2 Supercritical Fluids in Ionic Liquids

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ABSTRACT

Ionic liquids and supercritical fluids are both alternative environmentally benign solvents, but their properties are very different. Ionic liquids are non-volatile but often considered highly polar compounds, whereas supercritical fluids are non-polar but highly volatile compounds. The combination of these two types of solvents has some unique features. It has been discovered that the solubility of supercritical carbon dioxide in several ionic liquids is very high but that the solubility of ionic liquids in supercritical carbon dioxide is negligibly low. Therefore, organic solutes can be extracted from an ionic liquid using supercritical carbon dioxide without any contamination by the ionic liquid. The phase behaviour of many binary or ternary (ionic liquid + supercritical carbon dioxide) systems was subsequently studied. Combined with the fact that ionic liquids are excellent reaction media for catalysed reactions, this led to the development of chemical processes where the reaction was carried out in the ionic liquid and the product was extracted afterwards with supercritical carbon dioxide. Newest developments include the multi-functional use of supercritical carbon dioxide as extraction medium, transport medium, and miscibility controller in these processes, resulting in higher reaction and separation rates.

2.1 INTRODUCTION

Both ionic liquids and supercritical fluids have been described as alternative "green" solvents, which are highly tuneable. The properties of an ionic liquid can be tuned by the choice of the cation and the anion [1]. The properties of a supercritical fluid can be adjusted to be more "gas-like" (low solvency power) or "liquid-like" (high solvency power) by adjusting the pressure [2, 3]. Most commonly used supercritical fluids include carbon dioxide (CO_2), ethane, propane, ethane, and fluoroform (trifluoromethane, CHF_3) above their critical point. Supercritical CO_2, in particular, has attracted a lot of interest, because it is non-toxic, non-flammable, relatively inert, abundant, and inexpensive. Moreover, it is relatively easy to reach the critical conditions (304 K, 7.4 MPa) [3].

The properties of ionic liquids and supercritical CO_2 are very different. Ionic liquids are non-volatile but often considered as highly polar compounds, whereas CO_2 is a non-polar but highly volatile compound. The combination of these two types of solvents has some unique features. In 1999, it was reported that the solubility of supercritical CO_2 in [C_4mim][PF_6] was very high but that CO_2 is not able to dissolve these ionic liquids [4]. Therefore, it was found to be possible to extract a solute from an ionic liquid using supercritical CO_2 without any contamination by the ionic liquid [5]. The phase behaviour of many binary or ternary (ionic liquid + supercritical CO_2) systems was subsequently studied, and is addressed in Section 2.2. Combined with the fact that ionic liquids are excellent reaction media for catalysed reactions, this led to the development of chemical processes where the reaction was carried out in the ionic liquid and the product was extracted afterwards with supercritical CO_2. Newest developments include the multi-functional use of supercritical CO_2 as extraction medium, transport medium, and miscibility controller in these processes, resulting in higher reaction and separation rates. These applications of (ionic liquid + supercritical fluid) systems are described in Section 2.3. The chapter ends with some conclusions and an outlook with regard to (ionic liquid + supercritical fluid) systems.

2.2 PHASE BEHAVIOUR OF (IONIC LIQUID + SUPERCRITICAL FLUID) SYSTEMS

2.2.1 Experimental Methods

Different methods to determine the phase behaviour of (ionic liquid + supercritical fluid) systems are available. Synthetic methods are most commonly used to determine the phase behaviour of these systems [6–9], whereby mixtures of (ionic liquid + supercritical fluid) of known composition are prepared and the phase transitions within a certain pressure and temperature range are subsequently observed. The synthetic method is suitable over wide pressure and temperature ranges and very reliable, but does not allow the analysis of

the phases in equilibrium. Another commonly used method is the static method [10–13], whereby the equilibrium cell at constant temperature is filled with a known amount of ionic liquid, which is brought into contact with a calibrated reservoir filled with supercritical fluid until equilibrium is reached as indicated by negligible pressure change. Dynamic methods are less commonly used and also less reliable, but allow analysis of the different phases [12]. However, the analysis of the supercritical phase is not always very useful, because many ionic liquids have negligible solubility (below detection limit) in the supercritical phase [4, 5]. The gravimetric balance, often used for determining gas solubilities in ionic liquids [14], is generally not suitable for measuring the phase behaviour of (ionic liquid + supercritical fluid) systems because of its low-pressure range (<2 MPa).

