HIGHLIGHTS
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Highlights

Markus Hölscher reviews some of the recent literature in green chemistry

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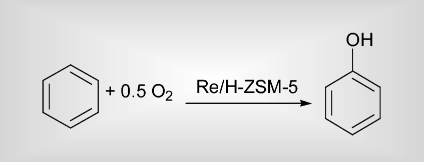
Oxidation of benzene to phenol with O_2 over rhenium/zeolite catalysts

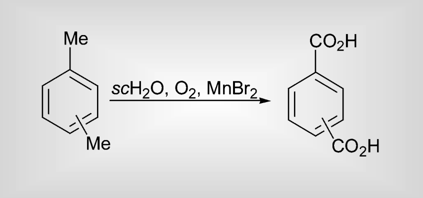
The cumene process, which is the industrial method of phenol production, suffers from by-product formation and low energy efficiency. Direct oxidation of benzene with molecular oxygen using selective catalysts would be economically and environmentally favourable. However, a suitable catalyst was not available. Iwasawa *et al.* from the University of Tokyo synthesized rhenium zeolites *via* impregnation and *via* chemical vapor deposition (CVD) of methyltrioxorhenium (MTO) and obtained active and selective catalysts for the direct oxidation of benzene to phenol, but only in the presence of ammonia (*Chem. Commun.*, 2004, 992–993).



The catalysts obtained by CVD were more active than zeolites impregnated with NH_4ReO_4 and among the different zeolite structures chosen the most active catalyst was H-ZSM-5. Its activity and selectivity did not decrease for at least 6 h. An excess of ammonia poisoned the catalysts and other bases like pyridine and isopropylamine also yielded inactive catalyst systems. According to EXAFS studies in H-ZSM-5 the rhenium centres are coordinated by three double bonded and two single bonded oxygen atoms. During the reaction the coordination number of the double bonded oxygen centres was reduced from 3 to 2 indicating the reduction of the Re^{7+} species to a Re^{6+} species. On Re/H-Mordenite catalysts the EXAFS results indicated aggregation of the Re-species, which explains the reduced activity.

Supercritical water as reaction medium for selective aerobic oxidations

Supercritical water has attracted much interest as an environmentally benign reaction medium. The physical and chemical properties of fluid water change drastically depending on temperature and pressure, which makes it possible to vary its performance in catalytic reactions. Catalyzed aerobic oxidations of methylaromatic compounds are reactions of significant importance for the chemical industry, since the resulting products are used almost everywhere in commodity and fine chemical production. Poliakoff *et al.* from the University of Nottingham investigated the performance of supercritical water in oxidations of xylenes and related compounds catalyzed by $MnBr_2$ (*Adv. Synth. Catal.* 2004, **346**, 307–316).



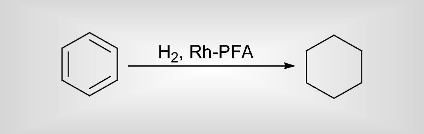
In an extensive study they developed reaction conditions in which *o*-, *m*- and *p*-xylene can be oxidized aerobically yielding the corresponding dicarboxylic acids with selectivities of 94, 97 and 95%, respectively. The yields were 46, 66 and 90%, respectively and the only by-product detected was benzoic acid (between 3 and 6%). The authors used a continuous flow reactor set up with residence times for terephthalic acid production of <20 s. Also mesitylene was oxidized successfully yielding trimesic acid in 78% yield and 93% selectivity. The only by-product found was phthalic acid (7%). In addition to chemical advantages, the new method is environmentally favorable since no acetic acid is used as solvent. Economical improvement is granted by small reactor volumes and fast processes (short residence times).

Aerobic oxidations using *N*-hydroxysaccharin (NHS) as promoter

One of the most challenging areas in modern oxidation chemistry is the selective oxidation of saturated hydrocarbons with molecular oxygen. Recently Sheldon *et al.* from the University of Delft showed that *N*-hydroxysaccharin (NHS) is an efficient promoter for oxidations of large ring cycloalkanes, ethylbenzene and a variety of alcohols in the presence of cobalt salts (*Adv. Synth. Catal.*, 2004, **346**, 286–296). Cyclododecane was oxidized with NHS in the presence of $Co(acac)_2$ with 64% conversion. Reaction products were shown to be the corresponding ketone (31%), the alcohol (8%) and the corresponding diacid (16%). A systematic variation of reaction parameters and co-catalysts showed Cu, Fe, and Ru compounds to be inferior to Co with regard to conversion. Chromium species also yielded lower conversions, however the yield of ketone could be increased to 57%. Also 2-octanol could be oxidized with high conversion (93%) and selectivity for the corresponding ketone (99%) when benzoic acid was added as additive. When ethylbenzene was oxidized to acetophenone in the presence of benzoic acid as additive a conversion of 71% was reached together with a selectivity of 96%. Mechanistic considerations based on bond dissociation energies are presented to help understand the mechanism of NHS action.

