these limitations, scCO_2 seems to offer a promising alternative to the before mentioned approaches. It is in many cases efficient in extracting a broad range of compounds out of ILs while maintaining extremely low cross-contamination, due to the fact that most ILs are virtually insoluble in CO_2 .

The idea of using CO_2 for extracting products out of the IL phase was first postulated by Blanchard et al., who successfully and near-quantitatively extracted naphthalene (as model nonvolatile organic solute) from $[\text{BMIm}][\text{PF}_6]$ at 40 °C and 138 bar, leaving behind the pure IL.⁶⁰ Later, Blanchard and Brennecke extended their studies and published a work investigating the recovery rates of several aromatic and aliphatic solutes from $[\text{BMIm}][\text{PF}_6]$ with highly promising results.¹¹⁴ The results of the extraction experiments are depicted in Figure 9.

The authors were able to recover in all cases at least 95% of the solutes. Interestingly, intermolecular interactions between the organics and $[\text{BMIm}][\text{PF}_6]$, although influential in the solubility of the solute in the IL, did not limit the degree to which a solute could be separated. However, the required amount of CO_2 differed considerably depending on the solute. Solute that are solids at room temperature (phenol, benzoic acid, and benzamide) required the largest amounts of CO_2 for 95% solute recovery. For liquid solutes (benzene and hexane families), the authors found a correlation between the amount of CO_2 necessary for 95% extraction and the dipole moment of the solute.

Sakellarios and Kazarian used infrared spectroscopy to study the partitioning of the model solute benzil (1,2-diphenylethane-1,2-dione) between $[\text{BMIm}][\text{PF}_6]$ and high-pressure CO_2 in order to investigate the partitioning between these two phases and further rationalize the feasibility of such extraction systems.¹¹⁵ This approach has the advantage that it not only allows calculation of the partitioning coefficient but also enables direct monitoring of the process by means of ATR- and transmission IR spectroscopy. Furthermore, this method yields insight into molecular interactions present as well as impurities, possibly influencing the partitioning behavior.

Brown et al. first used the scCO_2 extraction approach for a catalytic application in IL, namely the asymmetric hydrogenation of tiglic acid in $[\text{BMIm}][\text{PF}_6]/\text{H}_2\text{O}$ with high enantioselectivity (>85% ee) and conversion (>97%) using a $\text{Ru}(\text{O}_2\text{CMe})_2(\text{R-tolBINAP})$ catalyst at room temperature.¹¹⁶ The system could be reused without significant loss in activity and selectivity four times after subsequent scCO_2 extraction steps, while the catalyst remained completely in the IL phase.

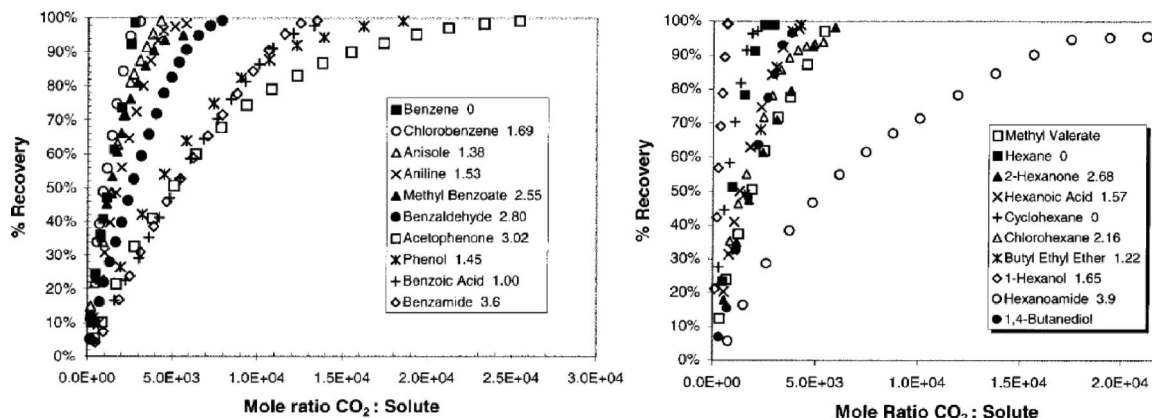


Figure 9. Extraction of aromatic (left) and aliphatic (right) solutes from [BMIm][PF₆] with CO₂ at 40 °C and 138 bar. Solute dipole moments (Debye) are given in the figure captions. Reprinted with permission from ref 114. Copyright 2000 American Chemical Society.

Similarly, Bortolini and co-workers used scCO₂ to efficiently extract the epoxidation products of several electron-deficient olefins from imidazolium-based ILs (with [BF₄][−], [PF₆][−], [OTf][−], and [Tf₂N][−] anions).¹¹⁷ For all the ILs employed, the products could be extracted almost quantitatively.

Another example of product separation by scCO₂ was presented by Yoon et al., who studied Heck coupling reactions of styrene and iodobenzene in [BMIm][PF₆] catalyzed by PdCl₂ and Et₃N.¹¹⁸ They found a crucial effect of the IL water content on their reaction, as a water content of more than 50 ppm decreased the catalyst activity considerably, which could not be explained sufficiently. However, as studies in our group indicated, scCO₂ is able to remove considerable amounts of water from [BMIm][PF₆] and other ILs upon continuous extraction, despite the relatively low solubility of water in scCO₂.¹¹⁹ This was not considered in the studies of Yoon et al., who successfully performed recycle experiments but after every cycle added fresh IL with fixed water content.

Furthermore, an equally crucial effect of the water content on a catalytic reaction was found by our group while studying the hydrogenation of acetophenone in [BMIm][PF₆] and other ILs catalyzed by IL stabilized Pd nanoparticles.¹²⁰ Water was causing a degradation of the [PF₆][−] anion, which led to the formation of HF and thus had a disadvantageous influence on the reaction. However, by scCO₂ extraction it was easily possible to remove HF (and also water), and the initial activity and selectivity of the catalyst could be reestablished by only this extraction step.

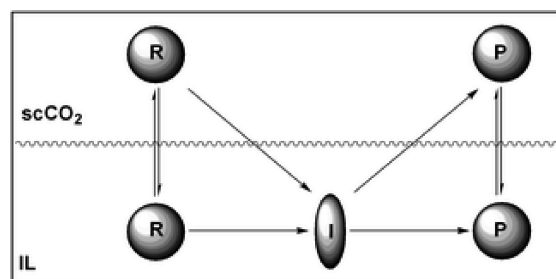
More examples of such extraction applications in reactions performed in ILs are summarized in a comprehensive review just recently published by Roth.¹⁸

3.2. Multiphase Catalysis

3.2.1. Biphasic (IL/CO₂) Batch Reactions

The first example of a biphasic IL/CO₂ batch system was actually reported by Jessop et al. in Noyori's group already in 1994, for their production of dimethyl formamide from scCO₂.¹²¹ Although the authors did not use the term "IL", the biphasic system consisting of dimethylamine, CO₂, H₂, and catalyst readily formed an IL phase at the bottom of the reactor. Formic acid catalytically generated from CO₂ and H₂ reacted with the amine and formed the salt dimethylammonium dimethylcarbamate, which became a liquid phase under the CO₂ pressure present. The catalyst remained in

Scheme 1. Schematic Illustration of a scCO₂/IL Biphasic System^a



^a R = reactant, P = product, I = polar intermediate (e.g. carbamate). Reprinted with permission from ref.¹²² Copyright 2001 Royal Society of Chemistry.

this IL phase while only the product dimethyl formamide was extracted into the scCO₂ phase.

Liu et al. later introduced the concept of such a biphasic IL/CO₂ catalytic reaction by successfully employing [BMIm][PF₆] for the hydrogenation of alkenes at 50 °C and the reaction of amines in IL/scCO₂ to produce formamides at 80 °C with a conversion of 100% and a selectivity of >99%.¹²² The basic concept is depicted in Scheme 1. Reactants and products are present in both phases, while their individual solubility (partitioning behavior) can be influenced by adjusting the CO₂ pressure (normally, a higher CO₂ pressure leads to a higher solubility in the CO₂ phase). The reaction occurs in the IL phase (including the creation of polar intermediates, e.g. carbamates), which ideally remain in the IL phase. Due to their possible polar or even charged nature and their short lifetime together with the slow mass transfer, this is also often the case. The product which is formed afterward is or can be extracted into the CO₂ phase and removed from the catalytic system, e.g. by extraction or continuous streaming.

Later, Bösmann et al. analyzed the hydrovinylation of styrene using the IL phase to immobilize organometallic catalysts (e.g., Wilke's catalyst) at 25 and 40 °C.¹²³ The catalyst was active in all ILs tested, but the efficiency appeared strongly dependent on the IL anion. The most promising results were obtained using [Al(OC(CF₃)₂Ph)₄] and [BARF] (tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) anions. An effect of the cation on the reaction was also observed, with better enantiomeric excess (ee) using [MBPy] instead of the more usual [EMIm] cation. ScCO₂ was used to recycle the IL-based catalyst system, while after three to four batchwise cycles the catalyst was rapidly deactivated.

Then the authors investigated this reaction under continuous flow conditions during three days and observed a stable activity of the catalyst with only a small decrease of the ee during the continuous reaction. Continuous flow reaction studies are discussed in more detail in the next section.

Hydroformylation reactions in IL/scCO₂ biphasic systems were studied by several groups in the past decade. Many of these works were performed partially using continuous flow conditions and are discussed in more detail in the next section. A recent investigation based only on batch reactions addressed the question which parameters need to be optimized in order to tune the system into the best conditions.¹²⁴ Scurto et al. carefully studied the hydroformylation of 1-octene with a rhodium-triphenylphosphine catalyst in a [HmIm][Tf₂N]/scCO₂/CO/H₂ system. The multiphase equilibria and mixture critical points between reactant, products, and IL with CO₂ and syngas (CO/H₂) were analyzed as well as the variation of viscosity of the IL phase, which decreased with the increase of CO₂ pressure, and the self-diffusion coefficient of IL and octane, which increased with the increase of CO₂ pressure. The authors pointed out that kinetics, phase behavior, and mass transport all are key parameters to elucidate such IL/CO₂ biphasic systems. In the case of the hydroformylation of 1-octene, the addition of CO₂ is facilitating the reaction by decreasing the viscosity and increasing the diffusion in the IL phase, up to a critical point. Afterward, the pressure of CO₂ is high enough to extract most reactant and product into the CO₂ phase and thus has a negative effect on the reaction.

Hou et al. investigated the oxidation of 1-hexene in biphasic scCO₂/[BMIm][PF₆] and compared the results obtained with the monophasic oxidation at 60 °C.¹²⁵ The initial composition for each experiment consisted of 1.5 g of [BMIm][PF₆], 0.032 g of PdCl₂, 0.25 g of CuCl₂, 1 mL of 1-hexene, and 2 mL of methanol in a 18 mL batch reactor. The conversion with and without IL at 125 bar total pressure (using an initial O₂ pressure of 21 bar) was very similar while the selectivity (toward 2-hexanone) increased from 70–75% to 85–90% when using an IL phase. Furthermore, the selectivity increased with time in the case of the biphasic system while it decreased in the monophasic system. Moreover, the selectivity also increased while increasing the pressure in the case of the biphasic system.

The positive or negative effect of scCO₂ in ILs for the enantioselective hydrogenation of unsaturated acids catalyzed by chiral transition metal complexes (e.g., Ru-BINAP complexes) was reported by Jessop and co-workers.¹²⁶ Depending on the substrate, the enantioselectivity of the hydrogenation was correlated with the pressure of hydrogen; thus, adding scCO₂ to the system should be beneficial while the enantioselectivity is known to be improved by increasing the H₂ partial pressure. The effect of CO₂ was shown to lead to an even better effect on the selectivity than the simple increase of the H₂ pressure. Similarly, the addition of a cosolvent (alcohol, toluene) to the IL could also reveal an improvement in the enantioselectivity of the hydrogenation. The study of the hydrogenation with different ILs revealed a limited influence of the IL cation on the reaction, and the results tend to conclude that viscosity and enantioselectivity are not directly correlated, and “many solvent parameters” should be taken into account for a better understanding of these catalytic systems. Apart from the results of the catalytic system itself, the solubility of the ruthenium-BINAP catalyst was analyzed by UV/vis spectroscopy, and the catalyst

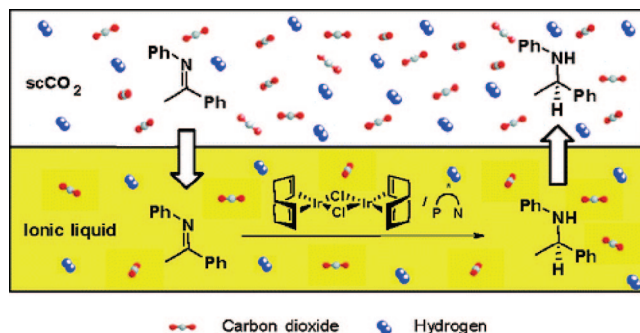


Figure 10. Biphasic reaction using a homogeneous catalyst in the IL phase. Reprinted with permission from ref 58. Copyright 2004 American Chemical Society.

showed a non-negligible solubility in the supercritical phase of 2.6×10^{-5} mol per mol in pure CO₂ at 205 bar and 40 °C, while adding H₂ to the system led to some antisolvent effects but did not completely eliminate the solubility of the catalyst in the supercritical phase.

