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Switching from water to ionic liquids for the production of methylchloride: Catalysis and reactor issues

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ABSTRACT

The synthesis of methyl chloride from methanol and hydrogen chloride catalysed by zinc chloride was investigated in water and in two room temperature ionic liquids in a CSTR reactor. Both Aliquat336 and BMICl drive to similar rate of reactions as the traditional process albeit at lower temperatures. More importantly, the formation of the side product Me_2O is decreased in ionic liquids. From the reactor point of view and on the basis of kinetics and simulations, a new process involving plug flow behaviour using ionic liquids is proposed which would lead to process intensification, i.e. (50×) productivity increase.

1. Introduction

Methylchloride is a large-scale bulk chemical with a production of more than 10^6 ton/year [1]. The use of methylchloride covers the silicone fluids and elastomers manufacture, the agrochemical and pharmaceutical industries, and also the preparation of quaternary ammonium compounds (used in water treatment and fabric softening compounds), methyl cellulose's (used as thickeners in adhesives) and halo-butyl rubbers (used in vehicle tyres and food stuffs). The industrial production of MeCl is achieved either by chlorination of methane at high temperature or by reaction of methanol with hydrogen chloride. The later process is very selective with yields above 95% and can be performed in the liquid aqueous phase using a transition metal salt, usually zinc chloride [1,2]. However, the later process still requires rather high temperatures (150–180 °C). Under such temperatures, the phase diagram of the zinc chloride/water mixture imposes a very large concentration (up to 80 wt%) of the metal salt. This thermodynamic constraint has two consequences: (i) the very large concentration of zinc induces costly and cumbersome down-stream treatments and (ii) the active catalyst concentration, thus the acidity, is fixed. On the contrary, ionic liquids offer the potential of very low vapour pressures, low water solubility (if desired), flexible and wide range of zinc chloride concentration and acidity. In this report, preliminary results concerning the use of ionic liquids to perform the reaction and potential benefits are discussed.

The target reaction is the nucleophilic substitution of the methanol hydroxyl group by hydrogen chloride (Eq. (1)). A side dehydration reaction leading to the undesired dimethylether occurs under the reaction conditions (Eq. (2)).

$$MeOH + HCl \Leftrightarrow MeCl + H_2O \quad (1)$$

$$2MeOH \rightarrow Me_2O + H_2O \quad (2)$$

This is a biphasic process with gaseous (HCl and MeOH) and/or liquid reactants (MeOH) and with products in the gaseous phase (MeCl and H_2O) at the operating conditions (temperature and pressure). From an industrial point of view, the process operates in a continuous reactor, open on the gas phase and closed on the liquid phase (i.e. the catalyst phase). The introduction mode of the methanol had an important impact on the thermal balance of the process (Table 1). A liquid phase introduction leads to a slight endothermic reaction (Eq. (3)) and a gas phase introduction results in an exothermic reaction (Eq. (4)). Hydrogen chloride dissolution in the aqueous displays the strongest thermicity, with a high exotherm (Eq. (5)).

$$MeOH_L + HCl_G \rightarrow MeCl_G + H_2O_G \quad (3)$$

$$MeOH_G + HCl_G \rightarrow MeCl_G + H_2O_G \quad (4)$$

$$HCl + H_2O \Leftrightarrow H_3O^+ + Cl^- \quad (5)$$

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Nomenclature

k	rate constant
k'	rate constant
m_{Zn}	mass of $ZnCl_2$ involved in the experiment (kg)
n_{Zn}	quantity of Zn involved in the experiment (mol)
P_i	partial pressure of component *i* in the reactor (MPa)
P_T	total pressure in the reactor (MPa)
r	rate of reaction ($mol\ mol_{Zn}{}^{-1}\ s^{-1}$)
X	conversion number for methanol

Greek symbols

τ_{CSTR}	residence time in the continuous stirred tank reactor (min)
τ_{PFR}	residence time in the plug flow reactor (min)

The main reaction is reversible (Eq. (1)). Thermodynamic calculations taking into account only a gas phase reaction show that the equilibrium is fully displaced to the formation of the desired product, methyl chloride. The computed equilibrium conversion reaches 99% at 300 K and 85% at 1000 K [6]. Albeit the straightforward extrapolation of those data to the liquid phase is not possible because of the non ideal character of the liquid phase, a maximum conversion of ca. 98% should be obtained under the operating temperature range and steochiometric ratio used in this study.

