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Carbon Dioxide, a Solvent and Synthon for Green Chemistry

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Abstract

Carbon dioxide is a renewable resource of carbon when we consider the reuse of existing CO₂ as a carbon source for producing chemicals. The development of new applications is of major interest from the point of view of carbon dioxide sequestration and within the scope of green chemistry. For example, using CO₂ instead of CO or COCl₂ for chemical synthesis constitutes an attractive alternative avoiding hazardous and toxic reactants. However, it has the lowest chemical reactivity, which is a serious drawback for its transformation. Supercritical CO₂ as a reaction medium offers the opportunity to replace conventional organic solvents. Its benign nature, easy handling and availability, non volatile emitting, and the relatively low critical point ($P_c = 73.8$ bar, $T_c = 31$ °C) are particularly interesting for catalytic applications in chemical synthesis, over a wide range of temperatures and pressures. The benefits of coupling catalysis and supercritical fluids are both environmental and commercial: less waste and VOCs emission, improved separation and recycling, and enhanced productivity and selectivity.

The case study described in this paper concerns the reaction of carbon dioxide with alcohols to afford dialkyl carbonates with special emphasis on dimethyl carbonate. It is of significant interest because the industrial production of this class of compounds, including polycarbonates, carbamates, and polyurethanes, involves phosgene with strong concerns on environmental impact, transport, safety and waste elimination. The future of carbon dioxide in green chemistry, including supercritical applications, is highly linked to the development of basic knowledge, know-how, and tools for the design of catalyst precursors and reactors.

Key words: carbon dioxide fixation, supercritical carbon dioxide, catalysis, dialkyl carbonate, dimethyl carbonate, phase equilibria, fractionation

Introduction

The development of environmentally-improved routes and the design of green chemicals are two facets of Green Chemistry devoted to reducing the impact of chemical processes and compounds on the environment (Anastas 2000). To reach the ultimate goals of cleaner production and sustainable development, new and improved syntheses of chemicals have to meet economics, ecological and social criteria (Vollenbroek 2002). The design of chemical reactions minimising waste, air emission, and hazardous reactants is on the way to environmentally benign technologies. For the academic chemist, minimisation of waste and emission relies on chemical yield, selectivity, and atom utilisation (Sheldon 1994). Therefore, catalytic processes likely to provide rapid and selective chemical transformations as well as effective recovery of both catalyst

and product, without creating environmental problems, do have a significant impact in the chemical industry. In most cases catalyst recovery and recycling is of paramount importance for the economics of the process due to multistage, sophisticated, and costly recycling operations. The alternative of leaving-in the catalyst is acceptable in few cases. For example, the latest generations of Ziegler-Natta and metallocene-based catalysts are so productive that the catalyst present in concentration at the ppm level is left in the polyolefin product (Mülhaupt 1995).

Carbon Dioxide as a Solvent

In organic synthesis, most reactions are performed in the liquid state by the addition of a solvent with several beneficial purposes: *(i)* bringing the reactants to a single phase for rate enhancement, *(ii)* decreasing the viscosity of the reacting mixture for better diffusion of the reactive species, and *(iii)* providing easier mastering of heat effects. It should be pointed out that when one of the reactants is in the gaseous state (dihydrogen, carbon monoxide, dioxygen, ...), the gas-liquid mass transfer is often rate determining. The use of toxic solvents contributes to air emission of volatile organic compounds (VOCs) and of chloro hydrocarbons; they are now considered as environmentally unacceptable (Eckert and Chandler 1998). In the field of soluble metal-based catalysts, a considerable progress has been achieved through the concept of diphasic liquid-liquid catalysis: here the catalyst is recovered in one liquid phase and the product in the other one. This has led to drastic technological improvements but it has only reached single cases of industrialisation (Keim 1984; Cornils and Kuntz 1995; Driessen-Hölscher 1998). Further possibilities deserve attention with promising results in the use of fluorous solvents (Horvath 1998), non-aqueous ionic liquids (Wasserscheid and Keim 2000), and supercritical media (Jessop and Leitner 1999). These systems are potentially cost-effective by combining reaction and separation into a single reactor (Freemantle 2000).