Nanoparticle catalysis in plastics swelled in supercritical CO_2

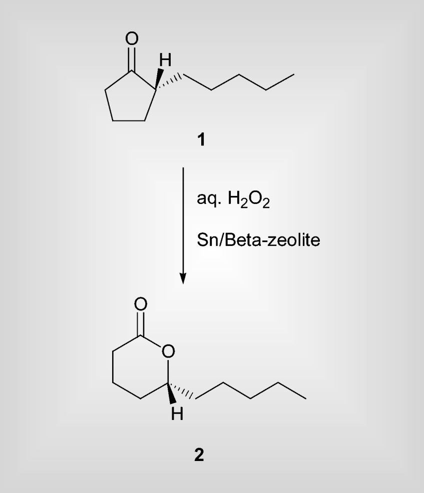
The tendency of nanometer-sized metal particles to agglomerate have been circumvented by different techniques, which render these unique metal species usable as interesting catalysts for green chemical technology. Wai *et al.* from the University of Idaho added another approach to this rapidly emerging field by stabilizing nanoparticles in plastics, which were swollen prior to use in supercritical CO_2 (*Chem. Commun.*, 2004, 930–931). They introduced the metal into high density polyethylene (HDPE) or fluoropolymer (PFA) by swelling the polymers in *sc*CO_2 and subsequently reduced molecular palladium and rhodium precursors with hydrogen to form the nanoparticles which resulted in metal loadings of 0.015–0.022 mmol. These materials were effective hydrogenation catalysts enabling the transformation of numerous aromatic compounds to saturated and partly saturated cyclic hydrocarbons.



The hydrogenation of benzene using Rh/PFA-material yielded cyclohexane at 50 °C with 100% conversion within 10 min. Napththalene was hydrogenated to tetraline with nearly 100% conversion at the same temperature in 15 min using Pd/HDPE-material. This catalyst system could be recycled 10 times without observable loss of activity. Olefinic double bonds and nitro groups can also be employed as substrates. The hydrogenation of nitrobenzene yielded aniline with a conversion of more than 98%. Advantages of these catalyst systems are their air stability, recyclability, easy handling and product separation.

Asymmetric lactone synthesis with Sn/beta-zeolite and H_2O_2

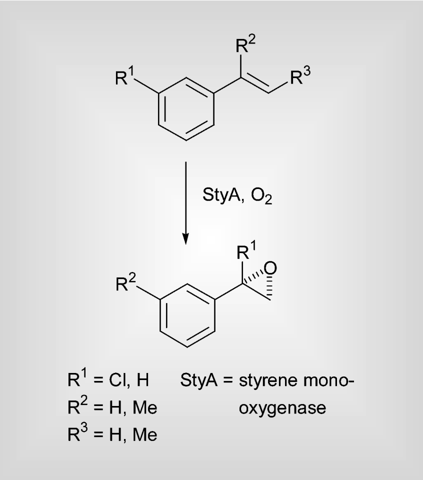
Asymmetric syntheses accomplished by zeolite catalysts with no or environmentally benign solvents such as water are currently under investigation in order to develop industrially useful alternatives to common oxidation procedures. Corma *et al.* from the Institute of Chemical Technology, Valencia, took a new step in this direction by investigating Baeyer–Villiger oxidations of ketones with H_2O_2 (*Adv. Synth. Catal.*, 2004, **346**, 257–262). Delfone (2-pentylcyclopentanone) **1** was transformed to the corresponding δ-lactone **2** (tetrahydro-6-pentyl-2*H*-pyran-2-one) with H_2O_2 as oxidant and a beta-zeolite modified with tin.



The stereochemical behaviour of the catalyst was the central focus of the authors. An enantiomerically enriched delfone mixture (87 : 13; (*R*) : (*S*)) could be reacted to the lactone with complete retention of configuration as was expected. The selectivity was 86% and could be optimized by varying reaction conditions to 92% (16% yield). These are promising results which should trigger more interesting research in this field.

Styrene monooxygenase in asymmetric epoxidations with molecular oxygen

The pharmaceutical and agrochemical industries rely on chiral oxofunctionalized hydrocarbons, which can be obtained *via* transition metal catalyzed reactions. However, enzyme catalysis with molecular oxygen as oxidant is an attractive alternative because of its high regio- and enantioselectivity, high turnover numbers and ecological friendly reaction conditions. Schmid *et al.* from ETH Zürich investigated the performance of styrene monooxygenase (StyA) coupled with regeneration of NADH in organic aqueous emulsions (*Angew. Chem.*, 2004, **116**, 2215–2218). This is the first report about the production and application of a bacterial monooxygenase for asymmetric cell free epoxidation of styrene derivatives.