Addition of zinc chloride in the aqueous liquid phase is known to catalyse the reaction and it is admitted that the reaction only takes place in the liquid phase. A 1974 Dow Chemical patent demonstrated that the reaction without catalyst is possible, albeit being very slow compared to the zinc catalysed process. A reaction mechanism depicting the role of the zinc species is described in Eqs. (6)–(12) [7]. The species X and X^+ are zinc chloride complexes of methanol, $ZnCl_2(MeOH)_n$, as described in the literature [8]. In this mechanism, the zinc distributes in five complexes X, X^+, $ZnCl_2$, $ZnCl_3{}^-$ and $ZnCl_4{}^{2-}$. The three species X, X^+ and $ZnCl_2$ are involved in the catalytic cycle whereas the two later species are chloride reservoir.

$$MeOH + H_3O^+ \Leftrightarrow MeOH_2{}^+ + H_2O \tag{6}$$

$$MeOH_2{}^+ + Cl^- \rightarrow MeCl + H_2O \tag{7}$$

$$MeOH + ZnCl_2 \rightarrow X \tag{8}$$

$$X + H_3O^+ \rightarrow X^+ + H_2O \tag{9}$$

$$X^+ + Cl^- \rightarrow MeCl + ZnCl_2 + H_2O \tag{10}$$

$$ZnCl_2 + Cl^- \Leftrightarrow ZnCl_3{}^- \tag{11}$$

$$ZnCl_3{}^- + Cl^- \Leftrightarrow ZnCl_4{}^{2-} \tag{12}$$

One important feature in this mechanism is the presence of the zinc coordination equilibrium as depicted in, e.g. Eqs. (11) and (12). The equilibrium position determines the actual concentration of $ZnCl_2$ and, subsequently, of the active catalytic zinc species X and X^+ through Eqs. (8) and (9). Furthermore, it not only varies with the concentrations of zinc chloride and chloride anion but also with that of methanol and water. The later concentrations are, in turn, functions of the temperature and pressure through the vapour–liquid equilibrium. Because of this coupling between the mechanism at the molecular level and the physical thermodynamics of phase equilibrium, this process is likely to exhibit complex and unpredictable overall kinetics leading to poor process design and operability.

Table 1
Thermodynamics of the reactions involved in the process

Reaction	ΔH°_{298}	ΔH°_{298}	ΔH°_{298}	ΔH_R
(2) [a]	−23.8	−24.7		−25.0
(3)				+5.2
(4)	−45.8	−30.3		−32.2
(5)			−74.77	
References	[3]	[4]	Computed from [5]	

All data in $kJ\ mol^{-1}$.

[a] For Eq. (2), all species are taken in the gas phase.

In this report, the industrial aqueous phase process is analysed through laboratory experiments, a different and simpler mechanism is proposed to account for the reaction in the aqueous phase and ionic liquids are evaluated in the hope to overcome the limitations imposed by the traditional aqueous phase process.