The ideal supercritical fluid (SCF) should be non-toxic for man and the environment, non-carcinogen, non-flammable, and its intrinsic chemical reactivity should not be the source of runaway reactions. Concerning carbon dioxide, its impact in the global warming may be a handicap, but, when CO₂ applications are implemented, carbon dioxide is never released to the environment. While commercial developments of supercritical carbon dioxide (scCO₂) technology are successful for separation and extraction, its application as a reaction medium and as a reactant are still in its infancy (Jessop and Leitner 1999; Noyori 1999). The wide range of miscibility of gaseous reactants, e.g. dihydrogen and dioxygen, in supercritical fluids simplifies greatly the design of reactors in comparison with conventional ones which operate under di- or triphasic conditions. Furthermore the good transport properties of these fluids (viscosity, diffusivities) allow to design small and efficient reactors, where catalysts may have longer lifetime. The post-reacting separation is likely to be easy. Small temperature or pressure variations lead to solvent-free products. Fractionation of the effluent is also possible without involving any further separating agent. The greatest safety concern of supercritical fluids is the use of high pressure components in the process equipment.

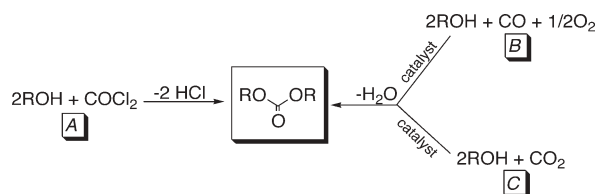
Carbon Dioxide as a C1-Building Block for Chemicals

Carbon dioxide, one of the major man-made greenhouse gases, is a renewable resource of carbon when we consider the reuse of existing CO₂ as a carbon source for producing chemicals. The industrial syntheses of urea, cyclic carbonates, salicylic acid, and methanol already involve carbon dioxide as a reactant. Nowadays, the development of new applications is of major interest from the point of view of carbon dioxide sequestration and within the scope of green chemistry (Dinjus and Fornika 1996). Using CO₂ instead of CO or COCl₂ constitutes an attractive alternative avoiding hazardous and toxic components (Aresta and Quaranta 1997). However, it has the lowest chemical reactivity which is a serious drawback for its transformation/incorporation to organic molecules. Several ways of activation are currently under investigation; among them catalysis offers a number of options, but it still is a challenge to find activities of practical interest.

We focused our research on new syntheses for open chain organic carbonates because their production is historically dominated by phosgene chemistry (Fig. 49.1, route A). The unfavourable opinion on the phosgene industry concerns the environmental impact, transport, safety and waste elimination. The lethal concentration threshold for a 30 min exposure is 10 ppm, as compared to 870, 4 000, and 30 000 ppm for dichlorine, carbon monoxide, and ammonia, respectively. In addition, the wastes contain hydrogen chloride as well as chlorinated solvents, and they have to be treated prior to disposal. These environmental and safety handicaps motivate the development of new technologies for commodity chemicals (>10 000 t yr⁻¹). Its industrial use is likely to be confined to small groups of experts who are properly equipped (Senet 2000). For the production of dimethyl carbonate (DMC), catalytic alternatives via the oxidative carbonylation of methanol (Fig. 49.1, route B) have provided an answer (Rivetti 2000). However, the use of carbon monoxide imposes safety constraints and the use of dioxygen requires a strict control of the kinetics.

Dimethyl carbonate (DMC) is an alternative to phosgene in carbonylation reactions, and a substitute for methyl halides and dimethyl sulfate in methylation reactions (Tundo 2001). Its current production is estimated to be around 80 000 t yr⁻¹ worldwide, with a growing demand for captive use by polycarbonate firms. DMC has a low toxicity, is not corrosive, and will not produce environmentally damaging by-products (no organics or salts). If the economics of the current technologies were more favourable, the market potential could be an order of magnitude higher because DMC is a good candidate for the replacement of methyl *tert*-butyl ether (MTBE) as a fuel additive (Pacheco and Marshall 1997). As a consequence, alternative reactions are under investigation. Among them, reacting methanol (or dimethyl acetals) and CO₂

Three reaction routes to open chain carbonates from alcohol and C1-building blocks



in the presence of a catalyst (Fig. 49.1, route C) leads to DMC under supercritical conditions (Isaacs et al. 1999; Ballivet-Tkatchenko et al. 2000); a drastic increase in activity is found if the experiments are conducted at ca. 2 000 bar and 180 °C (Sakakura et al. 1999). There is a real challenge from these very first results to commercial application, because on one hand the activity is low and on the other hand the most active systems are tin(IV) compounds which are not environmentally friendly. An important task is the knowledge of the reaction mechanisms involved to get structure-activity relationships. This paper addresses some issues on the chemistry and emphasises the reactor design under supercritical conditions for route C (Fig. 49.1). It also gives an insight to the complete process, including the post-reacting fractionation using potentialities of supercritical state.