As depicted in Figure 10, Solinas et al. analyzed the enantioselective hydrogenation of *N*-(1-phenylethylidene)-aniline using cationic iridium complexes with chiral phosphinooxazoline ligands in biphasic IL/scCO₂ systems to obtain (*R*)-phenyl-(1-phenylethyl)amine.⁵⁸ The first important conclusion in this work is the increased solubility of H₂ in ILs while adding scCO₂ (measured by high-pressure NMR spectroscopy) as well as the decrease of the viscosity of the ILs phase. At 25 °C (below the critical temperature of CO₂), the increase of H₂ is drastic; the concentration of H₂ in [EMIm][Tf₂N] is below 0.01 mol L⁻¹ at 30 bar H₂ and increased to 0.14 mol L⁻¹ with 30 bar H₂ and a total pressure of 120 bar after addition of CO₂. This effect of CO₂ appeared significant when the pressure of CO₂ was 80 bar or more. Secondly, an effect of the anion of the ILs was reported, showing an ee increase from 30% with [BF₄]⁻ to 78% with [BARF]⁻. This effect was explained by the decrease of the coordinating ability of the IL anion.

The enantioselective hydrogenation of methyl- α -acetamido cinnamate in [BMIm][BF₄] with a chiral rhodium catalyst was studied by Shariati et al.¹²⁷ [BMIm][BF₄] was chosen for the study as the solubility of H₂ in this IL is low, which can increase the enantioselectivity. A negative effect of CO₂ (at 5 and 35 bar) on the conversion and the enantioselectivity of the hydrogenation realized with 20 bar of hydrogen was found and explained by the decrease of the concentration of reactant and catalyst due to the presence of a high concentration of CO₂ in the liquid phase. The conversion decreased from 94.2% without CO₂ to 25.8% with 35 bar of CO₂. As the mole fraction of CO₂ at 25 °C and 32 bar in [BMIm][BF₄] is 0.41 (± 0.02),²² the dilution could explain a decrease of conversion. On the other hand, in such complicated systems, a macroscopic perspective is probably not sufficient, because the positions of CO₂ molecules are very probably specific and the knowledge of molecular interactions would give a better understanding of the positive and negative effects of CO₂ on such biphasic catalytic systems. Moreover, the authors follow the conversion and selectivity of the hydrogenation based on the partial pressure of CO₂, while a more accurate way would perhaps be to use the concentration of H₂ and CO₂ in the liquid phase, although this is more difficult to achieve accurately and could lead to false results.

The polymerization of styrene, using aluminum chloride (AlCl₃) as initiator, was studied in several solvents, including

scCO₂, [BMIm][PF₆], and a scCO₂/[BMIm][PF₆] biphasic system.¹²⁸ The authors showed that the use of IL and scCO₂ (at 50 °C and 200 bar) resulted in better yields than the use of the other organic solvents.

Similarly, Ballivet-Tkatchenko and co-workers studied the palladium-catalyzed dimerization of methyl acrylate to yield dimethyl dihydromuconates in a mixture of imidazolium-based ILs with [BF₄][−] anion and scCO₂.¹²⁹ The authors reported no loss in activity under biphasic conditions (compared to a pure IL system), and the selectivity toward head-to-tail dimers also remained very high (>98%). Above 150 bar, the product showed excellent solubility in the CO₂ phase, and thus, the authors concluded that the CO₂ phase could act as a reservoir for products and reactants, as the catalyst remained in the IL phase, and hence, this process could possibly be extended to continuous reaction mode.

Another interesting application of an IL/CO₂ biphasic system was reported by Zhao et al., who studied the electro-oxidation of benzyl alcohol to benzaldehyde while making use of the good electrolyte properties of ILs.¹³⁰ As they analyzed several parameters, the authors found an increase of the Faradaic efficiency (FE) and selectivity toward benzaldehyde at pressures below 93 bar. At higher pressures, the activity decreased. From the two ILs tested, [BMIm][BF₄] appeared to be a more suitable reaction medium than [BMIm][PF₆], affording higher activity. The products could be conveniently extracted by scCO₂ after the reaction, and the IL was completely reusable.

While some studies summarized so far simply show the possibility to perform a specific reaction in IL/scCO₂ biphasic systems, others are going further and try to demonstrate what the key parameters of such systems are. Solubility, viscosity, diffusion, mass transfer, temperature, pressure, effect of cosolvent or antisolvent in the CO₂ phase, degradation of the catalyst, molecular interactions, choice of IL (anion and cation), and reaction time are some of the parameters which must be taken into account. Batch reactor studies (monophasic in IL or biphasic) are a first step to investigate and rationalize a reaction system and to evaluate its potential for a future continuous reaction mode. While the advantages of a real biphasic (batch or continuous) reaction system are often tremendous (in the ideal case, the CO₂ phase acts as a reservoir for reactants and as a sink for products), in reality not all reactions gain benefits from this approach. For instance, if a reactant has a much higher solubility in the CO₂ phase than in the IL phase, the reaction will be hampered by addition of CO₂, as it separates reactant and catalyst. In such cases, as shown above, CO₂ may still have a beneficial impact on the reaction, as it can be added after the reaction is completed to extract the products. However, from an industrial point of view, the goal should be to design, if possible, continuous reactions with stationary, more or less constant, pressure, and temperature conditions. Like this, energy- and time-losses due to repeated pressurization and depressurization should be avoided. Thus, already in an early stage of biphasic IL/CO₂ research, many groups aimed toward finding such continuous applications.

3.2.2. Biphasic (IL/CO₂) Continuous Reactions

The group of Cole-Hamilton has been the most productive in the studies of biphasic IL/CO₂ continuous catalytic reactions without the use of a solid support and they have been focusing on the important case of the hydroformylation of alkenes (depicted in Figure 11). Sellin et al. reported in a

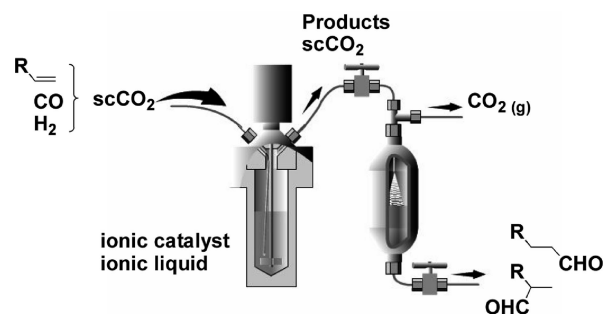
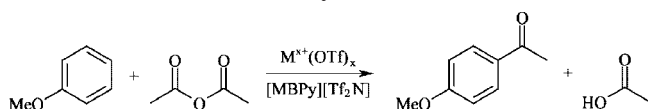
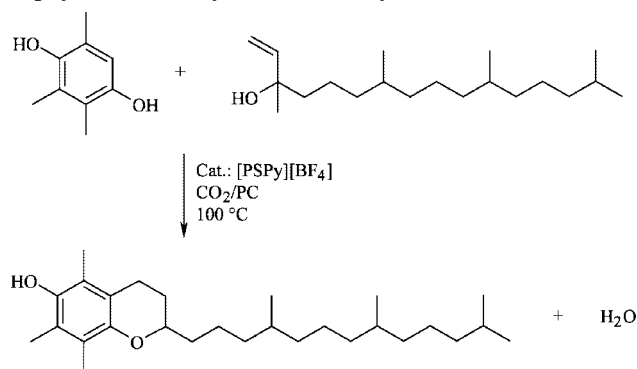


Figure 11. Continuous flow hydroformylation of alkenes in supercritical fluid-ionic liquid biphasic systems. Reprinted with permission from ref.¹³² Copyright 2003 American Chemical Society.

communication the hydroformylation in IL/scCO₂ biphasic systems with the initial motivation that scCO₂ should facilitate the diffusion of the reactants into ILs and act as the carrier for a flow system.¹³¹ The aldehyde selectivity in the hydroformylation of hex-1-ene was improved by using a biphasic IL/scCO₂ system employing rhodium complexes. Working with batch reactors, the reactants were extracted using scCO₂, and the reaction was repeated with the same catalyst and showed a loss of activity and selectivity after 23 recycle times which was explained by the reaction of the [PF₆][−] anion to release HF. In continuous flow, the hydroformylation of oct-1-ene was performed for 30 h with a rhodium catalyst at 100 °C.

Later in the same group, investigations on the hydroformylation of alkenes were continued.¹³² In the case of repeated batch reaction, the formation of HF occurred in the IL phase, and the decrease in the selectivity of the system studied could be explained by oxidation of the phosphine ligand, which yielded a different catalyst complex with different selectivity.

In continuous flow reactions many parameters were studied, including the effect of the IL (by screening imidazolium-based ILs bearing different anions, such as chloride, [PF₆][−], [Tf₂N][−], and others), flow rate, temperature, gas composition, and purity of CO₂ used. The effect of the alkyl group of the 1-alkyl-3-methylimidazolium salt was studied, leading to the conclusion that increasing the alkyl chain improved the reaction. This fact was explained by a better solubility of alkenes in ILs containing long alkyl chains.⁹ Replacing [PF₆][−] by [Tf₂N][−] anion also improved the reaction, which could be explained by a lower sensitivity to moisture, decreased risk of foaming, better transport into ILs, and again an increase of the solubility of alkenes which the authors believed to be the more probable key factor. Another interesting parameter in this reaction is the partial pressure of CO/H₂ which is acting as an antisolvent in the scCO₂ phase, and thus increasing the amount of CO/H₂ can be used to decrease the leaching of the catalyst for a continuous flow reaction. This is a very nice example of the tuning possibilities of the solvent power of CO₂. The key there is to control the concentration of wanted (products) and unwanted (catalyst) molecules in the CO₂ phase, either by controlling directly the pressure and temperature of the CO₂ or by adding a cosolvent or antisolvent. Another interesting observation in this study was the effect of the purity of CO₂ used; impurities in the CO₂ can lead to oxidation of the phosphine which decreases the selectivity of the reaction. After optimization, the hydroformylation of alkenes with different chain length (up to 1-dodecene) appeared comparable to commercial systems and the catalyst leaching was as low as

Scheme 2. Friedel–Crafts Acylation in ILs¹³⁴**Scheme 3. Synthesis of D,L- α -Tocopherol Based on the Condensation Reaction of Trimethylhydroquinone and Isophytol with [PSPy][BF₄] as Catalyst¹³⁵**

3.6 μg per mol of product. Later the continuous flow homogeneous catalysis was used employing supercritical CO_2 in a biphasic system while the liquid phase was only reactant/product and ionic catalyst.

Several years later, Frisch et al. from Cole-Hamilton's group published another study on the continuous hydroformylation of 1-octene, catalyzed by an *in situ* generated IL catalyst, consisting of $[\text{Rh}(\text{acac})(\text{CO})_2]$, an imidazolium cation, and a coordinating sulfonated triphenylphosphine anion.¹³³ The study uses scCO_2 as mobile phase, while the homogeneous ionic catalyst is "immobilized" in the steady-state mixture of reactants and products present during reaction. The authors used an especially modified reactor suitable for such biphasic reactions in continuous mode. In order to establish a stable steady-state system, many parameters had to be optimized. One problem that appeared involved the mass-transport and miscibility of reactant, gases, products, catalyst, and IL/scCO_2 , as these parameters changed with conversion. Eventually, stable conditions were found, where at 140 °C a TOF of approximately 180 h^{-1} was achieved. While this process may be too complex to exploit industrially, it yielded valuable information on the complex reaction mixtures present in IL/scCO_2 hydroformylation reactions, which could be used in corresponding SILP systems (*vide infra*).

Zayed et al. demonstrated the possibility to use an IL/scCO_2 biphasic system for the continuous Friedel–Crafts acylation (Scheme 2) while screening 10 different catalytically active metal salts at 60 °C under high pressure of 300 bar.¹³⁴ Among the catalysts tested in this work, yttrium triflate was giving the best results ahead of scandium, gadolinium, ytterbium and bismuth.

A condensation reaction recently reported (Scheme 3) was producing D,L- α -tocopherol with a conversion of 97.4% and a yield of 90.4% after optimization of temperature (100 °C), pressure (200 bar), molar ratio of different components, and residence time of 12.6 min using a sulfonic acid-functionalized IL.¹³⁵ The continuous reaction was carried out during 6 h, and the process of reaction coupled with separation was stable.

While the results obtained with such biphasic continuous reaction systems are highly promising, an often encountered

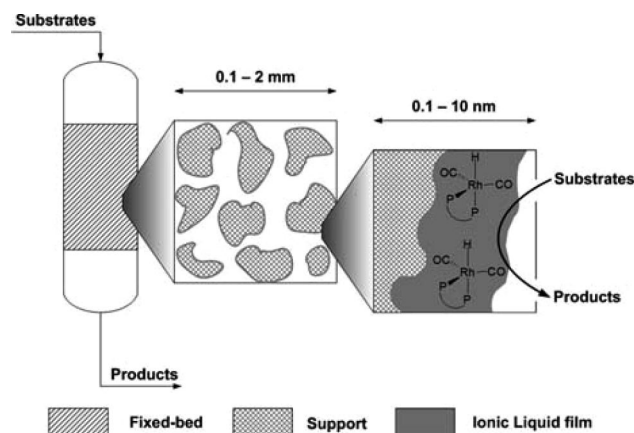


Figure 12. Schematic illustration of supported ionic liquid phase (SILP) catalysts for fixed-bed reactor technology. Reprinted with permission from ref 6. Copyright 2006 Wiley-VCH.

intrinsic problem is the slow diffusion of reactants inside the IL phase, especially when catalyst concentration is relatively low. Furthermore, if potential industrial (or large scale) applications are targeted, vast amounts of ILs create a financial burden that limits the applicability of such systems considerably. Hence, the goal should be to use as little IL as possible, especially also given the fact that the extremely low solubility in CO_2 would also make a very thin layer of IL a suitable stationary phase in continuous reactions. As it is difficult to achieve a homogeneous thin layer of IL in a continuous reaction system, and the stability of such a layer toward agglomeration especially in continuous reaction mode would be doubtful, another approach was taken to circumvent this problem, which led to the development of SILP catalysis.