2.2.2   Phase Behaviour of Binary (Ionic Liquid + Supercritical Fluid) Systems

2.2.2.1   *The Binary Ionic Liquid + Supercritical CO_2 System.*   The most widely investigated binary (ionic liquid + supercritical fluid) systems are the mixtures of 1,3-dialkylimidazolium ionic liquids with supercritical CO_2 [4–14]. A typical phase diagram of these systems is depicted in Figure 2.1.

From Figure 2.1, it can be concluded that the CO_2 solubility in a 1,3-dialkylimidazolium ionic liquid is high at lower pressures, but a nearly infinite bubble-point slope is present at a specific maximum concentration of CO_2, beyond which increasing the external pressure hardly increases the CO_2 solubility in the ionic liquid. According to Huang et al. [15], the reason for this sharp pressure increase at a certain maximum CO_2 concentration is that at this
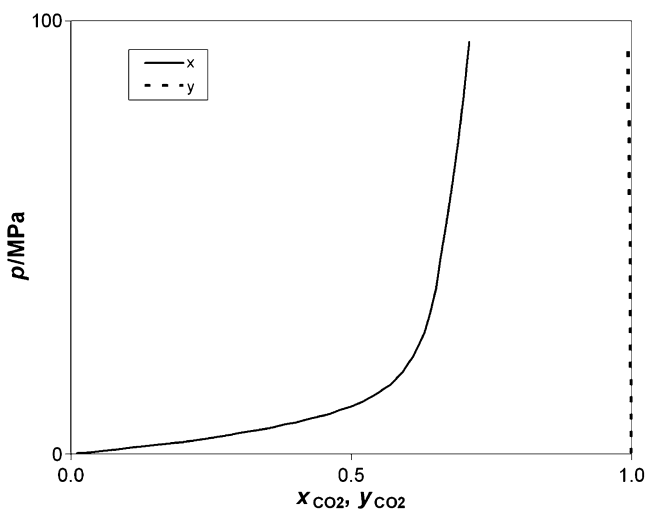

Figure 2.1   Typical phase behaviour of binary (ionic liquid + CO_2) systems.

point all cavities in the ionic liquid phase are occupied by CO_2, so that further insertion of CO_2 would require "breaking" the cohesive structure of the ionic liquid.

It was found that the anion predominantly determines the CO_2 solubility in 1,3-dialkylimidazolium ionic liquids [11]. Ionic liquids with anions containing fluoroalkyl groups, such as the $[NTf_2]^-$ anion, show highest CO_2 solubility [9, 11]. It was also observed that an increase in the alkyl chain length on the cation increases the CO_2 solubility in the ionic liquid [7, 8]. The solubility of CO_2 in an ionic liquid decreases with increasing temperature [16].

The extremely low solubility of 1,3-dialkylimidazolium ionic liquids in supercritical CO_2, as indicated by the straight dew point line at a CO_2 mole fraction of 100% in Figure 2.1, resulted in the use of supercritical CO_2 to extract products from these ionic liquids without solvent contamination [5]. However, some ionic liquids that do not incorporate a 1,3-dialkylimidazolium cation show completely different phase behaviour. For example, the ionic liquid $[P_{6\,6\,6\,14}]Cl$ was found to be able to dissolve in supercritical CO_2 up to a mass fraction of 7% [17], indicating that one has to be extremely cautious when stating that ionic liquids cannot dissolve in supercritical CO_2.

2.2.2.2   *The Binary (Ionic Liquid + Supercritical ChF₃) System.*   While supercritical CO_2 is not able to dissolve any 1,3-dialkylimidazolium ionic liquid [4], other supercritical fluids do. Ionic liquids are especially soluble in hydrocarbons that have a strong molecular interaction with the ionic liquid, such as supercritical CHF_3 [18, 19]. Figure 2.2 shows the general phase
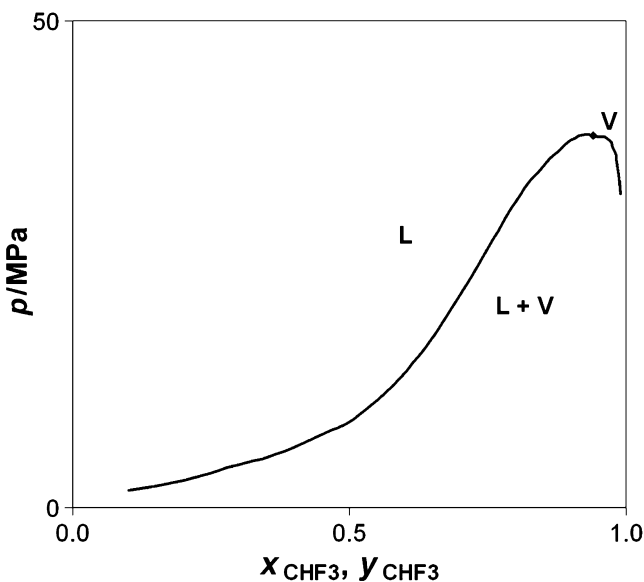