Experimental

General

All reactions were carried out under dry argon using Schlenk tube techniques. The solvents were purified by standard methods. The organotin compounds n -Bu₃SnCl, n -Bu₂SnCl₂, n -BuSnCl₃, (n -Bu₃SnO)₂, and (n -Bu₂SnO)_{*n*} were used as received from Aldrich and Acros Chimica for the syntheses of the alkoxytannanes derivatives according to already published procedures (Ballivet-Tkatchenko et al. 2000). CO₂ N45 was purchased from Air Liquide. The ¹H, ¹³C, and ¹¹⁹Sn nuclear magnetic resonance (NMR) spectra were measured at 500.132, 125.770, and 186.501 MHz, respectively, on a Bruker DRX 500 spectrometer. For a detailed description and assignment of the experimental spectra see (Ballivet-Tkatchenko et al. 2000). Infrared spectra were obtained with a FT-IR Bruker Vector 22 spectrometer, the sample being placed between NaCl windows either as neat or dispersed in Nujol. Elemental analysis was performed at the Laboratoire de Synthèse et Electrosynthèse Organométalliques, Université de Bourgogne, Dijon.

Volumetry

A Schlenk tube containing 1 mmol of the tin compound in 1 ml of toluene was connected to a pressure transducer and to a CO₂ reservoir of known pressure and volume, maintained at 19 °C. The amount of CO₂ gas absorbed by tin compound was calibrated by reference experiments. The calculated CO₂:Sn molar ratio was at ±0.05.

Reaction under CO₂ Pressure

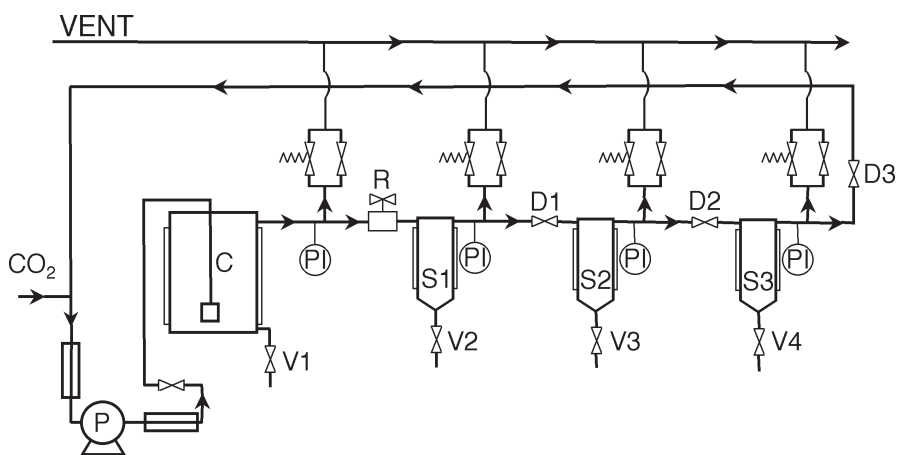
In a 100-ml stainless steel batch reactor, a solution (10–30 ml) of the tin compound (4 mmol Sn) was introduced. The reactor was pressurised with CO₂, heated to 145 °C,

then the CO₂ pressure was adjusted to the desired value, typically between 90 and 220 bar. After the run, the reactor was cooled to 0 °C, depressurised, and the liquid phase was analysed by gas chromatography (Fisons 8000, FID detector, J&W Scientific DB-WAX 15 m megabore column) and gas chromatography-mass spectrometry for identification (Fisons MD 800, EI 70 eV, J&W Scientific DB-1 60 m capillary column). Evaporation of the volatiles under vacuum at room temperature allowed to characterise the residue by NMR.