2. Experimental

The laboratory pilot is a gas–liquid well stirred gas sparged reactor of 120 cm^3 open to the gas phase (Fig. 1). Gaseous hydrogen chloride (anhydrous) was preheated at 150 °C. Methanol can be feed as a liquid at ambient temperature or as a gas by vapourisation and pre-heating at 150 °C. The reactor, made of quartz, allows working at $P_{max} = 5$ bar and $T_{max} = 180\,^\circ C$. Materials in contact with reactants and products are glass, PTFE and PEAK. Stirring was ensured by a 6-blades turbine (Rushton type) or a 4-blades impeller associated with an in-line magnetic coupling. Glass baffles can be added. The gas distributor is placed directly in the liquid closed to the turbine. A PTFE capillary tube placed under the turbine at the bottom of the reactor was used for the methanol liquid distribution. The reactor was equipped with a pressure sensor, a Teflon protected thermocouple and a jacketed tank to ensure efficient heat transfer. At the outlet of the reactor, the gas phase was released to atmospheric pressure with a PTFE back pressure regulator. The condensable products are collect with a water condenser and the remaining gas flow was measured and analysed.

The chemicals, methanol (Fisher Scientific), hydrogen chloride (Air Liquide), methylchloride, dimethylether (Sigma–Aldrich), Aliquat336 (tricaprylmethylammonium chloride) (Aldrich) and BMICl (butylmethylimidazolium chloride) (Aldrich) were used as received. The liquid condensate was sampled and analysed by gas chromatography. On-line analysis of the gas phase was performed with an automatic injection valve on a gas chromatograph HP 5890 series II equipped with a TCD and a FID detector mounted in serial and a Porabond U column supplied by Varian-Chrompack. The amount of dimethylether (thus the purity of the methyl chloride produced) was determined. Quantification and qualification of the liquid phase by acidic tritration and liquid GC injection of a neutralized solution allows the determination of the molar flow rate of production and the reactants consumption. The carbon and chlorine balance were calculated for each experiment and was always between 0.9 and 1.1.

3. Results and discussion

First, an exhaustive study on possible mass transfer limitations was performed. Gas to liquid mass transfer limitation is anticipated within the range of operating conditions used. Thus, different type of impeller and turbines have been evaluated, the gas and liquid distributors injectors and the liquid phase volume have been change without any noticeable effects on the reaction rate. This supports the view that no gas to liquid mass transfer limitations occurred in the set-up.