Figure 2.2   Typical phase behaviour of binary (ionic liquid + CHF_3) systems.

behaviour of binary (ionic liquid + CHF_3) systems [18–20]. This phase diagram is completely different from the phase diagram of binary (ionic liquid + CO_2) systems. The binary ionic liquid system with CHF_3 shows a closed phase envelope, including the occurrence of a critical point [18], whereas the CO_2 binary system with the same ionic liquid has an immiscibility gap between the CO_2 phase and the ionic liquid phase, even up to very high pressures. This has been attributed to the stronger molecular interactions between CHF_3 (with its strong permanent dipole moment) and the ionic liquid compared to those between CO_2 (no dipole moment) and the ionic liquid [8]. Again, it can be concluded that one has to be extremely cautious when stating that ionic liquids cannot dissolve in supercritical fluids. This is simply not true. In fact, the solubility of an ionic liquid in a supercritical phase depends on the curvature of the critical line in type III systems, according to the classification of Scott and van Konynenburg [21].

2.2.2.3   Classification of Binary Ionic Liquid + Supercritical Fluid Systems.
Scott and van Konynenburg [21] found that six different types of fluid phase behaviour exist, which are presented in Figure 2.3. With an exception of type VI, all types could be retrieved from the van der Waals equation of state. Although the original classification of Scott and van Konynenburg is still accepted, a detailed study on the occurrence of "holes" in ternary fluid multiphase systems [22], with CO_2 as one of the components, showed that acceptance of the existence of types I and V for binary CO_2 systems leads to inconsistency in the fluid phase transformations in ternary systems. For
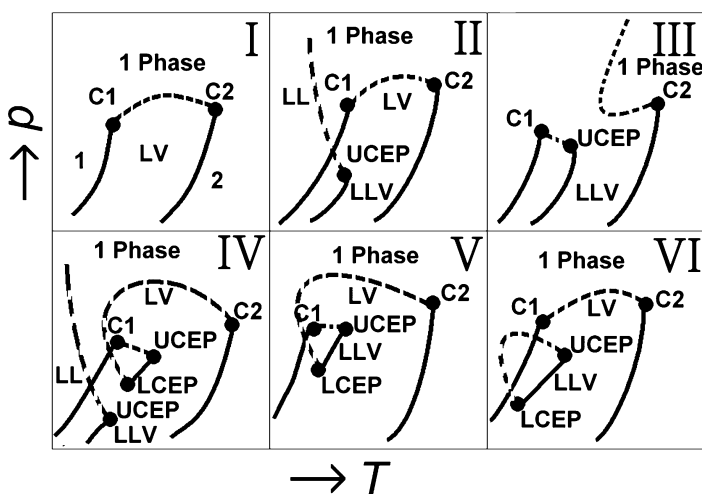

Figure 2.3   Classification of the liquid–vapour phase behaviour of binary systems according to Scott and van Konynenburg [21]. C, critical point; L, liquid; V, vapour; UCEP, upper critical end point; LCEP, lower critical end point.

instance, if in the ternary system (CO_2 + A + B), the binary system (CO_2 + A) has type III and the binary system (CO_2 + B) has type V fluid phase behaviour, a continuous transformation from type III into type V, by gradually replacing molecules A by molecules B, cannot be made. The same observation applies if type II or type IV is combined with type V or type I. These inconsistencies can only be overcome if it is assumed that type V in reality is type IV and, similarly, that type I in reality is type II, that is, both type I and type V must have a low-temperature liquid–liquid immiscibility region, as is the case in type IV. In all, this means that the original classification of Scott and van Konynenburg only comprises three independent types of fluid phase behaviour (II, III, and IV). From experiments in ternary CO_2 systems, it became apparent that between types II, III, and IV, continuous transformations are always possible, which is not the case if a type I or a type V is accepted to exist [22].