Experimental Set-up for the Fractionation Study

For the fractionation study, we have used an experimental process schematically shown on Fig. 49.2, comprising a 200 ml contacting vessel C (the reactor) followed by three cyclonic separators S₁, S₂, and S₃ (ca. 20 ml each). As an efficient immobilised catalyst has not yet been found, the reaction could not be operated experimentally. We therefore worked with a mimicked reacting mixture in the contacting vessel where an intimate contact between a methanol-dimethyl carbonate-water mixture and CO₂ entering the process takes place. A constant feed flow rate of CO₂ of ca. 4 kg h⁻¹ is kept. The outgoing fluid from the contactor C composed of a CO₂-methanol-dimethyl carbonate-water quaternary mixture undergoes a three successive depressurisation stages S₁, S₂, and S₃, in order to recover the targeted components (DMC and water), and to recycle CO₂ and methanol.

Liquid phase analyses were done by gas chromatography with a Hewlett-Packard 5890 series II chromatograph equipped with a Supel-QTM Plot capillary column (30 m, 0.53 mm ID) from Supelco (USA) and a thermal conductivity detector (TCD). Synthetic mixtures were prepared from distilled water, dimethyl carbonate (Aldrich, 99%, D15,292-7), and methanol (Prolabo Chromanorm, min. 99.8%, 20834.291).



Pilot SF200. C: contactor; D₁, D₂, D₃: depressurization valves; P: pressure pump; PI: pressure indicators; R: back pressure regulator; S₁, S₂, S₃: separators; V₁, V₂, V₃, V₄: sampling valves

Numerical Methods for Thermodynamic Calculations

In this study, phase equilibria are calculated using the cubic equation of state proposed by Redlich and Kwong (Redlich and Kwong 1949), modified by Soave (Soave 1972), and named SRK equation. To account for interaction taking place between components in the mixture, the “MHV-2” mixing rules, developed by Huron and Vidal (Huron and Vidal 1979) and modified by Michelsen (Dahl and Michelsen 1990), are used. This type of modelling is now commonly recognised as a good choice for high pressure phase equilibrium calculations involving polar compounds, as it is the case in this study. Equations of state such as SRK equation give satisfying results at high pressure but have to be used only when dealing with apolar or poorly polar compounds. Conversely, activity coefficient models (differently named γ - ϕ approach) cannot be used at high pressure but are particularly appropriate for thermodynamic calculations involving polar compounds. The MHV-2 approach conciliates these two application domains, involving an activity coefficient model into mixing rules of an equation of state. The UNIQUAC activity coefficient model (Abrams and Prausnitz 1975) has been chosen to determine the value of the free excess Gibbs energy needed in the calculation of the mixture parameters.

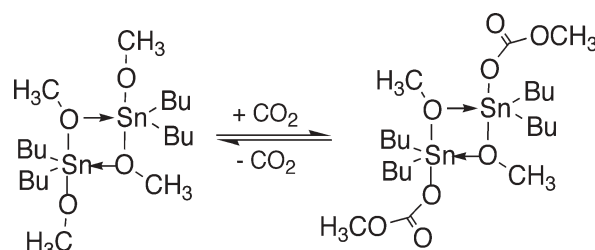
Thermodynamic models have proved to be of great help in predicting thermodynamic behaviour of mixtures. However, these models need specific mixture parameters, reflecting interactions between the components in the mixture, that are obtained by fitting a limited set of experimental equilibrium data. The data used to determine mixture parameters can be equilibrium data from the binary or ternary sub-systems constituting the quaternary methanol-CO₂-water-DMC mixture. In our case, some binary or ternary data can be found in the existing literature. For DMC-water and DMC-CO₂ mixtures, no experimental work is available, and experiments have been necessary. Such new results are now available from our recent publication (Camy et al. 2002). Binary interaction parameters are calculated using the commercial software ProReg™ (PROSIM S.A., France). This model fed by adequate binary interaction coefficients allows us to describe the thermodynamic behaviour of the reacting mixture in the reactor itself and in the separation system.

Results and Discussion

Mechanistic Approach for Dimethyl Carbonate Formation

Our interest in the reaction of carbon dioxide with alcohols to afford dialkyl carbonates led us to focus on the mechanistic approach with tin compounds. These compounds were chosen because ¹¹⁹Sn NMR spectroscopy provides useful information on the number of tin species and their coordination (Hani and Geanangel 1982) in addition to ¹H and ¹³C spectra. IR spectroscopy was also used to monitor the presence of absorption bands of the carbonate moieties. It is not intended to report here in details the synthesis and characterisation of the compounds as preliminary results have already been published (Ballivet-Tkatchenko et al. 2000). It is more important to summarise and emphasise some elementary reaction steps for the purpose of reactor design.