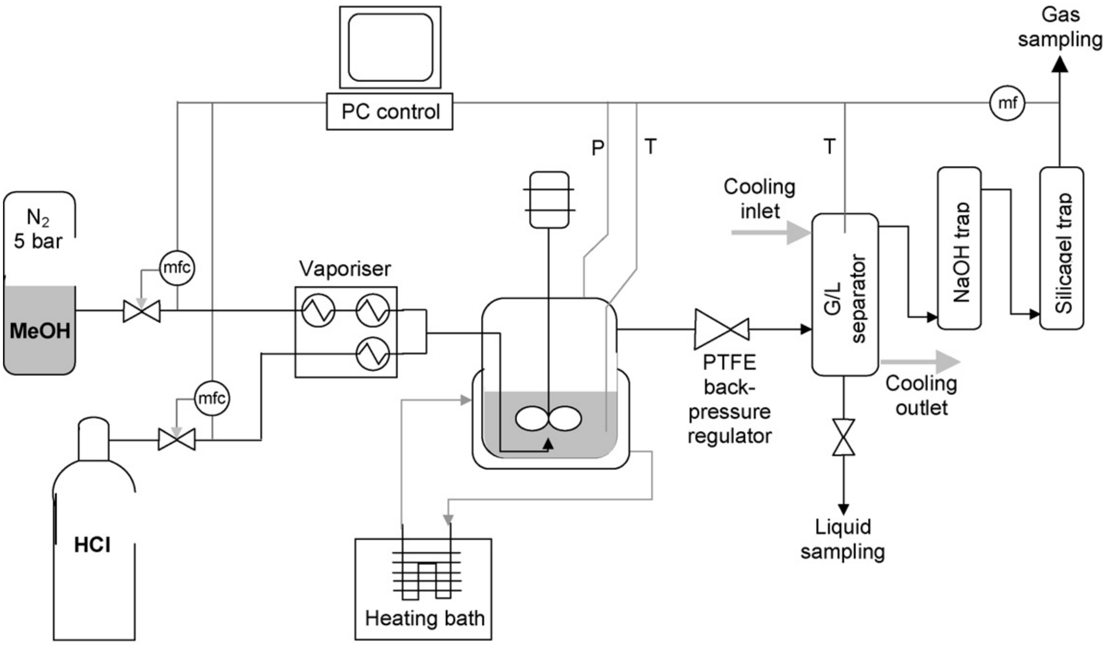

Fig. 1. Experimental set-up.

The effect of temperature was then investigated. According to the gas phase equilibrium constant [6] conversions up to 97% are allowed within the temperature range of the study. However, no effect on the conversion, thus on the reaction rate, was observed when the reaction temperature was changed from 130 °C to 170 °C, except for the formation of dimethylether which increases with temperature. The apparent (measured) activation energy is closed to zero within the experimental error (ca. 1––2 kJ mol^{-1}). This is likely due to the change in the liquid phase composition. Literature data on the quaternary (reactive) mixture HCl–MeOH–$ZnCl_2$–H_2O is obviously not available but measurements on the $ZnCl_2$–H_2O vapour pressure diagram reveals a strong change in the zinc chloride and water concentrations with temperature (Fig. 2). Such a change will translate into a displacement of the equilibrium between the zinc chloride species (Eqs. (11)–(14)). It may well push the equilibria backwards, leading to a decrease of the actual active catalytic species, e.g. $ZnCl_4{}^{2-}$ that may compensate for the activation energy of the methylchloride reaction. No thermodynamic data on equilibria of Eqs. (11)–(14) are available to support this idea but it may explain the measured abnormal Arrhenius behaviour.

The catalytic performances of fresh and spent catalysts were identical, even concerning the by-products formation. However, they reveal a different behaviour with respect to the start-up of the reactor (Fig. 3). A fresh catalyst requires ca. twice the time to reach the quasi steady-state regime. This likely corresponds to the time required to reach the equilibrium of Eqs. (11) and (12). For the fresh catalyst, the zinc in solution may be in the form $ZnCl_2$ at low pH (ca. pH 3), large amount of hydrogen chloride introduced during the first minutes being used to shift the equilibrium and not to form methyl chloride. This would explain this smaller gas flow rate measured at the outlet of the reactor. For the spent catalyst, a

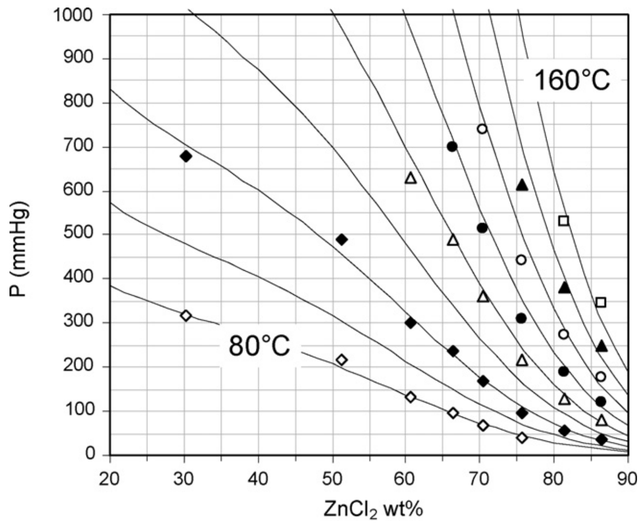

Fig. 2. Vapour pressure of a $ZnCl_2$–H_2O binary mixture in the range 80–160 °C. The lines corresponds to the model: $\log P = -(A \times Zn + B)/T - C \times Zn^3 + D \times Zn^2 - E \times Zn + F$.