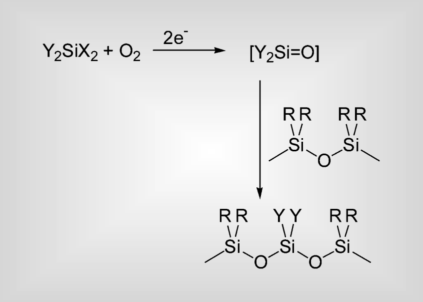


In a two phase dodecane–water reaction mixture reactants and products are dissolved in the organic phase while the enzymes for reaction and regeneration reside in the aqueous phase. 3-Chlorostyrene, α-methylstyrene and *trans*-β-styrene were epoxidized with conversions between 88 and 95% and very high selectivities of >99.9, 98.1 and 99.7% *ee*, respectively. The volumetric productivities of these catalyst systems have already reached the performance of their all-cell-based counterparts and turnover numbers of 1800–2800 were achieved, which outperform chemical catalysts by far (TON *ca.* 1000).

Focus on ionic liquids

Electrosynthesis in ionic liquids

The usage of room temperature ionic liquids (IL) as reaction media for electrochemical transformations attracts increasing attention. Good electrochemical stability, selective miscibility with organic solvents and their conductivity make these solvents interesting electrolytic media. Jouikov and coworkers from the University of Murcia, Spain, showed that the reaction of diorganyl dichloro or dialkoxy silanes with reduced forms of oxygen in the presence of siloxanes furnishes functional siloxanes without destruction of the solvent (*Chem. Commun.*, 2004, 674–675), which is a common problem with many solvents when the superoxide anion is generated.

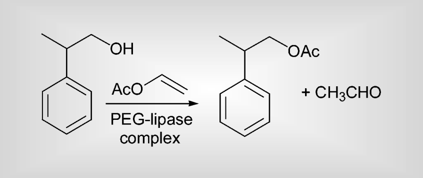


The reaction proceeds presumably *via* a silanone intermediate. Pyridinium based ILs with fluorinated side chains were suited best for these transformations with yields reaching 64% of the corresponding product. Recycling of the reaction media is possible.

Ionic liquids as solvents for highly active and enantioselective poly(ethylene glycol)-lipases

Catalytic enzymatic reactions in ionic liquids are attracting increasing interest, since in stoichiometric reactions it can be shown many times that enzyme activity and selectivity are higher in ILs than in common organic solvents. Goto *et al.* from Kyushu University reported lipase catalyzed alcoholysis between 1-phenylethanol and vinyl acetate in different ILs with the same or superior enantioselectivity compared to *n*-hexane (*Org. Biomol. Chem.*, 2004, **2**, 1239–1244).

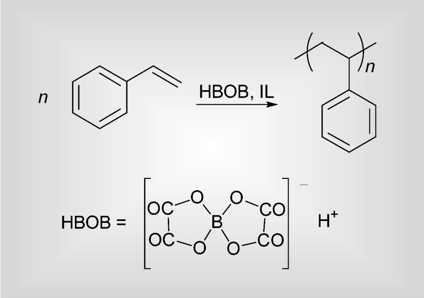
They showed that the activity of the native lipase is tremendously enhanced



when poly(ethylene glycol)-lipase complexes are used and interestingly ILs [BMIM][PF_6] and [OMIM][PF_6] yielded the same *ee* as *n*-hexane (80%), whereas [BMIM][Tf_2N] gave 98% *ee*.

Ionic liquids as reaction media for living cationic polymerizations

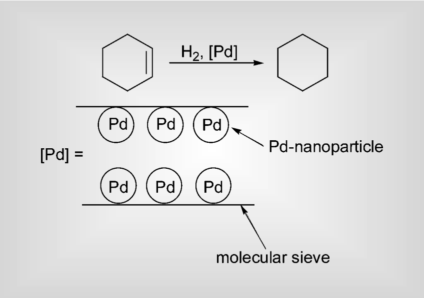
One of the main drawbacks of Lewis acid catalyzed cationic polymerizations of vinyl monomers is the generation of large amounts of waste and a difficult product separation. Furthermore, when $AlCl_3$ is used as the catalyst, chlorinated solvents are inavoidable to solubilize the aluminium compound. MacFarlane and Vijayaraghavan from the Monash University, Australia, introduced a novel catalyst and an ionic liquid as reaction media into the field and in this way developed a much greener version of this reaction (*Chem. Commun.*, 2004, 700–701). The IL chosen was *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide [P14][Tf_2N], the reaction to be investigated was the polymerization of styrene and as catalyst the authors used bis(oxalato)boric acid (HBOB).



They compared their results with experiments in which $AlCl_3$ was used as the catalyst both using IL and commonly used dichloromethane (DCM). At 0 °C experiments with $AlCl_3$ in IL yielded polymers with lower molecular weights compared to DCM and HBOB was inactive as catalyst. At 60 °C HBOB yielded polymers with a small polydispersity index indicating a narrow molecular weight distribution. Conversions were as high as 96% and the living character of the polymerization could be proved.

Immobilization of Pd nanoparticles on molecular sieves by ionic liquids—solvent-free hydrogenation of olefins

An interesting combination of the use of ILs, molecular sieves and nanoparticle catalysts was set up by Han and coworkers from the Chinese Academy of Sciences, Beijing (*Angew. Chem.*, 2004, **116**, 1421–1423). The authors used 1,1,3,3-tetramethylguanidinium lactate (TMGL) as IL for immobilizing Pd-nanoparticles on the inner surface of molecular sieves. The resulting catalyst was used for solvent-free hydrogenation of cyclohexene, cyclohexadiene, and 1-hexene.