Dimeric arrangements for $n\text{-Bu}_2\text{Sn}(\text{OCH}_3)_2$ and its carbonated form



Several tin(IV) compounds were studied, $n\text{-Bu}_3\text{SnCl}$ (Bu = butyl), $(n\text{-Bu}_3\text{SnO})_2$, $n\text{-Bu}_3\text{SnOR}$ (R = phenyl, methyl), $n\text{-Bu}_2\text{SnCl}_2$, $(n\text{-Bu}_2\text{SnO})_n$, $n\text{-Bu}_2\text{Sn}(\text{OR})_2$ (R = phenyl, methyl, isopropyl, *tert*-butyl), $n\text{-BuSn}(\text{OCH}_3)_3$, $\text{Ph}_3\text{SnOCH}_3$ (Ph = phenyl), and $\text{Ph}_2\text{Sn}(\text{OCH}_3)_2$. The fixation of carbon dioxide was effective for compounds containing OR groups, preferably methoxy and isopropoxy. The new species formed is the result of carbon dioxide insertion in the Sn-OR bond, leading to the carbonate fragment Sn-OC(O)OR. At room temperature and atmospheric pressure, the reaction is reversible leading back to Sn-OR. Volumetric experiments showed that reaction stoichiometry is $\text{CO}_2:\text{Sn} = 1$, whatever the initial number of alkoxy fragments. Therefore, only one OR group is reacting. This result has been assigned to the dimeric structure of the polyalkoxystannanes as shown in Fig. 49.3 for $n\text{-Bu}_2\text{Sn}(\text{OCH}_3)_2$. A recent X-ray single crystal structure determination of $(\text{CH}_3)_2\text{Sn}(\text{OCH}_3)_2$ and its carbonated form strengthens this assignment (Choi et al. 1999).

The formation of dialkyl carbonates was only found for the polyalkoxybutylstannanes. For example, starting from $n\text{-Bu}_2\text{Sn}(\text{OCH}_3)_2$ dimethyl carbonate is quantitatively produced (DMC:Sn = 1) upon heating a methanolic solution at 150 °C under 200 bar of carbon dioxide. Further experiments conducted in toluene instead of methanol point out that methanol is not directly involved in DMC formation (Ballivet-Tkatchenko et al. 2002). An intra-molecular rearrangement of the tin coordination sphere is taking place, but, in the overall reaction, methanol and carbon dioxide should be the reactants for the catalytic cycle (Fig. 49.1, route C). Under these experimental conditions, CO_2 reaches the supercritical state ($P_c = 73.8$ bar, $T_c = 31$ °C). Supercritical CO_2 as a solvent and a reactant has a great potential for optimising chemical reactions (Jessop and Leitner 1999); however, in our case the origin of the enhanced chemical reactivity is not clear as the phase behaviour under reaction conditions have a great influence. It can also be expected that CO_2 pressure has a beneficial effect on the carbonation reaction, which was found to be reversible at room temperature and atmospheric pressure.

Dimethyl Carbonate Synthesis Using Supercritical CO_2

Operation of chemical reactions in supercritical media is regularly emphasised by experts in the domain as a very promising field of research. Nevertheless, conception of reactors, as well as optimum choice of operating conditions, are still to be developed.

It is now well admitted in chemical engineering strategy, that conception of the post-reacting separation as early as the conception of the reactor, leads to more effi-

cient processes. It is particularly true for supercritical media, because their adjustable solvation power is a very convenient way to operate the purification of products. In the case of the carbonation reaction of methanol (Fig. 49.1, route C), there is an additional reason, because one product of the reaction, water, has a detrimental effect on a possible reversal of carbonation reaction, as well as on the good operation of the catalyst. This implies that it would be preferable to eliminate reaction products as the reaction proceeds, in order to shift the equilibrium of the reaction. As a consequence the study of the entire process could be of a great help for optimising the reaction, and investigation of the fractionation process implemented at the output of the reactor has to be undertaken.