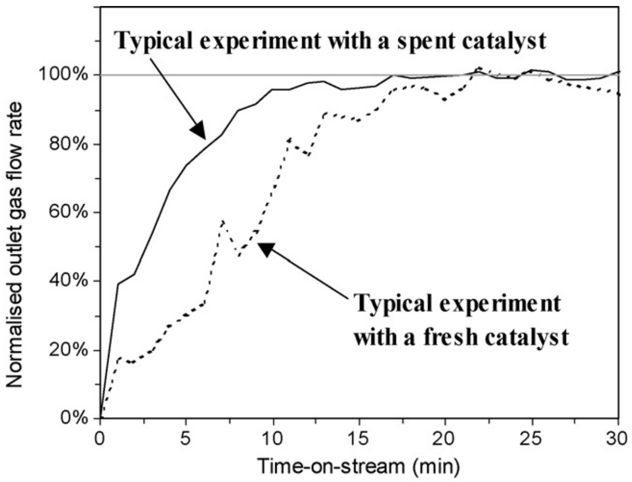

Fig. 3. Influence of the catalyst aging on the start-up of the reactor under similar operating conditions.

large quantity of $ZnCl_4^{2-}$ could already be present in the solution, which is supported by the very low pH (<1) of the solution. These observations point $ZnCl_4^{2-}$ as being the active catalytic species.

Literature data on zinc chloride aqueous solutions also support $ZnCl_4^{2-}$ as the pre-eminent species. They reveal that the equilibrium between the different species $ZnCl_2$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ favours the later tetrachloride complex, the effect being more pronounced in hydrochloric solutions [9,10].

All these observations point to a mechanism in which the tetrachloride complex $ZnCl_4^{2-}$ is the actual active catalyst (Eqs. (5), (6) and (11)–(13)). In this new mechanism, the species X, X^+ are no longer needed, the reaction taking place through the nucleophilic attack of the methyloxonium $MeOH_2^+$ by the strong nucleophile $ZnCl_4^{2-}$.

$$HCl + H_2O \Leftrightarrow H_3O^+ + Cl^- \tag{5}$$

$$MeOH + H_3O^+ \Leftrightarrow MeOH_2^+ + H_2O \tag{6}$$

$$ZnCl_2 + Cl^- \Leftrightarrow ZnCl_3^- \tag{11}$$

$$ZnCl_3^- + Cl^- \Leftrightarrow ZnCl_4^{2-} \tag{12}$$

$$MeOH_2^+ + ZnCl_4^{2-} \rightarrow MeCl + Zn(H_2O)Cl_3^- \tag{13}$$

$$Zn(H_2O)Cl_3^- + Cl^- \Leftrightarrow ZnCl_4^{2-} + H_2O \tag{14}$$

Ionic liquids would be ideally suited to perform this reaction: (i) they display very low vapour pressure thus would not lead to the coupling between the mechanism at the molecular level and the physical thermodynamics of phase equilibrium, (ii) high chloride concentrations that would shift forward equilibrium of Eq. (14) can be reached by choosing adequate anions, (iii) the water solubility and acidity range can be tuned, thus offering a large potential for process improvement.

Considering point (ii), solutions of $ZnCl_2$ in ethylmethylimidazoliumchloride up to 50 mol% have been prepared for electrodeposition of zinc metal [11]. It is also generally assumed that melts containing less than 33 mol% $ZnCl_2$ are basic, because of the large excess of "free" chloride ions, the major zinc species likely being the monomeric $ZnCl_4^{2-}$ anion. Conversely, solutions that contain more than 33 mol% $ZnCl_2$ are "acidic", because there is not enough chloride ions to fully coordinate the zinc cation, thus leading to under-coordinated species like $ZnCl^{3-}$, $Zn_2Cl_7^{3-}$ and $(ZnCl_2)_n$ [11]. Several papers reporting the preparation of various ionic liquid solutions with zinc chloride and their use in organic synthesis and catalysis have been published [12,13], but none concern the very simple nucleophilic substitution targeted here.