3.2.3. Supported Ionic Liquid Phase (SILP) Catalysis

Supported ionic liquid phase (SILP) catalysis has gained considerable interest in catalytic applications and was recently reviewed by Riisager et al.⁶ Figure 12 depicts the concept schematically: A very thin layer of IL is covering a solid support (e.g., silica) while still acting as a "liquid" IL phase containing the catalyst. The thus obtained full powder material can be employed like any other solid catalyst and be used for instance in fixed-bed flow reactors. So far, especially hydrogenation, oxidation, and hydroformylation reactions were improved by using IL-supported solid catalysts, both in batch and in continuous reactions. The fact of having a thin layer of ILs covering a solid support while dissolving (and at the same time immobilizing) catalytically active species diminishes diffusion barriers and facilitates the handling of the catalyst material compared to bulk ILs. Apart from a thorough view on SILP catalysis in general, Riisager et al. also investigated the influence of CO_2 cofeeding on their reported SILP hydroformylation, thus replacing the inert gas otherwise used. Indeed, using subcritical CO_2 enhanced the catalytic activity by up to 35% compared to a system using helium while the selectivity remained equally high around 94.5%. They attributed the beneficial effect to the high solubility of CO_2 in the ILs, a lowered viscosity thereof, and thus a higher solubility of other gases in IL, as normally mass transfer is indirectly correlated to viscosity.

The concept of supported ionic liquid phase (SILP) catalysis in combination with scCO_2 was introduced and first reported for the aerobic alcohol oxidation by Ciriminna and co-workers.¹³⁶ They used a sol–gel entrapped perruthenate

as catalyst and investigated two different synthetic routes to yield this silica-IL-supported species. These synthetic routes included, on one hand, a silica catalyst obtained by methylation of a neutral imidazole-bearing anchor group, followed by ion exchange with perruthenate, and, on the other hand, a silica xerogel obtained directly by copolycondensation of silane monomers with an ionic imidazolium-functionalized organosilane compound, also followed by RuO_4^- ion exchange. The latter method yielded a catalyst with significantly higher activity than the former and exhibited no detectable Ru leaching. A screening of different alcohol substrates (including benzyl alcohol and primary and secondary aliphatic alcohols) showed excellent selectivity toward the aldehyde or ketone, respectively, while completely waiving the use of additional solvents during the whole process. Apparently, the only disadvantage of this promising green catalytic process is the relatively high pressure of 220 bar employed.

A very similar reaction system was reported by Xie et al., who also studied the aerobic oxidation of benzyl alcohol using SILP catalysts, however following a different immobilization strategy.¹³⁷ While the catalytically active species, perruthenate, was the same, they obtained an IL-functionalized support by radical copolymerization of divinyl benzene with 1-vinyl-3-butylimidazolium chloride, which afterward was loaded with Ru by ion exchange. The thus synthesized SILP catalyst showed good performance at 80 °C and a pressure of 140 bar. Different organic solvents for the apolar phase were tested, but scCO_2 proved to be superior, reaching almost quantitative yield after 8 h with a TOF of 5.5 h^{-1} . Recycling tests however revealed a relatively fast deactivation (after the fourth run only 33% of the first-run yield was reached). This was attributed by the authors to self-aggregation of Ru derivatives, a claim which however was not experimentally supported.

Hintermair et al. from the group of Cole-Hamilton reported another excellent example of employing SILP catalysis together with scCO_2 .^{138,139} They investigated the hydroformylation of 1-octene in continuous reaction mode over a fixed-bed SILP catalyst consisting of $[\text{Rh}(\text{acac})(\text{CO})_2]$ dissolved in imidazolium-based ILs supported on silica. Earlier studies with a batch reaction system (vide supra) suffered from a continuous drop in product selectivity (linear/branched) from 3.7 to 2.5 over nine reuse cycles, probably stemming from ligand oxidation due to technical reasons connected with the recycle tests and too high solubility of the thus formed catalyst complex in the scCO_2 phase, hence also showing increased leaching.¹³¹ These difficulties could be circumvented by the reported continuous reaction process. A prolonged catalyst usage on stream, which showed no deactivation whatsoever during at least 40 h, yielded a constant product ratio of 3.1 (linear/branched) and leaching of less than 1 ppm. Extensive tests with different IL loadings revealed that, unlike in SILP systems without scCO_2 , the reaction rate is not significantly influenced by the IL loading. This is an interesting finding, as normally in SILP catalysis (using gases other than CO_2 as mobile phase), the IL layer thickness shows an optimum in terms of reaction rate, on the lower boundary limited by disadvantageous solid support–catalyst interactions and on the higher boundary limited by diffusion barriers.⁶ This effect was not observed in this study using scCO_2 , probably due to a facilitated transport of the reactant molecules (1-octene, H_2 , and CO) into the IL by scCO_2 . Optimization of the process, mainly

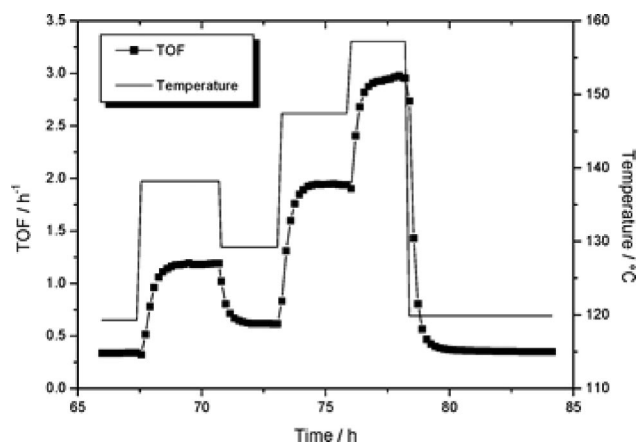


Figure 13. Dependence of TOF on temperature. Reprinted with permission from ref 140. Copyright 2009 Royal Society of Chemistry.

by tuning the substrate flow rate, led to TOF values of 800 h^{-1} , being higher than those of corresponding batch systems (527 h^{-1}) and even commercial alkene hydroformylation reactions ($550\text{--}700 \text{ h}^{-1}$).

Recently, a RuCl_3 catalyst in $[\text{BMMIm}][\text{OTf}]$ on a porous silica support was used in a tubular fixed-bed reactor for the water-gas shift reaction (WGS) at low temperatures ($120\text{--}160 \text{ }^\circ\text{C}$), ambient pressure ($p_{\text{CO}} = 0.1 \text{ bar}$, $p_{\text{water}} = 0.2 \text{ bar}$), and a residence time of 5.5 s.¹⁴⁰ The reported system is very promising; however, some minor doubt may arise given the fact that the authors claim an IL film thickness of 0.3 nm on the support, which was probably calculated based on the surface area of the support and the amount of IL used in the synthesis. In this case, it is supposedly more likely that the IL does not form a completely homogeneous film in terms of thickness but rather areas with higher coverage where also the catalyst is dissolved (e.g., in pores) and others with no or very little coverage.

The reported RuCl_3 –SILP system was stable for at least 150 h time on stream even at $140 \text{ }^\circ\text{C}$. After 67.5 h at $120 \text{ }^\circ\text{C}$ (to reduce distortion of the kinetic data by the catalyst deactivation), the temperature was changed. Figure 13 shows the evolution of the TOF for different temperatures, which allows calculating the activation energy of the reaction (84 kJ mol^{-1}) and also demonstrates the ability of this SILP system to work under moderate temperature. Moreover, no side products of the reaction were detected. Finally, the apparent reaction orders were 1.05 and 0.01 for water and CO, respectively. Very recently, the authors published a communication reporting a tremendous improvement of their system, which now exceeds the activity of commercially employed low temperature WGS systems.¹⁴¹ By IR spectroscopic measurements, they were able to identify the active catalytic species, a carbonyl complex, and by using $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ instead of RuCl_3 as precursor, the initiation time of the reaction could be eliminated. The introduction of basicity (via support, organic base additive, or IL) and extensive parameter studies led to outstanding maximal TOFs up to the range of $20 \text{ mol (CO}_2\text{) mol (catalyst)}^{-1} \text{ h}^{-1}$.

In a subsequent work, the same group reported a further development on their SILP WGS system by extending it to a screening technique for various catalysts using highly porous Silica 100 and $[\text{BMMIm}][\text{OTf}]$ as support.¹⁴² Instead of employing elaborative batch experiments, they used a fixed-bed continuous gas-phase reactor to screen under steady-state conditions the activity and stability of 36

different catalyst systems, including a series of transition metal chlorides, carbonyls, and more complex derived catalyst systems. This is indeed a very promising approach, as active species formation and deactivation phenomena can be studied more efficiently compared to classical batch screenings. Furthermore, the study highlights the strengths of SILP catalysis, including extremely simple preparation of the immobilized catalysts, high leaching stability (especially for continuous reactions in the gas phase and of course also the scCO_2 phase), and a high tunability of the catalyst system in terms of metal precursor, IL, and support.

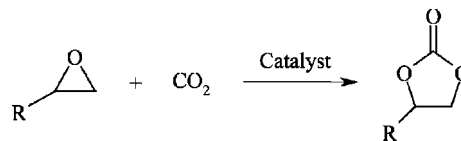
Very recently, Hintermair, Leitner, et al. reported another interesting application of SILP catalysis, the continuous enantioselective hydrogenation of dimethyl itaconate using a scCO_2 flow system.¹⁴³ The catalyst consisted of a Rh(I) complex bearing a chiral phosphine-based ligand immobilized in imidazolium-based ILs on dehydroxylated silica. Screening of different IL loadings revealed an optimal pore filling degree α of 0.36. Tests with and without solid support showed that the enantiomeric excess (ee) was in both cases higher than 99%; thus, the SILP method does not appear inferior to homogeneous catalysis in these terms, which is a very promising finding. Screening of different ILs revealed a strong dependence of the activity on the IL employed. Hydrophobic imidazolium-based ILs with a $[\text{Tf}_2\text{N}]^-$ anion yielded the highest activity and selectivity, while more hydrophilic ILs with $[\text{BF}_4]^-$ or $[\text{OTf}]^-$ anions only yielded poor results. The best IL, $[\text{EMIm}][\text{Tf}_2\text{N}]$, was used to create a SILP catalyst which ran 65 h on stream without loss of activity and excellent leaching resistance. However, the enantioselectivity could not be kept stable during the whole long-term test. The authors reported no drop in ee until at least 10 h on stream, but after that, a slow decrease down to 70–75% was observed. This was attributed to partial decomposition of the catalyst to less selective species. However, this interesting study shows that SILP catalysis in continuous flow reactors can also be employed for rather difficult enantioselective processes.

3.2.4. Carbon Dioxide as Reactant

The promising results obtained while researching IL/ CO_2 biphasic systems also open doors for new ways of chemically transforming CO_2 into more valuable chemicals. The unique features of IL/ CO_2 systems, of course, remain when CO_2 is not only employed as solvent but also serves as a C_1 -building block with potential to replace toxic and hazardous chemicals such as phosgene or carbon monoxide. Indeed, a vast number of reports were published in the past decade addressing highly interesting applications of chemical CO_2 transformation where ILs play a crucial role. The beneficial impacts of ILs on CO_2 transformation are not limited to mere solvent properties (as in electrochemical reactions or biocatalysis); the strong interactions of some IL anions with the CO_2 molecule also lead in some cases to an activation of the latter, which efficiently enhances the possibilities of CO_2 activation compared to “classical” reaction systems.

3.2.4.1. Cyclic Organic Carbonates. The synthesis of cyclic organic carbonates from epoxides and CO_2 (Scheme 4) is one of the major pathways nowadays to chemically transform carbon dioxide.^{144–151} As a considerable amount of CO_2 can be dissolved in ILs, they potentially offer a suitable reaction medium for this reaction. Furthermore, typical ILs such as ammonium or phosphonium salts are known to catalyze (or at least promote) the cycloaddition of

Scheme 4. Catalytic Synthesis of Cyclic Organic Carbonates from Epoxides and CO_2



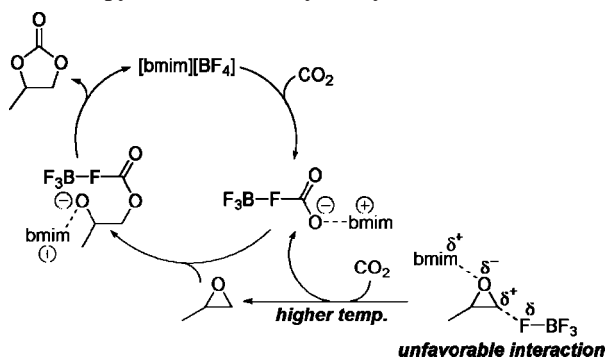
CO_2 to epoxides.^{152,153} Numerous publications report catalytic systems where ILs play an important role, either as reaction medium, as catalyst, or both. The results in this field up to 2005 are summarized in a review by Sun et al.,¹⁹ but research was extended considerably during the past years.