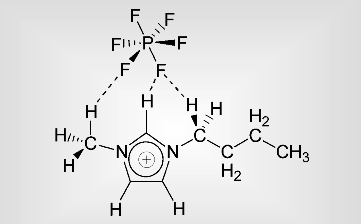
Even at room temperature conversion was 100% in most cases, with reaction times of up to 10 h. The alkadiene was hydrogenated to cyclohexene in high selectivity. Recycling experiments proved the catalyst system to generate product reproducibly at least four times without loss of activity. Among other results TEM analysis showed that the Pd-nanoparticles did not agglomerate significantly upon immobilization on the molecular sieve, which is probably part of the explanation why these catalytic systems are so active. The authors mention the size and Si/Al ratio of the molecular sieve (6.7 nm pore diameter and Si/Al = 1 : 1, respectively), but they do not provide its structure, which is unfortunate on the one hand, but might trigger even more research interest.

Gold nanoparticles modified with ionic liquids

Novel technical applications based on gold nanoparticles include usage as extinction dyes exploiting the high molar absorptivity in the visible region. Itoh, Naka and Chujo from Kyoto University combined the synthesis of gold nanoparticles and surface modification with ILs and developed an interesting device to sense anions in water colorimetrically (*J. Am. Chem. Soc.*, 2004, **126**, 3026–3027). By reducing $HAuCl_4$ with $NaBH_4$ in the presence of 3.3′-[disulfanylbis(hexane-1,6-diyl)]-bis(1-methyl-1H-imidazol-3-ium)dichloride (**1**) they generated gold nanoparticles with surface bound **1**, which are soluble in water. Upon addition of HPF_6 and HI to **1**-modified gold nanoparticles in aqueous solution the colors changed from red to purple and blue, respectively. Since **1**-modified gold nanoparticles are soluble in water in the presence of Cl^- as counterion, but immiscible with PF_6^- the nanoparticles can be moved from aqueous to IL phases by simply exchanging the anion, thus enabling the synthesis of ILs with gold nanoparticles. ILs of this type constitute a promising tool for recyclable biphasic catalytic processes.

Physicochemical properties of IL [BMIM][PF_6]

Besides the many reported applications of ionic liquids in chemical syntheses and other academic and industrial fields, relatively few investigations have contributed so far the underlying physicochemical basis of the unique properties of ILs. As ionic liquids are at the stage of becoming established solvents in many university laboratories around the world, researchers start to add the missing pieces. In a contribution by Dölle *et al.*, the well known IL [BMIM][PF_6] was subject to an investigation of molecular structure and dynamic behaviour (*Pure. Appl. Chem.*, 2004, **76**, 255–261).



Important F-H contacts in [BMIM][PF_6]

The authors used NMR derived data to establish the activation parameters for reorientational dynamics, which were found to be significantly higher for the aromatic ring of the cation. Semiempiric calculations showed clearly the existence of a hydrogen bond between the anion and the proton at C2 of the cation. Further analysis by molecular dynamics simulations in neat solution supported the existence of specific cation–anion interactions positioning the anion close to carbon atom C2 of the aromatic ring which is in accordance with quantum chemical structure calculations in the gas phase. Thus the formation of ion pairs of higher aggregates in solution can be assumed, which might explain the high viscosity of this IL.

Comparison of rate constants for solvent displacement in chromium complexes using ILs and common solvents

Displacement of a solvent molecule coordinated at a catalytically active metal complex can be the rate determining step in catalytic reactions. Since syntheses in

ILs have proven to be extremely valuable alternatives to the usage of common solvent systems, the need to acquire data about the new reaction media has grown. Using a model reaction, McLean, Gordon and coworkers investigated the displacement of solvent molecules by a “reactant” molecule in organic solvents and in ILs. They chose the photo-induced decarbonylation of $[(C_6H_6)Cr(CO)_3]$ yielding the solvent bound intermediate $[(C_6H_6)Cr(CO)_2(Solv)]$, in which the coordinated solvent molecule was displaced by acetonitrile. The reaction was carried out in cyclohexane, dichloroethane, methanol and in ILs $[BMIM][PF_6]$ and $[BMIM][(CF_3SO_2)_2N]$.

$$[(\mathrm{C_6H_6})\mathrm{Cr(CO)_3}] + \mathrm{Solv} \longrightarrow [(\mathrm{C_6H_6})\mathrm{Cr(CO)_2(Solv)}] + \mathrm{CO} \qquad (1)$$

$$[(\mathrm{C_6H_6})\mathrm{Cr(CO)_2(Solv)}] + \mathrm{L} \longrightarrow [(\mathrm{C_6H_6})\mathrm{Cr(CO)_2(L)}] + \mathrm{Solv} \qquad (2)$$

L = acetonitrile

The authors found that the Cr-solv interaction strength increased in the order cyclohexane, $[BMIM][PF_6]$, dichloroethane, methanol, whereas in the case of $[BMIM][(CF_3SO_2)_2N]$ acetonitrile was not able to displace the $(CF_3SO_2)_2N$ anion. These findings are in accordance with experimentally observed enhancement of turnover frequencies for nickel catalyzed reactions, when carried out in $[BMIM][PF_6]$ compared to dichloromethane or butane-1,4-diol, also suggesting the PF_6 anion to be more readily displaceable than chlorinated solvents like CH_2Cl_2.