In the targeted process however, because chloride is one of the reactant in the form of hydrogen chloride, it is believed that all the zinc would be displaced as $ZnCl_4^{2-}$ anion, thus leading to a high activity. However, since no literature data are available on the liquid–vapour equilibrium of Ionic Liquid–MeOH–H_2O–$ZnCl_2$ mixtures, it is impossible to predict the influence of the presence of water and methanol on the acidity and nucleophilicity of such catalytic solutions. Thus, the influence of the reaction temperature and of the zinc concentration have been investigated experimentally using two different ionic liquids: Aliquat336 and BMICl. The solubility of zinc chloride is clearly not a problem and mixtures with more than 60 wt% $ZnCl_2$ have been successfully prepared. However, one issue at the process level could be rather the high viscosity of those mixtures near ambient temperature.

Several experiments were performed to assess the efficiency of performing the target reaction in ionic liquids. The results obtained in ionic liquids are very close to those obtained in aqueous $ZnCl_2$ under the same conditions and also comparable to that reported in the literature (Table 2). However, the formation of the side product dimethylether is somehow decreased using ionic liquids (Entries 1, 2, 4 and 5). The might be due to a lower solubility of the substrate MeOH in the ionic liquid phase compared to the aqueous phase process which would disfavour the bi-molecular side reaction (Eq. (2)). Interestingly, ionic liquids can operate at lower temperature, albeit with a decrease in selectivity (Entry 3). Operating with comparable contact time, similar conversions are observed for the aqueous and BMICl systems (Entries 4 and 6). The activities are thus comparable. The higher conversion at shorter contact time reported in the literature is due both to the fact that a cascade of two CSTR and that an excess HCl have been used (Entry 8).

Table 2
Influence of temperature and contact time on conversion and selectivity for ionic liquids and water as solvents

	Entry	T (°C)[a]	Time (min)[b]	Conversion[c]	Selectivity[c]	
				MeOH	MeCl	Me_2O
Aliquat336	1	170	14	80.5	99.3	0.7
	2	150	64	88.2	99.4	0.6
	3	130	79	83.8	97.3	2.6
BMICl	4	170	9	90.2	99.5	0.5
	5	150	30	89.6	99.6	0.4
Water	6	150	9	88.9	97.5	2.3
	7	150	58	98.3	98.4	1.4
	8[d]	150	44	99.5	98.1	1.4

[a] Other conditions: total inlet flow rate 8.32 mol h^{-1}, MeOH/HCl 1/1, 800–1200 rpm.
[b] Contact time as defined in the text.
[c] Conversion and selectivity in mol%.
[d] Data from reference [9], MeOH/HCl < 1.

The reactors generally used for the industrial continuous production of methylchloride are continuous stirred tank reactors (CSTR) [2]. However, from a productivity point of view, it is probably the worst solution. Indeed, the kinetics of the target reaction is second order with respect to the reagents MeOH and HCl and may be considered as irreversible (Eq. (15)) [14]. Using basic chemical reactor engineering design, contact time required to achieve a given conversion can be expressed for both plug flow (PFR) and CSTR reactors (Eqs. (17) and (18)).

$$r_{MeCl} = kP_{MeOH}P_{HCl} \quad (\text{mol kg}_{ZnCl_2}^{-1}\,\text{s}^{-1}) \tag{15}$$

Considering the operating conditions $X = 0$, i.e. no MeOH conversion at the reactor inlet, and MeOH/HCl = 1, i.e. equal partial pressure for the reagents $P_{MeOH} = P_{HCl}$, Eq. (15) becomes:

$$r = 0.25k'(1-X)^2 P_T^2 \,(\text{mol mol}_{Zn}^{-1}\,\text{s}^{-1}) \quad \text{with}\; k' = km_{Zn}/n_{Zn} \tag{16}$$