3.2.4.1.1. Cycloaddition Reaction Catalyzed by ILs without Additives. The first report of ILs as catalysts for the cycloaddition of CO_2 to propylene oxide (PO) yielding propylene carbonate (PC) was published by Peng and Deng¹⁵⁴ using ILs containing $[\text{BMIm}]^+$ and $[\text{BPy}]^+$ as cations and Cl^- , $[\text{BF}_4]^-$, and $[\text{PF}_6]^-$ as anions. They reached quantitative yield after 6 h at 110 °C using 2.5 mol % $[\text{BMIm}][\text{BF}_4]$ and 25 bar CO_2 . The catalytically active IL phase was shown to be reusable with only minor loss of activity. Screening of the different ILs revealed a dependence of the catalytic activity on both cation and anion, in the order $[\text{BMIm}]^+ > [\text{BPy}]^+$ and $[\text{BF}_4]^- > \text{Cl}^- > [\text{PF}_6]^-$.

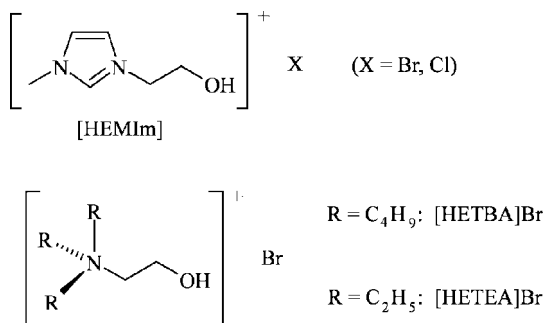
Shortly thereafter, Kawanami et al. published a work using different imidazolium-based ILs (bearing alkyl chains from C_2 to C_8) and various anions.¹⁵⁵ Due to the high solubility of supercritical CO_2 in ILs, they worked under a pressure of 140 bar at 100 °C and were able to reach 98% yield after 5 min, exhibiting extraordinary turnover frequencies. They showed that the chain length of the cation alkyl chain has a tremendous effect on the catalytic activity, rising proportionally from C_2 to C_8 , and they attributed it to a higher solubility of both epoxide and CO_2 in ILs with longer chain length. Of the anions used ($[\text{NO}_3]^-$, $[\text{CF}_3\text{SO}]^-$, $[\text{BF}_4]^-$, and $[\text{PF}_6]^-$), $[\text{BF}_4]^-$ turned out to be the most suitable in terms of activity. Another important finding was that a long alkyl chain (C_8) on the cation is only beneficial when using high pressures; at subcritical pressures the short alkyl chain (C_2) was more efficient.

The cycloaddition of carbon dioxide to propylene oxide catalyzed by 1-*n*-butyl-3-methylimidazolium- and 1-*n*-butylpyridinium-based ILs was later studied in our group by means of *in situ* ATR infrared spectroscopy.²⁶ Especially the molecular interactions of CO_2 with the anions $[\text{PF}_6]^-$, $[\text{BF}_4]^-$, and $[\text{Tf}_2\text{N}]^-$ were investigated, revealing Lewis acid–base interactions which lead to the formation of a new anionic species, $[\text{X}-\text{CO}_2]^-$, being more basic than the original IL anion X^- . The strongest effect of this kind, generating the strongest intermediate base, was found for $[\text{BMIm}][\text{BF}_4]$, which explains the highest activity of this IL for the given catalytic reaction. Also in the C–H region of the infrared spectrum, many changes were observed, and a catalytic mechanism was proposed based on the findings of the *in situ* study (Scheme 5).

The use of ammonium-based ILs as both solvent and catalyst for the synthesis of cyclic organic carbonates was first reported by Caló et al.¹⁵⁶ They used either molten $[\text{NBu}_4]\text{Br}$ or $[\text{NBu}_4]\text{I}$, or a mixture of both, as catalytically active solvent. The reaction using styrene oxide (SO) and a range of polymerization-sensitive epoxides as substrates was performed at 120 °C and under ambient pressure of CO_2 . The yields achieved were in most cases above 80% after reaction times between 1 and 24 h. In line with increased

Scheme 5. Proposed Mechanism for the Cycloaddition of CO₂ to Propylene Oxide Catalyzed by [BMIm][BF₄]^a

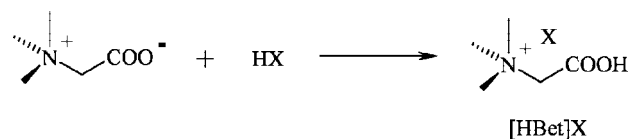
^a Reprinted with permission from ref 26. Copyright 2009 American Chemical Society.

Scheme 6. Hydroxyl-Functionalized ILs¹⁵⁷

nucleophilicity, the activity of the iodide salt was higher than that of the corresponding bromide species. Furthermore, the influence of the cation was studied, which showed that under the given conditions tetraalkyl ammonium salts were better than imidazolium, thiazole, or pyridinium salts. This led to the conclusion that the more bulky tetraalkyl ammonium cation had lower electrostatic attraction to the halide and therefore increased nucleophilicity compared to the other cations.

The next step in using ILs as catalysts for the synthesis of cyclic organic carbonates consisted of a task-specific tailoring of the ILs. Sun et al. synthesized hydroxyl-functionalized cations, based on both imidazolium and tetraethyl ammonium precursors (Scheme 6).¹⁵⁷ The highest activity was achieved using 1-(2-hydroxyethyl)-3-methylimidazolium bromide ([HEMIm]Br), yielding the desired product almost quantitatively after 1 h of reaction time at 125 °C and 20 bar CO₂. A range of substrates was screened, and a thorough comparison with nonmodified ILs proved the beneficial effect of the hydroxyl modification under the given conditions. Based on their findings, they postulated a reaction mechanism where the hydroxyl group plays an important role in activating the epoxide.

A similar approach was taken by Zhou and co-workers.¹⁵⁸ They synthesized a series of betaine-based ILs functionalized with a carboxylic acid group and various anions (Scheme 7). Several epoxides were tested as substrates. At a temperature of 140 °C and a CO₂-pressure of 80 bar, almost quantitative yield was achieved after 8 h with the most active catalyst [HBet]I. Interestingly, the activity of the screened catalysts was in the order I⁻ > Cl⁻ > Br⁻ > [BF₄]⁻ > [PF₆]⁻, which is not completely in line with decreasing nucleophilicity. The authors attributed this unusual finding to miscibility effects. Also, they proposed a reaction mechanism

Scheme 7. Carboxylic Acid-Functionalized (Betaine-Based) ILs¹⁵⁸

involving the carboxylic group, which is in good agreement with the one postulated by Sun et al. for the hydroxyl-functionalized IL.¹⁵⁷

Another approach was taken by Sun et al., who used a broad range of ILs, along with classical salts, as catalysts for the reaction while adding significant amounts of water to the reaction mixture.¹⁵⁹ The catalytically active ILs were only added in relatively small amounts, rather serving as catalysts alone than as solvents. Normally, a molar ratio of epoxide/water/ionic species of 200:67:1 was employed. The authors found an optimal water-to-epoxide ratio of approximately 1:3, which enhanced the activity of most catalysts, while higher water concentration led to increasing formation of glycolic side-products due to hydrolysis of the epoxide. The authors also carried out extensive parameter studies, including a wide range of different catalysts, various epoxide substrates, and added solvents. The best catalyst was [PPh₃Bu]I, which yielded 100% conversion of PO and 95% selectivity toward PC after 1 h of reaction time at 125 °C and 20 bar.

3.2.4.1.2. Cycloaddition Reaction Catalyzed by IL/Metal Systems. An improvement of the IL-catalyzed synthesis of cyclic organic carbonates can be achieved by adding metal salts or complexes which by themselves are active catalysts for the reaction mixture, as these often ionic species in most cases exhibit good solubility in ILs. Especially Zn(II) halide complexes have been known for a long time to be active catalysts for this reaction.^{160–165} Thus, Kim and co-workers reported a catalytic system where they added Zn(II) halide salts to imidazolium-based ILs, forming bis(1-alkyl-3-methylimidazolium) tetrahalide complexes of Zn.¹⁶⁶ These complexes, bearing either Cl⁻ or Br⁻ as anions, or both, turned out to be very active for the coupling of CO₂ with ethylene oxide and propylene oxide under the given reaction conditions of 100 °C and 35 bar during 1 h. Most active of the complexes studied were the purely bromide-containing species, while with increasing chloride content, the relative activity decreased. Also the influence of the alkyl-chain of the imidazolium cation was studied, which revealed the activity trend: benzyl > butyl > ethyl.

A very similar catalytic system was reported by Palgunadi and co-workers, also employing a series of bis(1-alkyl-3-methylimidazolium) tetrahalide Zn complexes for the coupling of CO₂ with various epoxides.¹⁶⁷ Although the reaction conditions including pressure and temperature were exactly the same, the activity in terms of turnover frequency (TOF) was generally lower than that in the work published by Kim et al.¹⁶⁶ However, a significantly lower substrate-to-catalyst ratio was used (a factor of 4 to 10), thus possibly adversely affecting the calculation of the TOF values. The authors tested the influence of the halide on the reaction, finding that higher bromide content had a beneficial influence on the activity. This is in agreement with the conclusions Kim et al. made and can be attributed to the higher nucleophilicity of bromide compared to chloride. The screening of different imidazolium-based cations with varying alkyl chain lengths revealed only a minor impact on the catalytic activity. More

important, the authors considered the influence of temperature, but not CO₂ pressure, on the reaction outcome. Finally, a screening of different substrates showed that bulkier epoxides were more difficult to convert to the corresponding carbonates. The structure of the catalytically active species was determined by X-ray diffraction for (1,3-dimethylimidazolium)₂Zn₂Br₂Cl₂.

Very similarly, Fujita et al. recently reported an interesting study where the authors extended the IL/Zn halide based catalysts to other ILs, including the cations [BMIm]⁺, [BPy]⁺, [Chol]⁺, and [NBu₄]⁺ using the substrate styrene oxide.¹⁶⁸ The catalyst systems thus obtained consisted of the general formula IL_{*n*}ZnX₂Y_{*n*}, where X and Y are halides. The best catalyst, [NBu₄]₂ZnBr₂Br₂, yielded 94% styrene carbonate after 30 min at 80 °C using a CO₂ pressure of 50 bar. The influence of the cation on the activity appeared in the order [NBu₄]⁺ > [BPy]⁺ > [BMIm]⁺ ≫ [Chol]⁺, while the Zn halide salt used in the synthesis influenced the activity in the order ZnBr₂ > ZnI₂ > ZnCl₂. Investigating this, it was found that the halide originating from the Zn halide salt (ZnX₂) had a higher influence on the activity than the halide originating from the IL ([IL]Y) used in the synthesis. Although the authors discussed a possible reaction mechanism, they could not completely rationalize this effect. Further investigations on the composition of IL_{*n*}ZnX₂Y_{*n*} revealed that the ratio of IL cation to Zn (*n* = [IL]/[Zn]) had an influence on the activity based on the cation used. For [NBu₄]⁺, an *n* > 2 did not lead to a further increase in activity, while, for [BMIm]⁺, the activity continued to increase linearly at least up to *n* = 4 (where full conversion was achieved under the given conditions). The explanation of this effect remained speculative in the publication, but it could perhaps be attributed to the fact that [NBu₄]X alone is a relatively active catalyst for this reaction.

Sun et al. used a series of metal bromide salts together with imidazolium-based ILs as catalyst system for the synthesis of styrene carbonate from the corresponding epoxide and CO₂.¹⁶⁹ Thorough screening of different catalysts, while varying metal cation, imidazolium alkyl chain length, IL anion, and metal salt anion, revealed that ZnBr₂ together with [BMIm]Cl yielded the best catalytic results under the given conditions. For example, they found a proportional dependence of the activity on the Lewis-acidity of the metal cation. Interestingly, using [BF₄][−] or [PF₆][−] as IL anions, the catalytic activity dropped compared to the case of chloride. Further parameter studies, including temperature and CO₂ pressure, revealed a strong dependency of the reaction on both parameters. Higher temperature led to higher yields, while for the CO₂ pressure an optimal regime was found around 40 bar. The authors furthermore provided view-cell experimental results for phase-behavior studies, alongside with a proposed reaction mechanism, which is in good agreement with mechanisms published on similar systems.^{170,171}

Very recently, Yu and co-workers used the same catalysts, mainly imidazolium-based chloride ILs with varying alkyl chain lengths and partially with Zn(II) halides as cocatalysts.¹⁷² As substrate they chose the rather unusual butyl glycidyl ether to synthesize the corresponding cyclic carbonate. The authors found very similar trends as reported by Sun et al.¹⁶⁹ The alkyl chain length showed an influence on the catalytic activity in the order [EMIm]⁺ < [BMIm]⁺ < [HMIm]⁺, and for the anions, the dependence of the activity was in the order [BF₄][−] < Cl[−] < Br[−], being in line with nucleophilicity and in agreement with other published results.

The same anion dependence was also revealed for the Zn halide cocatalysts. The study did not report extremely high TOFs for the catalytic system; however, it contains useful kinetics investigations comparing the different ILs.