Sixth Summer School on Green Chemistry

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The Summer School on Green Chemistry became a reality in 1998 with a grant from the European Commission's IV Framework Programme (FP) Training and Mobility of Researchers (TMR) programme. Currently, within the VI FP, the Summer Schools are part of the "Improving the Human Research Potential and the Socio-economic Base" programme.

Additional funds to cover participation of students from the Russian Federation and Latin America have been provided by the Italian Ministry for Foreign Affairs. Admitted European, Russian, and Latin American students benefit from complete scholarships.

Each year the School pays particular attention to the description of existing industrial processes, case histories and examples of clean organic processes. In addition topics related to current research in Green Chemistry are addressed with the aim of familiarizing the students with the strategies behind the planning and designing of efficient and "greener" synthetic routes.

Its chief aim is to train more young graduate and postgraduate chemists all over Europe on Green Chemistry, *i.e.* how to approach pollution prevention from a chemical standpoint.

The Summer School on Green Chemistry has run yearly in Venice, and this year will be the seventh (Venice, Italy, September 5–11, 2004).

The last Postgraduate Summer School, the sixth, was held at the Istituto Canossiano (see http://helios.unive.it/inca/summer_school.htm

Like the five preceding Summer Schools, the sixth one has been organized by the Italian National Interuniversity Consortium "Chemistry for the Environment", INCA (www.unive.it/inca).

The sixth School was attended by 64 students selected from approximately 90 applications received, and by 14 teachers. The students represented 20 different nations (Argentina, Egypt, Estonia, Finland, France, Germany, Hungary, Israel, Italy, Poland, Portugal, Romania, Russia, Slovakia, South Africa, Spain, Switzerland, the UK, Ukraine, Uzbekistan), while teachers were from Australia, Germany, Hungary, Italy, Switzerland, Denmark, the UK, and the USA. Participants, whose ages ranged from 25 to 35, represented both academia and industry.

The teachers were selected among the foremost experts in the fields of Green Chemistry.

This sixth School covered all the usual aspects of green chemistry, with special emphasis on catalysis:

Topics were
- alternative solvents
- alternative feedstocks
- catalysis
- alternative reaction conditions

This innovative approach to the design of clean chemical reactions and processes proved attractive to young scientists, as was immediately obvious from the growing number of applicants year after year.

Two poster sessions gave students the opportunity to establish new contacts, and to exchange information about their research in Green Chemistry. Posters of a high scientific level were presented by most of the students attending (an Abstracts book can be looked up and/or downloaded on the web page http://helios.unive.it/inca/); three were judged outstanding, and were presented with a book award and a certificate by the instructors.

Tutorial sessions were held during this year's Summer School. These involved dividing students into small (5–10 people) groups and assigning each group to an instructor, to discuss selected topics and to pose questions out of the classroom. Discussion ensued from these sessions which was lively and open.

Each session often evolved into an interactive discussion, rather than a traditional lecture, which followed the course laid out by the speaker. Some speakers gave more than one lecture, one being an introductory lecture to a general subject, and the second a more focused lesson on a specific research topic.

In addition, more industrial speakers were present, in order to convey to students the idea that Green Chemistry is a practical approach to solving real world industrial problems.

1. **Paul Anastas** (White House Office of Science and Technology Policy – USA) is one of the foremost experts and supporters of Green Chemistry. He gave the opening lecture on the general principles and on the objectives of Green Chemistry, thereby immediately putting the topic into context for the students.

2. **David Black** (University of New South Wales – Austria) lectured twice, the first time as Secretary General of IUPAC on the international activities carried out on Green Chemistry by IUPAC, and the second, on homogeneous enantioselective catalysis as a tool for green chemistry.

3. **Istvan Horvath** (Eotvos Lorand University – Hungary) described how homogeneous catalysis is green chemistry, and how molecular design is an art which can lead to beautiful and useful achievements.

4. **Wolfgang Hölderich** (RWTH Aachen – Germany) spoke twice. The first time he discussed the outlook for heterogeneous catalysis as a tool for green chemistry: "Environmentally Benign Processes Catalyzed by Heterogeneous Catalysts", where industrial processes in the field of acid, base and acid–base bifunctional catalysis as well as oxidation and enzymatic catalyzed processes were covered. In the second lecture processes based on renewable feedstocks were described.

5. **Walter Leitner** (RWTH-Aachen – Germany) described the use of enantioselective catalysis for green chemistry and in the second lecture spoke about "Supercritical CO_2 as a reaction medium for chemical synthesis".

6. **Mario Marchionna** (Enitecnologie – Italy) linked the oil and gas industry to green chemistry, and described new applications of green chemistry in the field of energy and of the petrochemical industry.