According to the foregoing discussion, the dispute whether binary (ionic liquid + CO_2) systems show type III or type V phase behaviour is not relevant and should be replaced by the question of whether we are dealing with type III or type IV [23]. As can be seen from Figure 2.3, type III has an upper critical end point (UCEP) of the nature $L_1 = V + L_2$, while type IV has, coming from higher to lower temperature, a UCEP ($L_1 = V + L_2$), followed by a lower critical end point (LCEP) of the nature ($L_1 = L_2 + V$) towards lower temperature and finally another UCEP ($L_1 = V + L_2$) as the beginning of the lower temperature branch of the three-phase equilibrium L_1L_2V. This means that if both a UCEP and an LCEP are present in the system, it will have type IV fluid phase behaviour. However, if only a UCEP can be identified in the system, it will have a type III fluid phase behaviour. An additional indication that we are dealing with type V phase behaviour is that this type has a critical line running from critical point 1 (C1) to critical point 2 (C2), which can be easily identified both experimentally and computationally, while type III phase behaviour shows a range of temperatures at which there are two immiscible phases up to infinite pressures. From the foregoing discussion, it follows that computational studies [14] suggesting that type V has to be assigned to (ionic liquid + CO_2) systems are not correct, and should be most likely type III [8, 24] or type IV, in case also an LCEP is present in the system. As it is experimentally observed that (1,3-dialkylimidazolium ionic liquid + CO_2) systems show the existence of two immiscible phases even up to extremely high pressures (>0.3 GPa) [5], binary (ionic liquid + CO_2) systems most likely will show a type III phase behaviour [8, 24]. In line with the foregoing discussion, (ionic liquid + CHF_3) systems, which show a critical line running from C1 to C2 as indicated in Figure 2.3 for type IV, most likely show a type IV fluid phase behaviour [25].

2.2.2.4 *Modelling of Binary Ionic Liquid + Supercritical Fluid Systems.*
Different types of equations of state have been used to model the phase behaviour of binary (ionic liquid + supercritical fluid) systems. Cubic equations of state such as the Peng–Robinson equation [18] and the Redlich–

Kwong equation [14, 25] have been used to describe the solubility of CO_2 and CHF_3 in ionic liquids. Because these cubic equations of state require the critical parameters of ionic liquids, which are unknown and have to be estimated by using group contribution methods [14], it is unreliable to apply cubic equations of state to ionic liquid systems. Moreover, cubic equations of state can only describe the CO_2 solubility in ionic liquids at low concentrations and pressures (below the critical pressure of CO_2), but cannot predict the dramatic increase in bubble-point pressure at higher CO_2 concentrations [18]. This is the reason why type V (type IV according to the previous discussion) phase behaviour was wrongly assumed for binary (ionic liquid + CO_2) systems on the basis of numerical calculations [23].

More reliable phase behaviour predictions for binary ionic liquid systems with CO_2 come from group contribution equations of state, such as the non-random lattice fluid equation of state [13] and the group contribution equation of state of Skjold–Jørgensen [26]. In group contribution methods, molecules are decomposed into groups which have their own parameters. Generally, ionic liquids are decomposed into a large group, consisting of the anion and the methylated (aromatic) ring of the cation, and a CH_3 group and various CH_2 groups that form the alkyl chain of the cation [13, 26]. For example, Figure 2.4 shows how the ionic liquid $[C_4mim][BF_4]$ is decomposed into one CH_3 group, three CH_2 groups, and one $[mim][BF_4]$ group. Pure group parameters are regressed from liquid density data [13]. Binary interaction parameters are fitted from infinite dilution activity coefficients and vapour–liquid equilibrium data of binary (ionic liquid + CO_2) systems [26]. In this way, the unknown critical parameters and vapour pressures of ionic liquids are not needed to determine group contribution equation of state parameters. Consequentially, phase equilibrium data can be predicted with higher accuracy [13, 26].

Statistical-mechanics-based equations of state are most predictive because they account explicitly for the microscopic characteristics of ionic liquids. The statistical association fluid theory models tPC-PSAFT [27, 28] and soft-SAFT [29] have successfully been used to model the phase behaviour of binary ionic liquid systems with CO_2 over a wide pressure range (0–40 MPa). These statistical mechanics-based equations of state consider the ionic liquids to be asymmetrical neutral ion pairs, either with a dipole moment to account for the charge distribution of the ion pair (for tPC-PSAFT) [27, 28] or with an
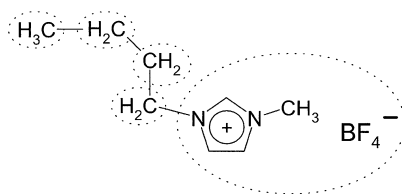

Figure 2.4   Decomposition of the ionic liquid $[C_4mim][BF_4]$ into separate groups.

associating site mimicking the interactions between the cation and anion as a pair (in the case of soft-SAFT) [29]. Also, the associating interactions between ionic liquids and CO_2 are accounted for. All pure-component parameters for ionic liquids are calculated from available physicochemical data of the constituent ions, such as size, polarisability, and number of electrons [27]. This means that all parameters are physically meaningful. Only one binary interaction parameter for each possible binary pair is adjusted in order to fit the model to experimental vapour-liquid equilibrium data [26–28]. Statistical associating fluid theory models predict the phase behaviour of ionic liquid systems with CO_2 with high accuracy [27–29]. However, it is less suitable to predict the phase equilibria of ionic liquid systems with more polar compounds (e.g., CHF_3), because ionic liquid dissociation into its constituent ions is not taken into account [28].