A similar catalytic system was reported by Li et al., using ZnCl₂ together with [BMIm]Br as IL for the synthesis of various cyclic carbonates at 100 °C and under 15 bar CO₂ pressure.¹⁷³ Excellent activity in terms of turnover frequency of up to 5410 h^{−1} was achieved using a molar ratio of Zn/IL/substrate of 1:6:5700. The screening of different IL anions exhibited a similar outcome as published by Sun et al.,¹⁶⁹ as Br[−] was superior to Cl[−], while the complex anions [BF₄][−] and [PF₆][−] only yielded traces of the desired cyclic carbonate product. An interesting finding of the study was that, when using cyclohexene oxide as substrate, only the *cis*-cyclic carbonate was formed.

Zhang and co-workers focused on the production of chiral cyclic carbonates using not only a chiral catalyst but also a chiral IL as reaction medium.¹⁷⁴ The catalyst employed was a cobalt(III)–salen complex with chiral salen ligand being a well-known catalyst for the cycloaddition of CO₂ to epoxides.¹⁷⁵ Together with chiral ILs consisting of tetrabutylammonium-based salts with amino acidic anions, they could reach ee values of 85.2% but with only a low yield of 10%. Higher yields unfortunately were accompanied by a decrease in ee.

Another approach was taken by Kossev et al., employing CaCl₂ and a series of onium salts (ammonium and phosphonium) as catalysts for the synthesis of different cyclic carbonates.¹⁷⁶ As in the systems mentioned before, the role of the calcium salt is to provide a Lewis acid which enhances the catalytic activity of the IL. Unfortunately, the reported activity of these systems was lower compared to the ones using Zn²⁺ and imidazolium-based ILs. However, the authors could show a crucial synergistic effect of the onium salts and CaCl₂, as the yield of the desired cyclic carbonate product after 4 h reaction time increased from less than 20% using 1 mmol of triethylbenzylammonium chloride to almost quantitative yield using double that amount. Without the calcium salt, the increase was similar, but in both cases, it was 1 order of magnitude lower compared to the case where CaCl₂ was used. In general, to achieve full conversion, the authors had to employ comparably high reaction temperatures of 120–170 °C, which still required reaction times of at least 4 h.

Several years later, Sibauhi and co-workers used a similar approach while combining onium (ammonium, phosphonium, and imidazolium) salts with Co(II) salts as catalytic system.¹⁷⁷ The reaction conditions involving 120 °C, 10 bar CO₂ pressure, and 1 h of reaction time appear moderate for the excellent activity reported; however, the addition of small amounts of CH₂Cl₂ was necessary to solubilize the catalyst system. As in the report by Kossev et al.,¹⁷⁶ also Sibauhi et al. found a significant synergistic effect of the Co(II) salt together with the onium species.¹⁷⁷ Interestingly, in this system, chloride as IL anion appeared to be superior to bromide or acetate. In screening tests comparing the onium salts, it was found that phosphonium was more active than ammonium, while the imidazolium-based ILs were the least active. The study is further enriched with ESI-MS experiments in order to analyze the reaction mechanism, which revealed the presence of an intermediate [onium]⁺ [CoX₃][−] ion pair.

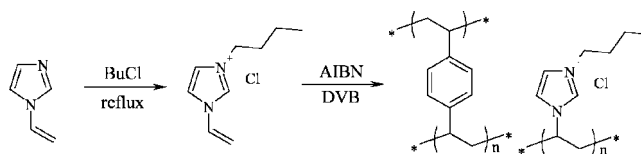
The combination of metal salts with ILs as catalytic system for this reaction was further enhanced by Ono et al. using microwave irradiation as energy supply.¹⁷⁸ They employed various Zn salts, including halides and triflate, but the most efficient appeared to be the rather unusual zinc phenolsulfonate octahydrate (ZnPO). The ILs employed included tetrabutyl ammonium halides and imidazolium-based bromide ILs. In a reaction system using ZnPO and Bu₄NBr, an outstandingly high TOF of 20,371 h⁻¹ was achieved with 30 bar CO₂ pressure and 120 °C under microwave irradiation. The comparison between conventional oil bath-heating and microwave irradiation showed a significant enhancement (at least 1 order of magnitude) using the latter energy supply in every experiment. Reaction parameter screenings concluded optimal temperature (120 °C) and pressure (30 bar) regimes, while IL screening revealed that ammonium-based ILs were superior to imidazolium-based species. The authors also investigated the influence of microwave irradiation on the reaction kinetics and reported that the activity-enhancement was not likely to be due to superheating or similar effects but rather due to a decrease in activation energy for the reaction, a claim that was supported by kinetic experiments. The microwave-assisted reaction process was likewise employed using other epoxide substrates, also yielding high TOF values. Another example of using microwave irradiation is described in section 3.2.4.2.

3.2.4.1.3. Cycloaddition Reaction Catalyzed by Supported IL Catalysts. The next generation of IL-catalyzed (and/or promoted) synthesis of cyclic organic carbonates from epoxides and CO₂ consisted of the immobilization of such catalytic systems on solid supports, which adds, in analogy to the before-mentioned SILP catalysis, the advantage of very easy product separation by filtration techniques, alongside with a possible high dispersion of the catalytically active species. The first report of such a system was published by Wang and co-workers, employing tetrabutylammonium halides immobilized on silica by a simple adsorption technique.¹⁷⁹ The activity of the reported system was however comparably low, as full conversion was reached only after 5–10 h at 150 °C and 80 bar CO₂ pressure. Parameter studies involved the screening of different halides as IL anions, and various ammonium cations. Apart from iodide, which showed a lower activity than expected, the halides rose in activity according to their nucleophilicity. For the cations, the effect of, for example, the alkyl chain length appeared negligible.

Shortly thereafter, Wang et al. extended the principle of using such immobilized catalysts to imidazolium-based ILs supported on silica.¹⁸⁰ Among the ILs tested, [BMIm][BF₄] immobilized on silica proved to be the most active, exceeding the Br⁻ and the [PF₆]⁻ species. Thorough parameter studies, including temperature, pressure, and reaction time, revealed an optimal regime for the reaction of 150 °C and 80 bar. Conversion tests after different times showed that the reaction was almost finished after 4 h. The authors also screened other epoxides as substrates and reused the catalyst four times without significant loss in activity.

Another example of physical impregnation to create a heterogeneous catalyst was employed by Zhu and co-workers.¹⁸¹ They used a combination of [Chol]Cl and urea (molar ratio 1:2) as catalyst system, immobilized on molecular sieves. After 5 h of reaction time at 110 °C, PC was obtained from PO in 99% yield. Similarly high activities were achieved for other substrates, and a reaction mechanism was reported. The role of urea as cocatalyst was mainly attributed

Scheme 8. Synthesis of a Cross-Linked-Polymer-Supported IL¹⁸²



to a beneficial hydrogen-bonding between the chloride anion of the IL and urea, which also leads to a drastic decrease in melting point down to 12 °C.

A different approach was used by Xie and co-workers.¹⁸² They synthesized a series of ILs grafted onto a polymer matrix by radical copolymerization (depicted in Scheme 8). The thus obtained highly cross-linked polymer possessed a particle size in the micrometer range and a rough surface. The imidazolium-based IL catalysts exhibited good activity; full conversion was reached after 7 h at 110 °C and 60 bar CO₂ pressure. Excellent reusability could be shown with no loss of activity after at least five runs. Interestingly, the copolymer catalyst showed higher activity than an equimolar amount of monomeric catalytically active IL. This behavior was explained by bad miscibility of the monomer in the substrate epoxide during the solventless synthesis, a fact which could be circumvented by the reported grafting technique. This effect was also observed by Qiao et al., who synthesized a very similar catalyst system consisting of a linear copolymer of the same IL as that Xie et al.¹⁸² used, and styrene.¹⁸³ Their polymeric catalyst showed excellent activity in the synthesis of styrene carbonate from SO and CO₂, reaching a TOF of 3808 h⁻¹. When they employed the same catalyst in homogeneous form (not polymerized), the TOF was slightly lower, only reaching 3363 h⁻¹. Regardless of that, it has to be noted that such high TOF values can sometimes be misleading, depending on how they were calculated. If the authors calculated their TOFs based on the metal content of the catalyst (which is a usual approach in catalysis), it has to be taken into account that the metal-free system consisting only of IL also is catalytically highly active. Thus, for catalysts consisting of individually active components (which may exhibit synergistic catalytic activity), the calculation of a meaningful TOF is not trivial. Nevertheless, these TOF values still provide a reasonable basis for comparing reaction parameters, especially within the same study, and are in many cases more informative than the product yield.

An overview of the methods employed to obtain covalently immobilized ILs on various supports is summarized in Table 3. Support materials consisted of silicas (both yielded by synthesis and commercially available products),^{184–190} other oxides,¹⁸⁵ polystyrene resins,^{187,191} zeolites,^{192,193} and organic polymers (chitosan).¹⁹⁴ The ILs used as catalyst include ammonium, phosphonium, and imidazolium-based species with mostly halide anions. The versatility in synthetic approaches is equaled by the broad range of reaction conditions and substrates employed, and in several reports, cocatalytic metal salts were added.^{183,184,186,189}

Although the catalytic systems summarized in Table 3 are not easily comparable due to their broad range of differing reaction parameters, some careful conclusions can be drawn by comparing selected features. The choice of the support material, for instance, has apparently a tremendous influence on the activity. Most studies use silicates as support, which have the advantages of high thermal and chemical stability, wide structural versatility (including mesoporous, amorphous,

Table 3. Catalytic Activity Data for Several Covalently Immobilized IL-Based Catalysts Employed for the Cycloaddition of CO₂ to Epoxide-Type Substrates

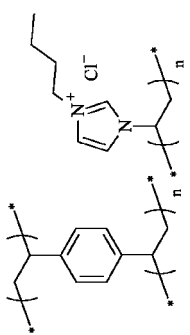
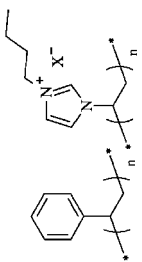
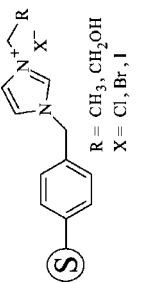

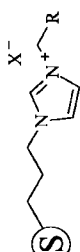
| IL structure Support | Catalyst | Metal | Substrate | Reaction conditions | | | Catalytic results | | | Additional features | Ref. |
|---|---------------------------|-------------------|-----------|---------------------|-----------|----------|-------------------|--------------------|---------------------------|---|-------|
| | | | | p (bar) | T (°C) | t (h) | Yield (%) | Selectivity (%) | TOF (h ⁻¹) | | |
|  | IL copolymer with DVB | - | PO | 60 | 110 | 7 | 97.4 | - | - | - Recycle tests - Parameter studies | (182) |
| | | - | ECH | 60 | 110 | 3 | 95.8 | - | - | - | |
| | | - | GPE | 60 | 110 | 3 | 96.4 | - | - | - | |
| | | - | SO | 60 | 110 | 7 | 79.3 | - | - | - | |
| | | - | CHO | 60 | 110 | 72 | 93.1 | - | - | - | |
|  | IL copolymer with styrene | ZnBr ₂ | SO | 30 | 120 | 8 | 35.0 | - | 1397 | - Recycle tests | (183) |
| | | ZnBr ₂ | SO | 30 | 120 | 8 | 97.5 | - | 3808 | - Parameter studies - Characterization | |
|  | Polystyrene resin | - | PO | 25 | 120 | 4 | 98 | 99 | - | - Recycle tests | (191) |
| | | - | ECH | 25 | 115 | 3 | 92 | 92 | - | - Parameter studies | |
| | | - | GPE | 25 | 115 | 3 | 99 | 99 | - | - Characterization | |
| | | - | SO | 25 | 120 | 6 | 93 | 99 | - | - Mechanism | |
| | | - | CHO | 25 | 125 | 20 | 80 | 99 | - | - | |
|  | Modified MCM-41 | - | AGE | 21.7 | 110 | 6 | 93.6 | 94.5 | 4.5 | - Characterization | (192) |
| | | - | AGE | 17.6 | 110 | 6 | 97.0 | 97.9 | 4.9 | - Mechanism | |
| | | - | AGE | 17.6 | 110 | 6 | 97.5 | 98.2 | 4.4 | - | |