And the reactor models are:

$$\tau_{PFR} = \frac{2}{k'P_T^2}\frac{X}{(1-X)} \tag{17}$$

$$\tau_{CSTR} = \frac{2}{k'P_T^2}\frac{X}{(1-X)^2} \tag{18}$$

In these models, the normalised residence time τ (min) is just the ratio between the quantity of catalyst (n_{Zn}) in the reactor and the total reagents MeOH + HCl molar flow ($\text{mol}_{MeOH+HCl}\,\text{h}^{-1}$) fed at the reactor inlet. For closed (Batch) reactors, this contact time reduces to normal time t, for same substrate/catalyst ratio, i.e. for same (MeOH + HCl)/Zn. The CSTR reactor model and the experimental data in the aqueous system at 150 °C are in good agreement, excepted for the literature data from reference [9] which was performed in a different type of reactor arrangement (see above) (Fig. 4). It is also obvious that a plug flow reactor would be the best reactor type to perform the target reaction, much shorter time being necessary to achieve high conversions.

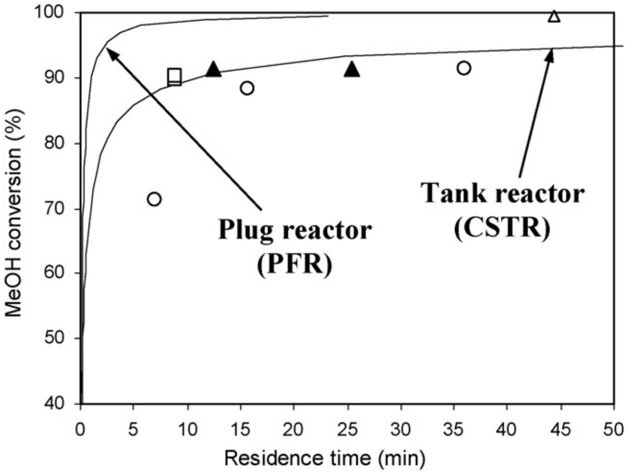

Fig. 4. Conversion vs. residence time plot. Water (▲) Aliquat336 (○) BMICl (□) US4922043 (△). The continuous and dash lines are CSTR and PFR model respectively. Conditions: 150 °C, 0.28 MPa.

Plug flow gas–liquid reactors are very difficult to design at the industrial scale, staggered bubble columns and cascade of CSTR being the traditional solutions to this issue. However, the use of ionic liquids may open other operating windows. They can act as H^+/Cl^- conveyors with the advantage of a pH window that is not limited by the presence of water, thus providing a high concentration of methyloxonium species $MeOH_2^+$. Thus a two step process can be design where in a first step, the ionic liquid/$ZnCl_2$ solution will be saturated with HCl in a simple tank reservoir then, in a second step, the so saturated solution will be contacted with methanol, forming a homogeneous liquid phase for which plug flow reactor design is well known. Such a switch from the CSTR to PFR technology would potentially result in a ca. fifty-fold improvement of reactor productivity (defined as the quantity of MeCl produced per mass unit of catalyst par time unit at 98% MeOH conversion). Furthermore, the very low vapour pressure of the ionic liquid will ensure a stable operation mode and easy separation of the product at the reactor outlet.

4. Conclusion

In this report, the use of ionic liquids has been investigated to replace water as a solvent in the preparation of methylchloride from methanol and hydrogen chloride, a large-scale industrial process. Analysis of the mechanism at the molecular level has lead to the use of ionic liquids for the targeted reaction. Albeit no spectacular improvement of the reaction efficiency was observed, it is demonstrated that the production of the side product Me_2O is somehow decreased in ionic liquids and that the reaction may be performed at lower temperature. From the reactor point of view, the analysis of the actual industrial reactors of CSTR type are not well suited. It is proposed that the use of ionic liquids can lead to process intensification resulting into a dramatic (50×) productivity increase through plug flow reactor design.

Acknowledgments

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