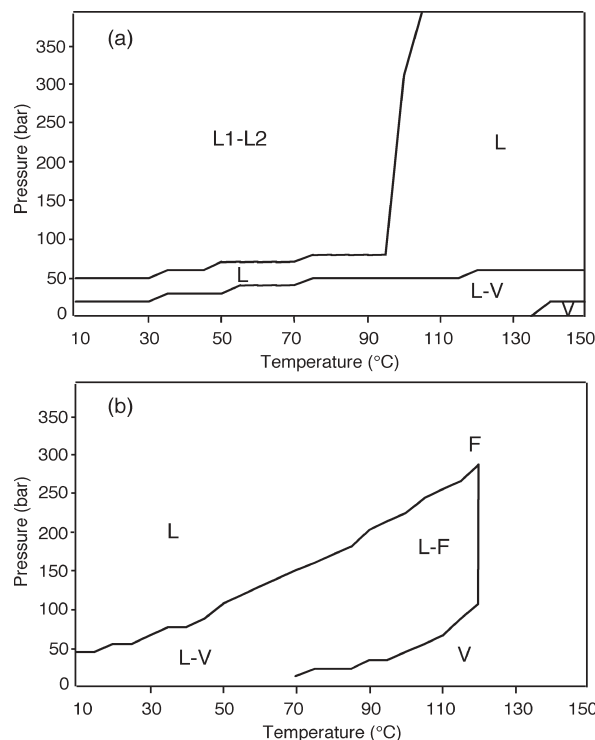
One first compulsory initial stage is to study the thermodynamic behaviour of the reacting mixture, i.e. the quaternary methanol-CO₂-water-DMC mixture. This knowledge is essential to characterize the possible coexisting phases in the reactor and define the optimum reaction conditions, as well as to design the post-reacting fractionation device.

Study of Operating Conditions in the Reactor

The main information needed is the description of phase equilibria existing in the reactor as a function of pressure and temperature. For this, a hypothetical perfectly mixed continuous reactor, fed with a methanol-CO₂ mixture, is considered. The DMC synthesis takes place with an arbitrarily chosen conversion, i.e. the concentrations inside the reactor are accordingly. Then the physical state of the mixture in this hypothetical reactor is calculated thanks to the thermodynamic model described above.

Figure 49.4 presents, for two different mixtures in the reactor, the coexistence zones of monophasic and diphasic states. In each diagram, qualitative information about the state of the mixture is marked for each domain. The letter L refers to a liquid phase, whose density is high (ca. 800–900 kg m⁻³). Conversely, the vapour state, marked with the letter V, refers to a low-density phase (<100 kg m⁻³). Finally, the letter F designates a fluid state whose density lies between that of a liquid and a gas. Because the critical line of this quaternary mixture was not calculated here, these denominations remain qualitative. Figure 49.4 shows that for a methanol rich mixture (diagram a), no fluid phase is present and there is a large diphasic liquid-liquid (L₁-L₂) zone, where a first liquid phase, mainly composed of water and methanol, is in equilibrium with a second liquid phase containing a large proportion of CO₂ and DMC. This equilibrium zone exists for low temperatures, at a pressure greater than about 80 bar. A second diphasic liquid-vapour zone (L-V) is present at low pressures, consisting in the equilibrium between a liquid phase and a CO₂ rich vapour phase. The main monophasic zone is a liquid (L); however, at high temperatures and low pressures, a restricted monophasic vapour phase zone (V) is evidenced. For a CO₂ rich feed (diagram b), the phase diagram undergoes perceptible modifications. Indeed, the diphasic zone is here further reduced and no liquid-liquid equilibrium is now observed. In this case, there is no longer liquid-liquid diphasic zone and a liquid-vapour zone (L-V) transforming into a liquid-fluid zone (L-F) is now present. At higher pressure and temperature we now observe a plain fluid phase.