Table 3. Continued

| IL structure Support | Catalyst | Substrate | | Reaction conditions | | Catalytic results | | | Additional features | Ref. |
|---|---|-------------------|-----|---------------------|----------|-------------------|--------------------|---------------------------|---------------------|--|
| | | Metal | p | T (°C) | t (h) | Yield (%) | Selectivity (%) | TOF (h ⁻¹) | | |
|  | R = C ₃ H ₇ , X = Br | - | AGE | 35.5 | 110 | 6 | 91.7 | 92.5 | 21.5 | - Characterization (188) |
| | R = C ₃ H ₇ , X = I | - | AGE | 35.5 | 110 | 6 | 93.6 | 94.8 | 14.2 | - Mechanism |
| | R = C ₃ H ₅ , X = Br | - | AGE | 35.5 | 110 | 6 | 90.4 | 91.8 | 15.8 | |
| SiO ₂ (mesoporous) | R = C ₃ H ₇ , X = Br | - | AGE | 8.6 | 110 | 6 | 60.2 | 86.7 | - | - Recycle tests, Characterization (186) |
| | ZnBr ₂ | ZnBr ₂ | AGE | 8.6 | 110 | 6 | 84.9 | 92.3 | - | - Mechanism |
| SiO ₂ | R = CH ₃ , C ₂ H ₅ , C ₃ H ₇ , C ₄ H ₉ , X = Cl, Br, I | - | AGE | 7.6 | 110 | 3 | 77.8 | 100 | - | - Recycle tests, Characterization (184) |
| | ZnI ₂ | ZnI ₂ | AGE | 7.6 | 110 | 3 | 60.4 | 93.4 | - | - Parameter studies |
| SiO ₂ | R = CH ₃ , X = OH | - | PO | 20 | 120 | 4 | 95 | 100 | - | - Recycle tests (190) |
| | R = CH ₃ , X = BF ₄ | - | PO | 20 | 120 | 4 | 24 | 100 | - | - Characterization |
| SiO ₂ (sol-gel method) | R = C ₃ H ₇ , X = Br | ZnCl ₂ | PO | 15 | 110 | 1 | 95 | >98 | 2712 | - Recycle tests (189) |
| | | CoCl ₂ | PO | 15 | 110 | 1 | 67 | >98 | 1913 | - Parameter studies |
| | | FeCl ₃ | PO | 15 | 110 | 1 | 55 | >98 | 1570 | - Characterization |
| | | NiCl ₂ | PO | 15 | 110 | 1 | 71 | >98 | 2027 | - Mechanism |
| | | CuCl ₂ | PO | 15 | 110 | 1 | 55 | >98 | 1570 | |
| | | AlCl ₃ | PO | 15 | 110 | 1 | 54 | >98 | 1542 | |
| SiO ₂ | R = CH ₂ OH X = Br | - | PO | 25 | 120 | 2 | 74.5 | 99.8 | - | - Recycle tests, Characterization (196) |
| SBA-15 | | - | PO | 25 | 120 | 2 | 98.7 | 99.8 | - | - Parameter studies |
| Al-SBA-15 | | - | PO | 25 | 120 | 2 | 97.7 | 99.8 | - | |

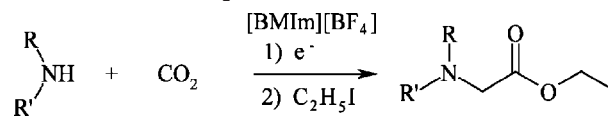
or zeolite-type structures), easily performed covalent anchoring of organic molecules by condensation of silanol-groups, and potentially beneficial interactions with substrate or catalyst molecules via surface free hydroxyls. Indeed, a comparison between SiO₂, Toyonite (a modified kaolinite (aluminosilicate)¹⁹⁵), and Al₂O₃ showed that, with higher Al content of the support, the activity was considerably lower.¹⁸⁵ However, pore structures seem to play a crucial role. Amorphous silica was reported to be inferior to mesoporous SBA-15, even when the latter was modified to contain Al.¹⁹⁶ Porous silicates appear to be generally a good choice, while the difference between unspecified mesoporous SiO₂¹⁸⁸ and zeolite structures such as MCM-41¹⁹² seems to be insignificant. Excellent results can also be obtained with the before-mentioned rather unusual copolymerization method,^{182,183} as this approach allows a much higher loading of catalytically active ILs (per mass or volume unit) compared to the case of silica. Furthermore, the apolar nature of the support may have a beneficial impact for certain substrates (or CO₂), as also the excellent results with an equally apolar polystyrene resin support indicate.¹⁹¹ In one study, the polystyrene support seemed drastically superior to a compared SiO₂ support exhibiting a surprising 10-fold excess in activity.¹⁸⁷

The type of IL used, of course, also has an influence on the catalytic behavior. Most of the studies summarized in Table 3 used imidazolium-based ILs, which clearly are a promising choice. However, one report directly compared an imidazolium-based IL with an ammonium-based one, and the latter appeared slightly more active in the case where short ethyl chains were attached to the ammonium ion.¹⁹³ Also, phosphonium-based ILs yielded excellent results in some reports,^{185,187} while in another study a pyridinium-based IL was slightly less active than its imidazolium counterpart.¹⁹⁷ Nevertheless, for the catalyst activity, more important than the IL cation seems to be the anion. The often used halides lead to active catalysts, while the activity mostly follows the nucleophilicity trend ($I^- > Br^- > Cl^-$), as reported in several studies.^{183,192,194} Interestingly, the [BF₄]⁻ anion, which is widely used in homogeneous systems for the same reaction, was only used in one study and yielded poor results.¹⁹⁰ In the same study, however, excellent results were obtained with the (in this context) unusual hydroxyl anion. These findings imply that certain parameters, such as the kind of IL anion, are not always transferable from, for example, a homogeneous catalyst system to a heterogeneous one, even if most of the other parameters are similar. Support effects and unexpected phenomena have to be taken into account.

One of the strengths of IL-based catalysis, the almost unlimited modifiability of the organic cations, offers further possibilities for optimization. As mentioned before, long alkyl chains on ammonium-based ILs, seem to inhibit the catalytic activity,¹⁹³ while in imidazolium-based ILs this effect seems to be much smaller.¹⁹² Furthermore, hydroxyl-substituents on the IL cation also seem to enhance the activity.^{194,196}

One factor that greatly enhances the catalytic activity is the addition of metal salts. Most often, for corresponding homogeneous systems, well-known Zn²⁺ halides (especially ZnBr₂) are employed,^{183,184,186} which indeed seem superior to other comparable metal halides. This was recently confirmed by Xiao et al., who among other parameters thoroughly screened various different metal salt additives for their SiO₂-grafted IL catalyst system.¹⁸⁹ Zinc clearly proved to be superior to Co, Fe, Ni, Cu, and Al.

Scheme 9. Electrochemically Promoted Synthesis of Carbamates from CO₂ and Amines²⁰¹



In summary, it can be concluded that such covalently immobilized IL-based catalysts are a promising approach for the cycloaddition of CO₂ to epoxides. Easy handling, product separation, and reusability of the catalysts are strong advantages compared to the cases of homogeneous systems. However, as the synthetic routes toward these materials are, in most cases, not trivial and the required functionalization of the ILs for covalent tethering makes the use of cheaper “standard” ILs impossible, it is doubtful that such catalysts will develop into an industrial application in the very near future.

3.2.4.2. Other Reactions Using CO₂ as Reactant in Combination with ILs. 3.2.4.2.1. Electrochemical Transformation of CO₂ in ILs.

Another promising application field of ILs is their use as solvents for electrochemical reactions. High conductivity, wide electrochemical windows, tunable solvent properties, and high chemical and thermal stability make them very useful electrolytes, for example, for batteries, electroplating, and electrochemical transformations.^{198,199} Thus, several research groups investigated the possibilities to use this approach in the IL-assisted electrochemical transformation of CO₂ into various useful products. The first report of this kind was published by Deng, Yang, and co-workers for the electrochemical synthesis of cyclic organic carbonates from epoxides and CO₂ under ambient pressure and temperature in a solventless process.²⁰⁰ The ILs tested included imidazolium- and pyridinium-based cations, while the anions consisted of either [BF₄]⁻ or [PF₆]⁻. The best results were obtained with [BMIm][BF₄], yielding 92% with 100% selectivity after 24 h. Temperature screenings revealed that lower temperatures (0 °C) had an adverse effect on the activity of the system, while higher temperatures (50 °C), at least in the case of styrene oxide as substrate, showed no change in activity or selectivity.

Several years later, Feroci and co-workers reported a study on the electrochemically promoted synthesis of carbamates from amines and CO₂ in [BMIm][BF₄], according to Scheme 9.²⁰¹ The reaction was performed at 1 bar CO₂ and 55 °C, and with various amines as test substrates which all produced good yields. Not surprisingly, the metal used for the cathode (in this study Cu, Pt, and Ni) had a tremendous influence on the reaction in terms of activity and reactivity. For instance, using Pt afforded a carbamate yield of 80%, without any byproduct.

Shortly later, Zhang et al. extended the method to synthesize organic carbonates (e.g., DMC) from CO₂ alcohols and alkyl iodides.²⁰² They used solely [BMIm][BF₄] as IL, while screening different alcohols and cathode materials. These tests revealed that Cu and Ag were superior to stainless steel, Ti, and Ni. Another important finding was the potential optimization. The crucial step of electrochemical CO₂-activation involves the reduction of CO₂ to the anionic radical CO₂^{•-} which is then stabilized via ion pairing by the IL cation. Thus, the best yields were achieved using a potential just above the CO₂ reduction potential (−1.71 V vs Ag/AgI). More positive values decreased the efficiency of the reduction, while more negative potentials were found to polarize the IL itself. Screening on different alcohols revealed that

primary and secondary alcohols were converted in good yields, while tertiary alcohols and phenols appeared non-reactive.

A later study by Yuan and co-workers tried to improve the electrochemical DMC production in imidazolium-based ILs by a different reaction system, using methanol and CO₂ as reactants, while employing methanolate salts as cocatalysts.²⁰³ Also this process, which does not use alkyl halides, was performed under ambient conditions (*p*, *T*), using a platinum electrode. The yield of DMC was relatively low, around 4% after 50 h of reaction time. Unfortunately, high concentrations of DMC at the electrode facilitated the formation of byproduct, such as trimethoxymethane.

A different goal for the electrochemical transformation of CO₂ in ILs was chosen by Zhao and co-workers. They used a biphasic system, CO₂–[BMIm][PF₆], to successfully convert scCO₂ and water to syngas at 45 °C.²⁰⁴ Traces of formic acid were found as byproduct; otherwise, the reaction yielded only the desired gas mixture. Recycling tests of the IL showed no deactivation or structural changes in the IL molecules after at least three runs, as performed IR and ¹H NMR analyses confirmed.

Barosse-Antle and Compton recently published a communication focusing on the electrochemical reduction of CO₂ in [BMIm][OAc], based on the previous finding that CO₂ has a very high solubility in that IL.²⁰⁵ Based on the assumption that CO₂ was not only physically absorbed in the IL, but rather chemically interacts with it, they explored the possibilities for fast CO₂ reduction for possible future sequestration purposes. Indeed, the CO₂ absorption appeared almost irreversible, and so was the reduction of CO₂ to CO₂^{•−} at 1.3 V vs Cc⁺/Cc (Cc = cobaltocene). They found a surprisingly high CO₂ solubility of 1520 mM in [BMIm][OAc] at ambient pressure. However, due to the probable high interaction, the diffusion of CO₂ in the IL was slow, which hampered the process somewhat and makes it less ideal for sequestration purposes.

Another promising utilization of electrochemically reduced CO₂ was reported by Lu and co-workers.²⁰⁶ They performed the electrocarboxylation of activated olefins in [BMIm][BF₄] at 1 bar CO₂ and 50 °C without using additional solvents. Monocarboxylic acids were obtained in yields between 35 and 55% in a one-compartment electrochemical cell using a Mg sacrificial anode and different cathodes. The cathode material had a significant impact on the reaction, as the yield decreased depending on the material used in the order stainless steel > Ti > Cu > Ni. As byproduct, mainly reduced olefins were obtained. The IL could be reused at least five times without apparent loss in activity.

Promising results were reported by Yuan et al. for the electrochemical dicarboxylation of arylacetylenes with CO₂ in a [Bu₄N]Br–DMF electrolyte system.²⁰³ They obtained the corresponding aryl-maleic anhydrides and 2-arylsuccinic acids in yields between 82 and 94%. Testing other ILs revealed a dependency of the activity in the order [Bu₄N]⁺ > [Et₄N]⁺ and Br[−] > Cl[−] > I[−]. The pressure of CO₂ also seemed to play a role, as, by increasing the pressure from 1 to 30 bar, the yield was almost doubled. This could be explained by the higher solubility of CO₂ in IL at 30 bar and the high requirement of CO₂ molecules in the reaction (2:1 compared to the olefin). The authors furthermore proposed a detail reaction mechanism, in which again the anionic radical CO₂^{•−} plays a key role as active intermediate.

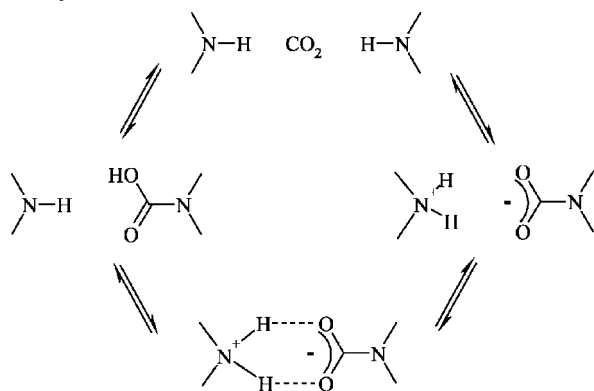
A similar electrochemical system was reported by Lu and co-workers who investigated the electrocatalytic carboxylation of benzyl chloride yielding phenylacetic acid as main product.²⁰⁷ The reaction was carried out under 1 bar of CO₂ and 50 °C in [BMIm][BF₄]. The reaction mechanism differs from the other reports in this field, as by using benzyl chloride, the reduction of this molecule (yielding PhCH₂[•] and Cl[−]) is the key step, and not reduction of CO₂. Therefore, the choice of electrode material had a great impact on the reaction outcome, as screening tests revealed. Using a silver cathode and a magnesium anode, almost no side products (apart from dimerization) were obtained, while when using Cu or Ni cathodes, the reduction potentials of benzyl chloride and CO₂ were much closer to each other. This then resulted in increased generation of CO₂^{•−} radicals and, hence, the formation of side products, such as oxalates, CO, and carbonates. In terms of temperature, the authors found an optimum range (around 50 °C), which was concluded to be governed on the lower side by higher CO₂ solubility at low temperatures and on the other side by lower viscosity (and facilitated mass transport) at higher temperatures.