2.2.3   Phase Behaviour of Ternary (Ionic Liquid + Supercritical Fluid) Systems

The number of different binary (ionic liquid + supercritical fluid) systems is already very large, but the number of possible ternary (ionic liquid + supercritical fluid) systems is orders of magnitude larger. However, the phase behaviour of only a few ternary (ionic liquid + supercritical fluid) systems has been investigated so far. Most studied ternary (ionic liquid + supercritical fluid) systems consist of an ionic liquid, supercritical CO_2, and an organic compound (*viz.* alkane, alcohol, ketone, ester, etc.) [30–40]. In some cases, the third compound is water [41–43].

   Figure 2.5 shows the general phase behaviour of ternary (ionic liquid (liquid) + CO_2 (vapour) + organic (liquid)) mixtures. When the ionic liquid and the organic compound are completely miscible at ambient conditions (liquid + vapour), it is possible to induce the formation of a second liquid
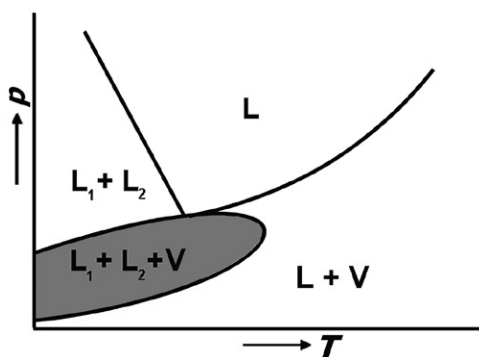

Figure 2.5   Phase behaviour of ternary (ionic liquid + supercritical CO_2 + organics) systems.
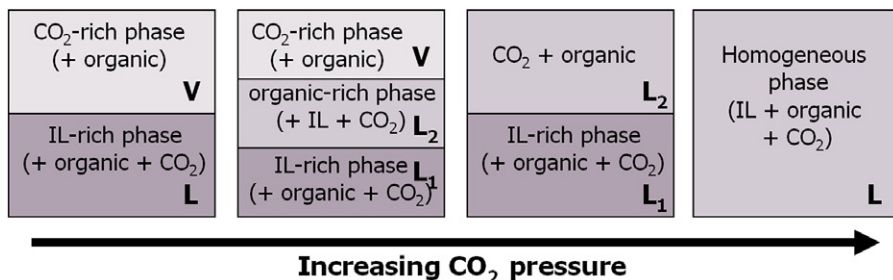
CO_2-rich phase (+ organic) **V**	CO_2-rich phase (+ organic) **V**	CO_2 + organic **L₂**	Homogeneous phase (IL + organic + CO_2)
	organic-rich phase (+ IL + CO_2) **L₂**		
IL-rich phase (+ organic + CO_2) **L**	IL-rich phase (+ organic + CO_2) **L₁**	IL-rich phase (+ organic + CO_2) **L₁**	**L**

Increasing CO_2 pressure →

Figure 2.6   Supercritical CO_2-induced "two-phase"–"three-phase"–"two-phase"–"one-phase" transition in ternary (ionic liquid + CO_2 + organics) systems.

phase by placing a pressure of CO_2 upon the mixture (liquid + liquid + vapour) [30–39]. The most dense phase is rich in ionic liquid, the newly formed liquid phase is rich in organics, and the vapour phase mostly contains CO_2 with some organics. Further pressurisation leads to expansion of the organic-rich phase with increased CO_2 pressure, while the ionic liquid-rich phase expands relative little. Eventually, this will lead to the disappearance of the vapour phase at the point where the organic-rich phase merges with the vapour phase [31–39]. At this moment, the last traces of ionic liquid that remained in the organic-rich liquid phase are expelled, and the resulting (CO_2 + organic phase) contains no detectable ionic liquid. Eventually, when the pressure is increased even further, one homogeneous liquid region is reached [36, 37].