7. **Michael Grätzel** (Lausanne Polytechnic – Switzerland) described how photochemistry can be applied to green chemistry, in particular for the construction of new optical devices using sustainable technologies.

8. **Bernd Jastroff** (University of Bremen – Germany) is an expert on toxicological and environmental aspects of chemicals; he therefore lectured on how industrial chemicals can be made green, and on how this can be assessed.

9. **Zhi Li** (ETH Zürich – Switzerland)

talked about biocatalytic processes and described the use of biocatalysis in the production of a variety of compounds, both in aqueous media and in organic solvents.

10. **Allen A. Jensen** (Federation of European Chemical Societies) described new initiatives for the promotion of Green Chemistry in Europe, in particular through the preparation of a EU Green and Sustainable Chemistry Award.

11. **Kenneth Seddon** (The Queen's University of Belfast, UK) gave a lecture on the use of ionic liquids as clean solvents. Among the advantages of such solvent systems are their high polarity, large liquid range, low vapor pressure, easy recovery, and stability to water. Ionic liquids can be designed to optimize a reaction, and are promising for two-phase catalysis.

12. **Alvise Perosa** (Università Ca' Foscari, Venezia, Italy) dealt with new methodologies for the detoxification of polychlorinated organic pollutants. It is now possible to transform toxic and dangerous halo-aromatics into the corresponding hydrocarbons, catalytically under very mild reaction conditions.

13. **Pietro Tundo** (University Ca' Foscari of Venice, Italy) spoke about "Dimethylcarbonate: a green reagent". DMC is now produced by oxidative carbonylation of methanol rather than from phosgene. It was shown that it can be successfully employed in methoxycarbonylation reactions and methylation reactions, in place of traditional toxic and dangerous reagents such as dimethyl sulfate and methyl iodide.

Fig. 1 Participants in the 2003 Summer School on Green Chemistry at Istituto Canossiano during a working session.

The updated edition of the book entitled *Green Chemistry – A collection of lectures from the Summer Schools on Green Chemistry* (2nd edition, edited by the INCA Consortium) was distributed to the students attending the Summer School. This volume was a product of the first four years' schools. It was used as a textbook for the fifth, and its updated versions, made for each series of Summer Schools, will continue to be the textbook for the future. These updated scientific contributions of international level scholars are available all over the world thanks also to the electronic version available for free download on the web site (http://helios.unive.it/inca/pubblicazioni.htm).

The Istituto Canossiano as a location was very suitable because it fully satisfied the requirements and the aims of the School. Students and teachers could all be accommodated together and did not need to move to take part in the sessions. This solution facilitated a closer interaction between all participants, and, most important of all, created an informal and friendly atmosphere which was very profitable for scientific exchanges. Furthermore, time was dedicated to the scientific aspects, but it also allowed for visiting Venice.

Markus Hölscher

COMMUNICATION

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A low cost environmentally benign CO_2 based hydrometallurgical process

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Green process technologies involving the use of liquid and supercritical carbon dioxide have shown much promise as sustainable extraction and reaction media in many applications such as homogeneous and heterogeneous catalysis, nanotechnology, polymer synthesis, organic transformations, and the hydrometallurgical processing of zinc. Commercialization of these technologies has been limited by the high capital equipment and utility costs of CO_2 based chemical processes. Incorporation of CO_2-philic groups such as perfluoroethers, perfluoroalkyls, perfluoracrylates, and siloxanes in molecules has led to organic materials capable of transporting otherwise insoluble polar and organometallic compounds into carbon dioxide at relatively moderate pressures. Combining solvating extractants and carbon dioxide has shown promise in commercial and developmental zinc recovery operations; however, transport of the metal species into carbon dioxide has been limited by the solubility of the charged organometallic compounds formed. Here we show that the use of a CO_2 soluble counterion such as perfluorocarboxylic acid will enhance the solubility of organometallic compounds in carbon dioxide provided the molecules are designed to strike a balance between low cohesional energy and high free volume. Following these simple thermodynamic rules, we have identified CO_2 soluble organometallic complexes that readily dissolve in carbon dioxide at a low pressure and temperature of 860 psi and 25 °C, respectively . Even though this study focuses on the design of highly CO_2 soluble organometallic compounds for hydrometallurgical processes, we surmise that our guidelines can be employed for the development of CO_2-philic compounds useful in applications such as catalysis, synthesis of nanoparticles, and organic synthesis in general.