Very recently, Hiejima et al. reported the electrochemical carboxylation of α -chloroethylbenzene to yield 2-phenylpropionic acid using not only well-known imidazolium-based ILs but also, for example, the rather unconventional IL *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)-imide [DEMe][Tf₂N].²⁰⁸ Interestingly, the reaction outcome depended greatly on the IL used. For example, if another cation (trimethylpropylammonium) was used, the reaction did not occur at all, which could not be explained convincingly. On the other hand, using [BMIm]⁺ as cation, the reaction proceeded well, but due to the more narrow electrochemical window, increased yield of undesired byproduct was obtained, which was attributed to reduction of the imidazolium-based cations. Mass transfer in [DEMe][Tf₂N] was enhanced by higher CO₂ pressures, due to lower viscosity, while the activity also increased with increasing temperature. Diffusion coefficient experiments were performed to investigate the mass transport behavior of [DEMe][Tf₂N], and the benefits of using a sacrificial Mg electrode for this reaction are discussed.

Another interesting way of electrochemical CO₂ conversion was reported by Chu et al., who synthesized low-density polyethylene (LDPE) from CO₂ on a nanostructured TiO₂ film electrode with 8–14% current efficiency.²⁰⁹ Rather dry [EMIm][BF₄] and [EMIm][BF₄] containing water were investigated as electrolytes, with the result that the latter appeared to be more suitable, as the catalytic activity was higher when water was present. For this study, the IL was chosen not only for its electrolytic properties but also (even mainly) because it would maintain a high CO₂ concentration at the electrode surface.

These examples prove that ILs have potential as reaction medium for electrochemical CO₂ conversion. Not only are ILs due to their intrinsic properties excellent electrolytes, they also exhibit sufficiently high CO₂ solubility to ensure reasonable reaction yield. The products obtained are in several cases highly valuable and—of course provided that inexpensive electricity is available—may lead to industrial applications, albeit not in the very near future.

3.2.4.2.2. Other, Non-electrochemical Transformations of CO₂ in ILs. There are other examples where CO₂ was successfully transformed into more useful chemicals by employing ILs as reaction medium. For instance, Tominaga

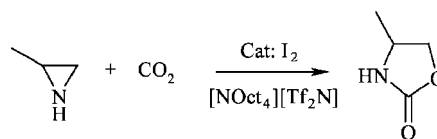
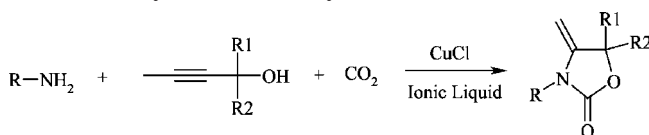
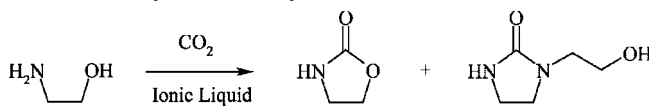
Scheme 10. Equilibria Existing in the Liquid Dimethylamine: CO₂ Adduct (Dimcarb)^{212,213}

and Sasaki developed a biphasic reaction system for hydroformylation of 1-hexene using CO₂ instead of CO as carbon source.^{210,211} Their unique reaction system, based on Ru₃(CO)₁₂ as catalyst, was initially using *N*-methyl-2-pyrrolidone (NMP) as crucial solvent, which later successfully was replaced by [BMIm]Cl, resulting in higher activity. They tested several apolar solvents for the biphasic system and found a trend in activity in the order cyclohexane < Et₂O < THF < toluene, in line with the miscibility with the IL used. Compared with their initial reaction system, the replacement of NMP by IL increased the yield of C₇ alcohols from 64% in the old system to 84% with IL.²¹¹ The regioselectivity, however, was not improved and remained at a ratio of almost 1:1 linear-to-branched. Later, they managed to avoid also the organic solvent by careful optimization of the system. The best results were obtained using a 1:1 mixture of [BMIm]Cl and [BMIm][Tf₂N] at 160 °C and 80 bar.²¹⁰

Another interesting example where IL could be used to successfully improve a reaction using CO₂ was reported by Stark et al. with the microwave-assisted Kolbe–Schmidt synthesis using ILs as reactive solvent and resorcinol (1,3-dihydroxybenzen).^{212,213} They investigated the use not only of ILs but also of Dimcarb as reactive solvent (Scheme 10), which can also be regarded as an “in situ” IL.

According to the authors, the use of Dimcarb offered some interesting aspects, especially concerning environmental questions, but actual ILs were significantly superior in terms of activity. Among the ILs studied were compounds containing imidazolium, pyridinium, ammonium, and phosphonium cations, which all worked similarly well. The anions consisted of hydrogencarbonate or methylcarbonate. Comparison between Dimcarb and such ILs proves the superiority of the latter, which generated almost double maximum yield (60%), while only 10% of the pressure was required (6 bar). With these parameters, and a working temperature of 100–160 °C, this IL-based Kolbe Schmidt reaction design could offer a true alternative to classical processes.

Similar to the synthesis of cyclic organic carbonates from epoxides and CO₂ (see section 3.2.4.1), the analogous reaction of aziridines and CO₂ in ILs (Scheme 11) was reported by Kawanami and co-workers.²¹⁴ Their very efficient system consisted of ammonium-based ILs and I₂ as catalyst, being able to yield 98% of the desired 2-oxazolidinone within 5 min, exceeding the TOF value in conventional solvents by more than 250 times. Their biphasic IL–CO₂ system at 40 °C and 100 bar pressure could reach TOFs of 838 h^{−1}. Interestingly, using an imidazolium-based [BF₄][−] IL (a very

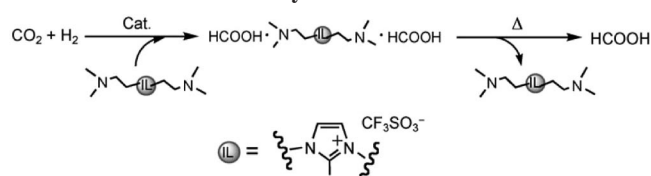
Scheme 11. Synthesis of 2-Oxazolidinones from Aziridines and CO₂²¹⁴**Scheme 12. Synthesis of Methylene Oxazolidinones in ILs²¹⁶****Scheme 13. Synthesis of Cyclic Urethanes in ILs²¹⁷**

active anion for the analogue reaction with oxiranes) led to complete deactivation, and almost no desired product was obtained. However, when they employed an ammonium-based IL (Scheme 11), excellent activity was achieved. Pressure tests led to the conclusion that an optimal pressure region at around 100 bar can be observed. This was explained by a too high solubility of the reactant in the scCO₂ phase at high pressures, thus hampering the reaction, while at too low pressures the decreased availability of CO₂ in the IL phase was the limiting factor.

Shi et al. from Deng's group reported another promising reaction in IL, the synthesis of symmetric urea derivatives from amines and CO₂.²¹⁵ They designed a reaction system using imidazolium-based ILs and CsOH or KOH as catalyst and achieved good yields of up to 98% after 4 h. Compared to industrial applications, their system does not require dehydrating agents (such as PCl₅ or POCl₃) and therefore offers promising green chemistry aspects. Different amines were tested, including aromatic amines, and good to excellent yields were obtained. Also, recycle experiments were successfully performed.

Shortly later, Gu et al., from the same research group, published a report on a similar reaction, the synthesis of 5-methylene-1,3-oxazolidin-2-ones from propargylic alcohols, amines, and CO₂ (Scheme 12).²¹⁶ Various amines and propargylic alcohols were tested, and good to excellent yields were achieved at 100 °C and 25 bar CO₂. The ILs tested consisted mainly of [BMIm]-based species, among which the one with a [BF₄][−] anion performed best. Also, some catalyst screening (involving the halide) was done, revealing an increase in activity in the order Br[−] = I[−] < Cl[−]. The authors stated that, for some products, the reported method involving ILs was better than other reported systems.

A similar reaction system was published by Fujita and co-workers, who synthesized cyclic urethanes from amino alcohols and CO₂ in ILs at 100 bar and 150 °C.²¹⁷ The reaction can yield not only 2-oxazolidinones as products but also consecutive products, such as 1-(2-hydroxyethyl)-2-imidazolidinone and other oligomeric heavier products (Scheme 13). A screening of different ILs (including imidazolium- and onium-based salts) showed drastic differences in product distribution depending on the IL used. The highest selectivity was achieved in [BMIm][BF₄], which almost only yielded 1-(2-hydroxyethyl)-2-imidazolidinone. Based on the reports of Deng et al., who used alkali metal

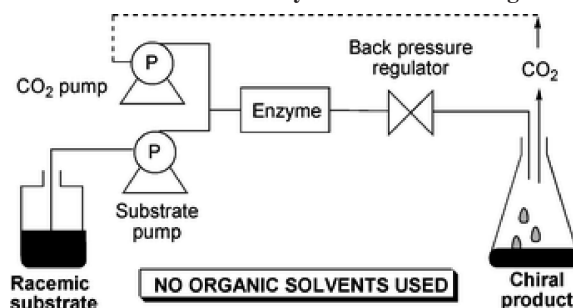
Scheme 14. Formic Acid Synthesis and Stabilization in ILs^a

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additives (such as CsOH),²¹⁵ the authors also tested such additives, finding that, among the tested salts, K₂CO₃ appeared beneficial, as it inhibited the formation of oligomers. Other additives did not have a significant impact. The influence of pressure was further studied, leading to the interesting finding that, around 100 bar, the selectivity for both main products was increased (especially for 2-oxazolidinone), but both higher and lower pressures lead to increased formation of oligomers. This was explained by phase-behavior effects, similar to the miscibility/solubility effects reported by others. Studies on a broad range of substrate amino alcohols and a proposed reaction mechanism further enrich this report.

Task-specific ILs are designed to improve a specific reaction based on their synthesis-based properties. As an example, new ILs with basic functional groups (e.g., a tertiary amino group on the cation) were synthesized and used for the hydrogenation of CO₂ to yield formic acid (HCOOH).²¹⁸ An IL containing a primary amino group (NH₂) could be used to absorb CO₂, but this NH₂ group would produce formamides with the formic acid, which would make it difficult to isolate the product (formic acid) and recover the IL after the reaction. A first IL with a tertiary amino group on the cation, namely 1-(*N,N*-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate ([MAMIm][OTf]), which can form a salt with formic acid and can be reused after separation, has been applied for this reaction.²¹⁸

As positive results were obtained from this first task-specific IL with one tertiary amino group on the cation, the same group continued with a second IL with two tertiary amino groups on the cation (1,3-di(*N,N*-dimethylaminoethyl)-2-methylimidazolium trifluoromethanesulfonate ([DAMI][OTf])), and they applied it for the hydrogenation of CO₂ to formic acid (CO₂ + H₂ → HCOOH) using a heterogeneous catalyst “Si”-(CH₂)₃NH(CSCH₃)-{RuCl₃(PPh₃)}, as depicted in Scheme 14.²¹⁹ The reaction shows high activity and high selectivity; moreover, increasing the water concentration, the pressure, or the temperature improved the reaction rate. In a batch system, the molar ratio of formic acid formed to the IL used can reach 2:1 in one reaction cycle, and recycling either the IL or the catalyst was possible. Indeed, Yasaka et al. very recently investigated the equilibrium reaction of formic acid production from H₂ and CO₂, with regard to using ILs as solvent.²²⁰ They compared the equilibrium constants in [PPMIm][HCOO], water, and vacuum (to study the gas phase reaction), and they found that the Coulombic solvation power present in the IL had a tremendously beneficial impact on the equilibrium toward the HCOOH side. The authors see in this method a possible future application for hydrogen storage, as formic acid can (unlike H₂) be easily stored and transported in the liquid state. This is a nice example of the unique properties of ILs as solvents for certain applications compared to “classical” solvents, and even water.