Interestingly, it is thus possible to induce ternary (ionic liquid + CO_2) systems to undergo a "two-phase"–"three-phase"–"two-phase"–"one-phase" transition by only changing the CO_2 pressure (Fig. 2.6) [36]. Although the simple phase transition from two to three phases by addition of CO_2 was already known to occur in ternary CO_2 systems without an ionic liquid, it was discovered only recently to occur in ternary CO_2 systems in the presence of an ionic liquid [30]. Initially this phenomenon was wrongly identified as LCEP [30]. Thereafter, the transition from three to two phases at further CO_2 pressure increase was discovered, and also wrongly identified as K-point [31]. After all, both transitions are normal phase transitions without any criticality involved [40]. More recently, the formation of a homogeneous liquid phase at even higher CO_2 pressures was found [36, 37]. The location of this homogeneous liquid phase is hard to locate because it occurs in a relatively narrow range of CO_2 concentrations [36].

Ternary (ionic liquid + CO_2 + water) systems show similarities to ternary (ionic liquid + CO_2 + organic) systems. The supercritical CO_2 can cause liquid–liquid separation in hydrophilic (ionic liquid + water) mixtures [41–43].

It is more difficult to model the phase behaviour of ternary (ionic liquid + supercritical fluid) systems compared with the binary ones. The only equation of state that has been successfully applied to model ternary (ionic

liquid + supercritical fluid) systems is the group contribution equation of state of Skjold–Jørgensen [44]. Excess Gibbs energy methods, commonly used to model ternary ionic liquid systems without any supercritical fluid added [45, 46], were not successful for this purpose.

2.3   CHEMICAL PROCESSING IN (IONIC LIQUID + SUPERCRITICAL FLUID) SYSTEMS

2.3.1   Separations in Ionic Liquid + Supercritical Fluid Systems

2.3.1.1 CO_2 Removal from Process Streams Using Ionic Liquids.   Super-critical CO_2 has a high solubility in ionic liquids [4]. Other compounds show much lower solubilities in ionic liquids. After CO_2, the supercritical fluids CHF_3 and hydrogen sulfide have the highest solubilities and strongest interactions with the ionic liquid [18, 47], followed by methane [48, 49]. Carbon monoxide is less soluble [49, 50]. Dihydrogen (H_2) is the least soluble of all supercritical fluids studied [49].

These differences in solubility can be used to separate CO_2 from high-pressure streams by using ionic liquids as selective extractants [51] or in sup-ported membranes [4, 52]. As opposed to conventional absorption techniques using amines, the lack of vapour pressure of ionic liquids minimises the loss of the capturing agent into the gas stream [52]. Examples include the separa-tion of acid gases from natural gas [51, 53] or purifying the products from steam reforming or water gas-shift reactions using ionic liquids [49, 51]. For example, the production of H_2 from fossil fuels by steam reforming/water gas shift can be enhanced by simultaneous removal of the by-product CO_2 using an ionic liquid [49].

2.3.1.2   Recovery of Organic Compounds from Ionic Liquids with Super-critical CO_2.   Because supercritical CO_2 is able to dissolve a wide range of organic compounds, but 1,3-dialkylimidazolium ionic liquids are not soluble in supercritical CO_2 [4], several studies have focussed on the recovery of organic compounds from these ionic liquids by using supercritical CO_2 as extractant [5, 54, 55]. Combined with the fact that ionic liquids are excellent reaction media for catalysed reactions [1], this led to the development of chemical processes where the reaction was carried out in the ionic liquid and the product was extracted afterwards with supercritical CO_2 [54, 55]. The main advantage is that the organic compound is recovered free of ionic liquid [5]. Disadvantages are the low extraction rate due to mass transfer limitations at the interface between the two phases, and the batch-wise operation of the process, making it is difficult to scale up [55].

A closer look at the phase behaviour of ternary (ionic liquid + supercritical CO_2 + organics) systems (Fig. 2.5 and Fig. 2.6) shows that this type of extrac-tion is only possible in the "two-phase" region (liquid + supercritical fluid)

[36]. Here, the supercritical CO_2 phase does not contain any ionic liquid, while the solubility of the organic compound in CO_2 is sufficiently high [36]. The conditions under which the different phase transitions ("two-phase"–"three-phase"–"two-phase"–"one-phase") occur depend on the type of organic, the type of ionic liquid, and the concentrations [32, 56]. Stronger interaction between the ionic liquid and the organic compound makes it more difficult for CO_2 to induce the formation of a second liquid phase, and also to recover the organic compound [56]. This difference in affinity can be used for selective extraction of specific organics from ionic liquids by using CO_2 [57].

CO_2 at low concentrations was found to work as co-solvent (increasing the solubility of organics into the ionic liquid phase), while CO_2 at higher concentrations worked as an anti-solvent (decreasing the solubility of organics in the ionic liquid phase) [58]. The same type of phase behaviour was also observed for systems in which the organic is a solid instead of a liquid [59]. Therefore, it is also possible to recover an organic compound from an ionic liquid by crystallisation using supercritical CO_2 as anti-solvent [59].