Coexisting zones of monophasic and diphasic mixtures at 60% conversion for: **a** methanol rich feed, **b** CO₂ rich feed



Study on dimethyl carbonate synthesis mechanism has shown that, for the moment, the most interesting results are obtained using polyalkoxybutylstannane catalysts, being active at about 150 °C. Moreover, to avoid mass transfer limitations which are likely to occur with the low-pressure diphasic system liquid mixture-gaseous CO₂ (Kizlink and Pastucha 1994, 1995), the reaction will advantageously be operated in a monophasic reacting mixture, and preferably in a “fluid” state, or vapour state. By comparison with the vapour state, the “fluid” state, that corresponds to higher pressures, is more interesting because (i) the volume of the reactor will be smaller (ii) the effect of pressure has been proved to be positive on the kinetics of the reaction, and (iii) the separation of the reaction products can be made easier by using the tunable solvent power of supercritical fluids. From Fig. 49.4 it can be concluded that, to be sure of running the reaction in a homogeneous fluid medium, a large excess of CO₂ is needed. Moreover, for such mixtures, a drop of pressure and temperature after the reactor would easily allow a return to a diphasic state, with a view to obtaining an efficient mixture fractionation. This last topic is the aim of the next part.

Study of the Mixture Fractionation

As previously mentioned, it is worthwhile to investigate the feasibility of the fractionation of the effluent methanol-DMC-water mixture, and to test a convenient and quite

simple process, generally used to run post-extraction fractionation in supercritical technology (Fig. 49.2). Due to the great number of parameters, this study of the post-reacting fractionation cannot only lean on an experimental approach. Modelling of the process must be developed in order to represent the dynamic behaviour of the whole experimental process. Indeed, even if this kind of pilot is often used to operate extraction operations, the literature proposes very few results dealing with its dynamic modelling.

Our description of the process is based on the conventional chemical engineering concept of theoretical stage of equilibrium. A simplified numerical approach used to solve dynamic mass balances has been proposed and validated in comparison with a rigorous resolution of the algebro-differential system of equations (Camy and Condoret 2001). The results of the modelling were compared to experiments and gave good results for the contactor, while it was not very satisfactory for the description of the separation. Even if discrepancies between experimental and calculated results may probably originate from experimental procedure, and because we think that thermodynamic modelling is correct, hydrodynamic description of the separators is here likely to be oversimplified. The cyclonic separators cannot be regarded as simple theoretical stages as it is often done in the literature (Cesari et al. 1989). We proposed an other description (Camy and Condoret 2001), that, although more suitable, needs still to be improved by taking into account, for instance, the imperfect collection of droplets.

Our work has shown that is not realistic to envisage the separation of the resulting methanol-dimethyl carbonate-water mixture with such a simple device because components have too strong affinities. The use of simple separators in order to separate a liquid mixture when volatility of components, as well as their solubility into CO_2 , are comparable, is not enough efficient. Under progress is now the use of modelling to investigate the feasibility of this separation, either using a greater number of separators, or by implementing a more complex strategy of separation. For instance a suitable way would be to consider the operation of one or several counter current columns of separation. Together with advances in the conception of an efficient catalyst, these approaches will be a useful contribution to the success of a viable process from CO_2 .

Conclusion

Supercritical CO_2 as a reaction medium offers the opportunity to replace conventional organic solvents due to its adjustable solvation property as regards to both temperature and pressure, either pure or through the addition of solubilizers. The relatively mild critical point of CO_2 , its benign nature, easy handling, availability, non volatile emitting are particularly attractive for catalytic applications in chemical synthesis, over a wide range of temperatures and pressures. The benefits of coupling catalysis and supercritical fluids are both environmental and commercial: less waste and VOCs emission, improved separation and recycling, and enhanced productivity and selectivity.

The case study described in this paper is of significant interest because the carbonation of alcohols to dialkyl carbonates replaces phosgene by carbon dioxide. Of course, carbon dioxide is much less reactive than phosgene, which means more energy input.

However, Life Cycle Analysis applied to the assessment of the environmental impact of the phosgene and carbon dioxide routes is greatly in favour of CO₂ (Aresta and Galatola 1999). The future of this molecule in green chemistry, including supercritical applications, is highly linked to the development of basic knowledge, know-how, and tools for the design of catalyst precursors as well as the technological conception of reactors and fractionation devices. The multi-component nature of a catalytic reaction (catalyst precursor, reactants, products), its changes upon time, and the pressure-temperature conditions make difficult the experimental approach. Synthetic chemistry, analytical chemistry, and chemical engineering are mandatory to cope with the above-mentioned requirements. Indeed, chemical engineering can bring better knowledge of the rather uncommon thermodynamics in the reactor, and has demonstrated the interest of studying the coupling of the reaction and the separation.

Acknowledgements

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