Scheme 15. Scheme of an Enzymatic Reactor Using IL/CO₂^a

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3.2.5. Biocatalysis (Enzyme Catalysis)

Also in the field of bio- or enzymatic catalysis, IL/scCO₂ biphasic systems have received considerable attention as reaction media, and several promising applications were reported (Scheme 15). As in other catalytic systems, the major advantage is the possibility to extract (as an alternative to distillation or extraction by organic solvents) nonvolatile or thermosensitive products from the catalytic IL phase. In this field, imidazolium-based [PF₆] and [Tf₂N] ILs are the most used ones, as they are rather hydrophobic and the size of the alkyl chain of the cation as well as the support appear to have a major impact on the catalytic activity.²²¹ *Candida antarctica* lipase (CAL A and CAL B) and *Mucor miehei* lipase (MML) are enzymes which can promisingly be used in such a reaction environment. Fan and Qian very recently published a concise review on lipase catalysis in IL/scCO₂ biphasic systems, including fundamentals as well as applications.²²² As an example, Miyawaki and Tatsuno reported a system, where scCO₂ was able to extract very selectively their butanolysis product butyloleate from the reaction mixture containing ceramic-immobilized *Burkholderia cepacia* lipase (PS-C I) in [MTOA][Tfa].²²³ Apart from the before mentioned extraction possibilities, the use of ILs alone already offers advantageous effects on enzymatic catalysis, as it leads to an overstabilization effect which enhances the half-life time of biocatalysts up to 2300-fold compared to classical organic solvents.²²² Enzyme-catalyzed transesterification reactions^{224–232} and acylation²³³ have also successfully been tested, and good activity was achieved, alongside with excellent long-term stability (weeks) and enantioselectivity (>99% ee). Lately, a few works pointed out some possibilities to further improve such biphasic systems. For example, a larger amount of enzyme can be dissolved in 1-hydroxy-1-propyl-3-methyl imidazolium nitrate ([HOPMIm][NO₃]) than in usual ILs used before.²³⁴ In order to improve the understanding of such complicated systems, vapor–liquid equilibrium (VLE) data for the ternary systems (CO₂ + IL + solute) have been studied in da Ponte's group.²³⁵ The authors explain that the separation factors (α), defined as ratios of partition factors for different solutes between IL and scCO₂ phases, do not change for pressures higher than 110 bar (at 35 °C). It is thus not necessary to apply higher pressure during the extraction cycle. A practical example of a complex synthesis is described in detail for the process of Levodopa production.²³⁶ For more details, biocatalytic reactions in ILs (including IL/scCO₂ biphasic systems) were discussed recently by Sureshkumar and Lee.²³⁷

As for other systems, the product yield and enantioselectivity of an enzymatic reaction in an IL-scCO₂ biphasic

system depend specifically on the transport phenomena, activity of the enzyme in the system, impurities, water content in the IL, leaching behavior, and specific parameters such as pH. The initial concentration of water within the range 0.5–2% (v/v) has a strong effect on the activity of the enzyme, as these biocatalysts normally stem from aqueous media. Nevertheless, as scCO₂ is known to be an efficient drying agent, for continuous systems, the water content should decrease with time and have an effect on the activity of the catalytic system, which has not been observed even with 100 bar and 50 °C under strong flow during 4 h.²²¹ Thus, the unexpected conclusion could be that scCO₂ is not able to extract the molecules of water necessary for the enzyme to do the catalytic reaction. This—alongside with the fact that a certain amount of water is required for many enzymatic reactions—might be an indication that a significant amount of water is very specifically and strongly bound to certain enzyme moieties and can therefore not be removed by scCO₂ extraction.

In summary, it can be concluded that, also in the field of biocatalysis, IL/CO₂ biphasic systems offer interesting possibilities. At least some ILs seem to be able to accommodate enzymes in a way that the narrow window of applicability is ensured (including pH, *T*, and maintained tertiary structure) while their solubility in CO₂ is sufficiently low to avoid leaching. Thus, also in this field further developments can be expected.

3.2.6. Potential for Industry

While several industrial applications have already been improved by replacing conventional solvents by ILs, to our knowledge, biphasic IL/CO₂ systems have not been implemented yet in larger scale. However, this is in our opinion only a matter of time. Highly successful applications using only IL (and no CO₂ yet) were only introduced less than a decade ago. Examples of such systems include the BASIL process (BASF),²³⁸ metathesis reactions (SASOL),²³⁹ the Dimersol process (Institut Français du Pétrole),²⁴⁰ and a hydrosilylation process using ILs (Degussa).²⁴¹ In all these examples, conventional solvents were replaced by ILs and the processes improved greatly in terms of activity, selectivity, or both. Many more processes are implemented or being currently modified by IL, tested, and upscaled for industrial application. A detailed discussion of the so far implemented industrial uses for ILs can be found in a recent critical review by Plechkova and Seddon.²⁴² The authors outline the potential of ILs in industry and attest them a bright future, mainly due to their extreme versatility and their possibility to be highly tailored to specific applications. The same can be expected for IL/CO₂ biphasic systems, as the examples of current academic research summarized in this review article show. Such developments may include mainly separations, but also continuous biphasic reactions (e.g., involving SILP catalysis) seem promising. Already there are studies which conclude that this combination might also be attractive from an economical point of view. As an example, Damen et al. proposed an industrially feasible process for the production of Levodopa based on an IL/CO₂ biphasic system and compared it to the conventional Monsanto process.²³⁶ The authors found that both the production costs and the energy requirement are lower when the IL/CO₂ system is used. The latter point is illustrated by the fact that the energy requirement for the evaporation of the conventional solvent (methanol) in the Monsanto process was calculated to be 24%

higher than the energy requirement for the compression of CO₂ in the postulated IL/CO₂ process to achieve the same separation. One drawback was found in the rather poor solubility of Levodopa in scCO₂, which contributed significantly to the energy costs of the new process. Still, even with suboptimal presuppositions, this IL/CO₂ process was found to be superior to the process using conventional solvents and, therefore, was patented.²⁴³ This example nicely shows the potential of IL/CO₂ biphasic systems for industry. The highly successful and increasing application of ILs²⁴² can be further extended for applications making use of the beneficial interplay of ILs and CO₂, as summarized in this review. As mentioned before, such applications are especially interesting for separations or SILP processes, but also IL-based processes using CO₂ as reactant may become attractive for industry, although, for example, the cyclic carbonates (see section 3.2.4) are probably still too expensive to be produced in this way. Nevertheless, we believe that IL/CO₂ systems will find industrial application in the not too distant future as a subsection of the increasingly attractive IL applications in industry, as CO₂ can broaden the task-specific properties of ILs which make them so unique (and often superior) compared to classical solvents.

4. Conclusions and Outlook

In this review the work on IL/CO₂ bi- and multiphasic catalytic systems published until early 2010 has been summarized and discussed, including fundamental aspects and with an additional focus on CO₂ conversion. The intrinsic properties of such IL/CO₂ systems, including but not limited to solubility phenomena, offer unique and extremely promising possibilities for applications in catalysis. The structurally highly versatile ILs with their unique properties (e.g., extremely low vapor pressure) can be tailored for desired reactions, while inexpensive, nontoxic, and abundantly available scCO₂ can be employed for facile product extraction without the problem of product contamination. Moreover, CO₂ improves the usability of ILs by lowering their melting point and viscosity and by facilitating mass transport and enhancing the solubility of gases. Thus, despite the still relatively high costs and still insufficient toxicity data for ILs, an almost ideal biphasic system for catalysis is now available, which has the potential to reduce the massive use of volatile organic solvents in certain industrial processes and to improve many catalytic systems. Especially IL/CO₂ SILP catalysis has enormous potential, as it makes use of all the before-mentioned intrinsic advantages while diminishing the problems of slow mass transfer in ILs and their high costs. Furthermore, it broadens considerably the possibilities to immobilize homogeneous catalysts and to design continuous flow systems, in cases where so far only batch systems were possible.

IL/CO₂ biphasic systems additionally widen the possibilities to chemically convert CO₂, a desirable goal for partially replacing toxic and hazardous substances such as carbon monoxide and phosgene in industry. For example, the high solubility of CO₂ in certain ILs facilitates electrochemical CO₂ activation, as ILs also have good electrolyte properties. Yet, the most intensively studied route to convert CO₂ by employing ILs remains the synthesis of cyclic organic carbonates, as many ILs act as highly active catalysts for this reaction.

Despite the fact that still a lot of research is necessary to completely understand IL/CO₂ biphasic systems, especially

Table 4. Alphabetical List of IL Cation and Anion Abbreviations and the Corresponding Chemical Names Used in this Review Article

| cations | | anions | |
|-----------------------|---|-----------------------|--|
| formula | name | formula | name |
| [BDMMA] | benzyldecyldimethylammonium | [BETI] | bis(perfluoroethylsulfonyl)-imide |
| [Bpy] | 1-butylpyridinium | [BF ₄] | tetrafluoroborate |
| [BzIm] | 1,3-dibenzylimidazolium | [DCA] | dicyanamide |
| [BMIm] | 1-butyl-3-methylimidazolium | [FEP] | tris(pentafluoroethyl)trifluorophosphate |
| [BMMIm] | 1-butyl-2,3-dimethylimidazolium | [HCOO] | formate |
| [Chol] | choline (<i>N,N,N</i> -trimethylethanol-ammonium) | [MeSO ₄] | methylsulfate |
| [DAMI] | 1,3-di(<i>N,N</i> -dimethylaminoethyl)-2-methylimidazolium | [methide] | tris(trifluoromethylsulfonyl)-methide |
| [DEME] | <i>N,N</i> -diethyl- <i>N</i> -methyl- <i>N</i> -(2-methoxyethyl)ammonium | [NO ₃] | nitrate |
| [DESMIm] | 1-(2-ethylsulfonyl)ethyl-3-methylimidazolium | [OAc] | acetate |
| [DMIm] | 1-decyl-3-methylimidazolium | [OTf] | trifluoromethanesulfonate |
| [EMIm] | 1-ethyl-3-methylimidazolium | [PF ₆] | hexafluorophosphate |
| [HBet] | betainium | [Tf ₂ N] | bis(trifluoromethylsulfonyl)-imide |
| [HDMIm] | 1-hexadecyl-3-methylimidazolium | [Tfa] | trifluoroacetate |
| [HDPy] | 1-hexadecylpyridinium | [TfePF ₃] | trifluorotris(perfluoroethyl)-phosphate |
| [HEMIm] | 1-(2-hydroxyethyl)-3-methylimidazolium | [tosyl] | 4-toluenesulfonate |
| [HETBA] | hydroxyethyltributylammonium | | |
| [HETEA] | hydroxyethyltriethylammonium | | |
| [HMIIm] | 1-hexyl-3-methylimidazolium | | |
| [HOPMIm] | 1-(1-hydroxypropyl)-3-methylimidazolium | | |
| [MAMIm] | 1-(<i>N,N</i> -dimethylaminoethyl)-2,3-dimethylimidazolium | | |
| [MBPy] | 1-butyl-4-methylpyridinium | | |
| [MTOA] | methyltrioctylammonium | | |
| [NBu ₄] | tetrabutylammonium | | |
| [NHep ₄] | tetraheptylammonium | | |
| [NHex ₄] | tetrahexylammonium | | |
| [NOct ₄] | tetraoctylammonium | | |
| [NPen ₄] | tetrapentylammonium | | |
| [OMIm] | 1-octyl-3-methylimidazolium | | |
| [PBu ₄] | tetrabutylphosphonium | | |
| [PMMIm] | 1-propyl-2,3-dimethylimidazolium | | |
| [PPh ₃ Bu] | butyltriphenylphosphonium | | |
| [PPMIm] | 1,3-dipropyl-2-methylimidazolium | | |
| [PPN] | bis(triphenylphosphine)iminium | | |
| [PSPy] | <i>N</i> -propane-sulfonic acid pyridinium | | |
| [THTDP] | trihexyltetradecylphosphonium | | |

on a molecular level, it can be concluded that the beneficial interplay of ILs and CO₂ will lead to many more interesting applications in SILP and biphasic catalysis, in biocatalysis, and also in noncatalytic applications such as CO₂ sequestration and gas separation.

5. Abbreviations

5.1. General Abbreviations

| | |
|------------|---|
| acac | acetylacetone |
| AGE | allyl glycidyl ether |
| AIBN | azobis(isobutyronitrile) |
| ATR-(FT)IR | attenuated total reflectance (Fourier-transformed) infrared |
| BARF | tetrakis[3,5-bis(trifluoromethyl)phenyl]borate |
| BINAP | 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl |
| CAL | <i>Candida antarctica</i> lipase |
| Cc | cobaltocene |
| CHO | cyclohexene oxide |
| COSMO-RS | conductor-like screening model for real solvents |
| DFT | density functional theory |
| DMC | dimethyl carbonate |
| DVB | divinylbenzene |
| ECH | epichlorhydrin |
| ee | enantiomeric excess |
| EoS | equation of state |
| ESI-MS | electrospray ionization mass spectrometry |
| FE | Faradaic efficiency |
| FTIR | Fourier-transformed infrared |
| GPE | glycidyl propargyl ether |
| HO | hexylene oxide |

| | |
|----------------------|--------------------------------------|
| IL | ionic liquid |
| LDPE | low-density polyethylene |
| LSER | linear solvation energy relationship |
| MML | <i>Mucor miehei</i> lipase |
| MPD | melting point depression |
| NMR | nuclear magnetic resonance |
| NMP | <i>N</i> -methyl-2-pyrrolidone |
| PC | propylene carbonate |
| PO | propylene oxide |
| PS-C I | <i>Burkholderia cepacia</i> lipase |
| RTIL | room-temperature ionic liquid |
| SAFT | statistical associated fluid theory |
| scCO ₂ | supercritical carbon dioxide |
| SILP | supported ionic liquid phase |
| SO | styrene oxide |
| <i>T_m</i> | melting point |
| TOF | turnover frequency |
| TON | turnover number |
| UV/vis | ultraviolet/visible spectroscopy |
| VLE | vapor–liquid equilibrium |
| VLL | vapor–liquid–liquid equilibrium |
| WGS | water–gas shift reaction |
| ZnPO | zinc phenolsulfonate octahydrate |

5.2. Ionic Liquids Abbreviations

The abbreviations for the IL anions and cations used throughout this article are given in Table 4, including their full chemical nomenclature in order to avoid ambiguity.

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