2.3.2   Combined Reactions and Separations in Ionic Liquid + Supercritical Fluid Systems

2.3.2.1   *Continuous Biphasic Processes with Ionic Liquids and Supercritical CO_2.*   After reaction, the formed organic products can be separated batch-wise from ionic liquids by extraction with supercritical CO_2. It was found that continuous operation could be achieved when the supercritical CO_2 was used not only as an extraction medium, but also as a transport medium [60–65]. In this case, the supercritical CO_2 phase acts both as a reactant and as a product reservoir (Fig. 2.7). The reactants are transported into the reactor using supercritical CO_2 as the mobile phase. In the reactor, the reactants dissolve in the ionic liquid phase with immobilised catalyst, where the reaction takes place. The products are continuously extracted with the supercritical CO_2 stream.
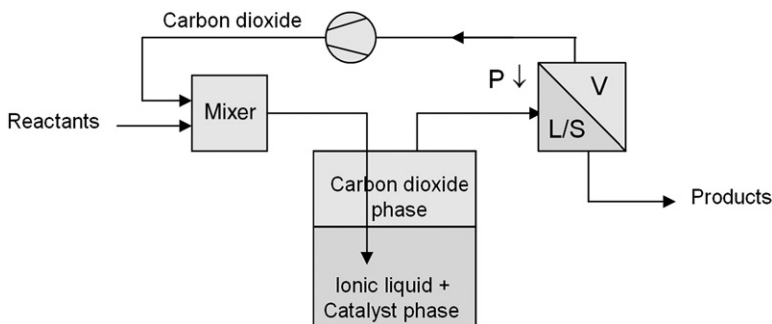

Figure 2.7 Continuous operation (reaction and separation) in biphasic (ionic liquid + supercritical CO_2) systems.

The product and CO_2 are separated downstream by controlled density reduction via pressure release or temperature increase. This biphasic process operation has been applied to hydrogenations [60], hydroformylations [61], dimerisations [62], (enzyme-catalysed) esterifications [63, 64], and the synthesis of cyclic carbonates (as CO_2 fixation method) [65].

Advantages of the biphasic operation are the ease of separation of the product and the catalyst, the enhanced stability and selectivity of the catalyst by the ionic liquid, and (in most cases) the increased reaction rate by adding supercritical CO_2 as compared to the biphasic operation without CO_2 [60–65]. However, the reported reaction rates in these biphasic systems are low compared with conventional catalytic single-phase processes, as a result of mass transfer limitations and low reactant solubilities. Moreover, mass transfer limitations also lead to low extraction rates [36]. The use of supported ionic liquid phase + supercritical CO_2 systems can overcome some of the mass transfer limitation problems [66].

In order to achieve high reaction rates, it is highly desirable to create a homogeneous liquid phase during reaction. In addition, instantaneous demixing into two phases, where the product is recovered from the phase that does not contain any ionic liquid, is desirable for a fast separation. In the next section, a continuous process that combines such features is presented.

2.3.2.2   Continuous Processes with Ionic Liquids, Supercritical CO_2, and the Miscibility Switch Phenomenon.

Figure 2.5 and Figure 2.6 show that it is possible reach a homogeneous phase in ternary (ionic liquid + supercritical CO_2 + organics) systems at high CO_2 pressures [36]. When the CO_2 pressure is subsequently lowered, the two-phase region (liquid + supercritical fluid) is reached again. This CO_2-induced switch in miscibility can be used to design a continuous process with high reaction and separation rates [67, 68].

The reaction is carried out in the homogeneous system, where the reactants as well as the catalyst dissolve in the ionic liquid [67]. The advantage of using an ionic liquid as reaction medium is that immobilised catalyst is stabilised against air and water oxidation by the ionic liquid, resulting in a longer lifetime of the catalyst without the need of regeneration [69]. The advantage of adding CO_2 to the reaction mixture is that the solubility of many reactants is increased (higher concentrations) and/or that reactants that are normally immiscible with pure ionic liquid can dissolve in (ionic liquid + CO_2) mixtures (the co-solvency effect) [70]. Therefore, it is possible to bring all components in high concentrations into one homogeneous phase. In this homogeneous system, the reaction takes place without any mass transfer limitations, which results in a high reaction rate [67]. Moreover, the addition of CO_2 to the reaction mixture leads to a lower viscosity of the reaction system and a higher diffusion rate of the reactants, resulting in a further increase in reaction rate [60]. The ionic liquid scarcely expands when CO_2 is dissolved because the CO_2 molecules

occupy the cavities in the ionic liquid phase [15]. Therefore, the reaction volume can be kept small, leading to small equipment size.