The requirement for large quantities of highly pure zinc metal product has placed stringent demands on separation technologies that have not been fully realized.[1] These include reductions in capital equipment and utility costs of recovery and purification techniques; minimizing environmental, health and safety risks; development of user friendly process strategies; and production of metals and alloys free of contamination. Satisfying these requirements has presented a significant challenge. For instance, to stay competitive with existing zinc refineries, the separation process of choice must be less energy intensive, consuming far less than 3 MWH per ton zinc produced[2] A single step zinc recovery process would be a novel accomplishment. Conventional process routes involve multi-stage processes as well as large volumes of acids and organic solvents. Based on information collected from the United States Geological Survey, there are currently no viable process alternatives which are more energy efficient, cost effective and sustainable as compared to conventional hydrometallurgical operations.[3]

We have developed a low cost environmentally responsible hydrometallurgical process which satisfies the guidelines specified above. This hydrometallurgical process involves extraction of transition metal ions into liquid carbon dioxide saturated with novel highly CO_2 soluble compounds to yield a highly pure zinc metal product. We recently reported the utility of a similar approach for metal recovery from aqueous systems. Experimental evidence demonstrated that quantitative recovery of zinc can be attained at relatively low pressure conditions employing sustainable materials which can be easily released from the valuable metal product.[4] While these efforts have addressed criteria such as environmental impact and performance, advancements must be made leading to extraction close to the vapor pressure of carbon dioxide (860 psi). Unlike past efforts, in this paper we report the recovery of high purity zinc for electrical, machinery and construction applications at low operating pressures of 860 psi and room temperature.

The CO_2 based hydrometallurgical process takes advantage of the physicochemical properties of nearcritical carbon dioxide, which in comparison to gases and supercritical fluids behaves as a liquid (Table 1). At these liquid conditions, the substance exhibits densities very close to organic solvents and are in the vicinity of 1 g cc^{-1} as illustrated by Table 1. It is these liquid densities which provide the nearcritical fluid with improved solvency characteristics as compared to a gas at ambient conditions. Nearcritical carbon dioxide at room temperature, and pressures close to 1132 psi, has been exploited as an environmentally benign solvent in laboratory and commercial efforts owing to the increased dissolution of organics and polymeric materials.[5–7] Unlike supercritical carbon dioxide, the lower temperature and pressure conditions allow for the development of energy efficient, sustainable and cost effective separation technologies. Finally, nearcritical carbon dioxide will allow for the fabrication of user friendly, simplified processing equipment.

Table 1 Comparison of properties of liquid, supercritical, and gaseous carbon dioxide

	Phase		
Property	Liquid	SCF	Gas
Density/g cc^{-1}	1	0.1–1	10^{-3}
Operating pressures/psi	Near 1132	Above 1132	14.7
System temperatures/°C	0–25	Above 31 °C	25

The ability to adapt conventional chemical processes for use in carbon dioxide has been realized through the molecular design of CO_2-philic compounds.[8–15] Compounds denoted as "CO_2-philic" incorporate functional groups such as perfluoroethers, perfluoroalkyls, perfluoroacrylates, and siloxanes into molecules. Inclusion of CO_2 philic groups enables miscibility with carbon dioxide at moderate pressures, resulting from the favorable thermodynamic interactions between the aforementioned functional groups and the nonpolar environment. Design and synthesis of CO_2-philic compounds has spawned the development and commercialization of many environmentally benign chemical processes. For instance, the design and synthesis of CO_2-philic phosphine ligands has led to CO_2 soluble catalyst systems capable of catalyzing the hydroformylation of olefins to aldehydes.[16–18] Development of CO_2-soluble surfactants has resulted in the creation of a CO_2 based synthetic route for the generation of microcellular polymeric foams[19] as well as the formation of nanoparticles in carbon dioxide.[20] Coupling CO_2-philic molecular design with an under-

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standing of conventional metal extraction processes, we have developed a low cost environmentally friendly process that yields an optimum zinc recovery of 97% at a CO_2 temperature and pressure of 25 °C and 860 psi. Recovery of zinc using CO_2 at such low pressure and temperature conditions provides a cost effective, sustainable process route as compared to conventional processes.

Currently, valuable zinc metal products are recovered and purified using a multi-step, energy intensive process.[1,2] First, recovery of zinc from metal laden solutions is accomplished *via* an electrowinning process. At a production rate of 950 tons day^{-1}, the electrodeposition of zinc is carried out in a cell house. This cell house contains 548 cells arranged in two sections of 132 cells and two sections of 142 cells, with each section powered by a rectifier with a capacity of 67,000 amps at 450 volts. The cells are placed in a cascade so that the metal laden solution flows under gravity from one cell to the next with the discharge from the last cell recycled back to return acid launders. Electrolyte solution is fed to the cells individually in each cascade with the overflow being accumulative. At the end of the electrolytic process, the cathodes deposited with zinc are removed and replaced with fresh ones. The 3 m^2 cathodes are stripped every 3 days using mechanized cathode handling and stripping units. Stripped zinc sheets are automatically stacked and conveyed to melting furnaces in the melting plant. In the melting plant, the zinc cathode sheets are melted and then the molten zinc is alloyed with other metals to adjust chemical properties to meet customer requirements. While the electrowinning operation results in a highly pure zinc product that is 99% zinc, this separation technique is very energy intensive as it consumes 3 MWH per ton zinc. At this consumption rate, the utility costs of the electrowinning operation alone total $500,000.

Other disadvantages inherent in this electrowinning operation include: need for a multi-stage process, removal of zinc from the cathodes, increased maintenance and manpower requirements, and use and handling of acidic solutions.