The separation is carried out in the biphasic system [67]. Application of the miscibility switch (pressure release) results in the instantaneous formation of a second phase out of the homogeneous liquid system by spinodal demixing [36]. The light phase consists of supercritical CO_2 with dissolved products (and reactants in case of incomplete conversion), but does not contain any ionic liquid (because CO_2 does not usually dissolve ionic liquid) [4, 5]. The heavy phase consists of ionic liquid with dissolved catalyst and some remaining products (and some remaining reactants in the case of incomplete conversion). These phases can be separated from each other, and the pressure of the light phase is further decreased, leading to precipitation of the product (as a liquid or as a solid) out of the CO_2. In this way, pure product is obtained without any detectable ionic liquid or catalyst (and no reactants when the reaction is complete). The catalyst remains in the ionic liquid phase and can be easily recycled, without negatively affecting the activity and enantioselectivity. Also, the CO_2 can be recompressed and reused [67]. The essential advantage of using instantaneous demixing instead of conventional extraction with CO_2 is the higher rate of product separation from the ionic liquid (no mass transfer limitations) [67]. Another advantage of carrying out the separation in the biphasic system is that the energy consumption is low. Energy is only required for recompressing the CO_2, but no energy-intensive distillation step is needed. Compared with the conventional separation processes, the energy consumption in the novel process setup can be decreased by 50–80% [67].

The continuous process set-up in which reactions and separations are combined using ionic liquids, supercritical CO_2, and the miscibility switch phenomenon is schematically depicted in Figure 2.8. It should be noticed that the CO_2 has a multi-functional purpose as co-solvent in the reaction step, viscosity decreasing agent, miscibility controller, and separation medium. Since the principle of miscibility windows is a general phenomenon [36], it is likely that this process set-up is applicable to many industrial processes.
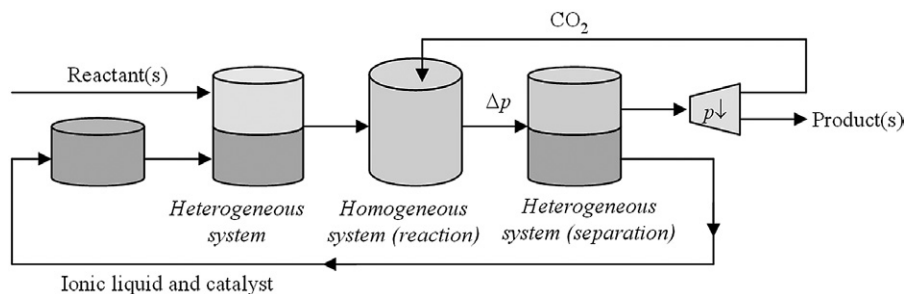

Figure 2.8 Continuous operation (reaction and separation) using ionic liquids, supercritical CO_2, and the miscibility switch phenomenon.

2.4 CONCLUSIONS AND OUTLOOK

Combining ionic liquids with supercritical fluids results in interesting phase behaviour. Binary (ionic liquid + supercritical CO_2) systems show a large immiscibility gap between the CO_2 phase and the ionic liquid phase up to very high pressures, and most likely have type III phase behaviour. Binary (ionic liquid + supercritical CHF_3) systems show a closed phase envelope and are therefore exhibit type IV phase behaviour. Supercritical CO_2 has high solubility in ionic liquids compared with other supercritical fluids. The solubility of 1,3-dialkylimidazolium ionic liquids in supercritical CO_2 is negligibly small, but this is not generally true for other ionic liquids. Ternary (ionic liquid + supercritical CO_2 + organics) systems can undergo a "two-phase"–"three-phase"–"two-phase"–"one-phase" transition by pressure increase.

Phase behaviour data of multi-component (ternary, quaternary, etc.) (ionic liquid + supercritical fluid) systems are relatively scarce. Future studies will therefore be directed to the phase behaviour of multi-component (ionic liquid + supercritical fluid) systems. Also, new modelling studies of the phase behaviour of multi-component (ionic liquid + supercritical fluid) systems are expected.

On the basis of the phase behaviour of multi-component (ionic liquid + supercritical fluid) systems, new applications will be sought. Combined (ionic liquid + supercritical fluid) systems will be used as "green" reaction and separation media, where the reaction product will be recovered from the supercritical phase (free of ionic liquid). A tendency to use the supercritical fluid for multiple purposes is observed. For example, supercritical CO_2 can act as extraction medium, transport medium, miscibility controller, and viscosity decreasing agent in these novel processes.

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