In an attempt to recover high purity zinc, we developed CO_2 soluble molecules[3,4] that would dissolve in carbon dioxide at low pressure conditions and form stable organometallic materials with zinc metal species. The combination of solvating extractants and carbon dioxide has proven useful for the recovery of metals in many developmental and industrial processes.[21] Although it is feasible to design solvating extractants that complex with zinc metal ions *via* coordination with electron-rich oxygen, nitrogen, or sulfur atoms, the positively charged organometallic material formed must be neutralized prior to solubilization into the non-polar extraction media. Neutralization of the charge on the organometallic compound is accomplished *via* association with negatively charged anions to form an ion pair. Since the polarized ion pair formed from the anions and the charged organometallic complex experience unfavorable thermodynamic interactions with carbon dioxide their solubility in carbon dioxide is expected to be low.

To aid in the molecular design of CO_2-philic organometallic complexes, we have developed design criteria based on CO_2 solution thermodynamics.[22–26] In this paper, we show that the solubility parameter can be used as a simple tool to design CO_2 soluble compounds which are highly miscible in carbon dioxide at low pressures. From such considerations, we conclude that a CO_2-philic organometallic complex should consist of a fluorocarbon ligand and counterion shell providing high free volume to enhance the entropy of mixing while at the same time exhibit a low solubility parameter to promote dissolution in carbon dioxide.

An understanding of the relationship between the molecular structure of organometallic compounds and their solubility in carbon dioxide can be realized through estimation of the solubility parameters of these materials. While many group contribution methods for the solubility parameter estimation have been developed, the technique described by Fedors[22] has been selected due to close agreement between calculated and documented solubility parameters and its prior use to correlate the solubilities of organic compounds in supercritical fluids.[27–29] Calculation of the solubility parameters of structurally complex molecules was accomplished by Fedor's group contribution method defined by

$$\delta = \left[\frac{\sum_i \Delta U_i}{\sum_i V_i} \right]^{\frac{1}{2}}$$

where ΔU is the molar cohesive energy and V is the molar volume of the CO_2 soluble molecules. Employing Fedors method, the solubility parameters of zinc alkylamine complexes were estimated and are given in Table 2. According to Table 2, substituting a CO_2 counterion such as perfluorodecanoic acid for a chlorine counterion, significantly lowers the solubility parameter from 22.11 to 17.17 $(cal\ cc^{-1})^{1/2}$. This decrease in the solubility parameter is due to the bulky and highly electronegative fluorine groups around the central metal ion of the metal alkylamine complex which reduce the cohesional energy and increase the volume contribution. Also, comparison of solubility parameters in Table 2 demonstrates the addition of the CO_2 soluble counterion results in minimizing the difference between the solubility parameters of the metal complex and carbon dioxide. According to the Scatchard–Hildebrand[24] equation, as the solubility parameter difference is minimized, optimum solubility in carbon dioxide results giving way to the concept of "likes dissolve likes".

Table 2 Solubility parameters of zinc alkylamine complexes estimated from Fedors group contribution method

Complex	$\delta/(cal\ cm^{-3})^{1/2}$
$Zn^{2+}(FL)_4 2Cl^-$	22.11
$Zn^{2+}(FL)_4 2PFDA^-$	17.17
CO_2 @ 1085 psi and 31 °C	10.73

The organometallic compound evaluated in this work was chosen to optimize the balance between cohesional energy and free volume contributions, as well as possess Lewis acid groups that form stable metal complexes with transition metal ions. With these thermodynamic guidelines in mind, we employ a bulky, highly electronegative shell consisting of a Fluorolink ligand[30] and perfluorodecanoic acid (PFDA) counterion[3] to adapt conventional solvating extractants for use in liquid carbon dioxide at low pressure conditions. Both of the CO_2 soluble compounds incorporate perfluoroether and carbonyl groups which are known to interact favorably with carbon dioxide. Our research group has observed that these model compounds exhibit high CO_2 solubility of 12–15 wt% at relatively low pressure conditions of 1500 psi and below. Coupled with their high CO_2-philic nature, these model compounds possess an amine chelate group (Fluorolink extractant) which targets the zinc metal ions and negatively charged anions (counterion) which neutralize the charge on the metal species. Using the thermodynamically favorable extractants and liquid carbon dioxide as the extraction media we have developed a low cost environmentally conscious hydrometallurgical process capable of extracting substantial amounts of zinc from metal laden aqueous solutions at low pressure conditions (Fig. 1A and 1B).[31–32]

The molecular design of a CO_2-philic organometallic compound proved to be an cost effective green process technique for recovering zinc into liquid carbon dioxide. First, comparison of extraction data using liquid carbon dioxide saturated with only Fluorolink and liquid carbon dioxide with Fluorolink and perfluorodecanoic acid showed a significant discrepancy. As demonstrated by Fig. 2a, the recovery of zinc using only the Fluorolink complexing agent was low at operating pressures close to the vapor pressure of carbon dioxide (860 psi). In stark contrast, these experimental data show that employing liquid carbon dioxide saturated with a Fluorolink complexing agent and perfluor-

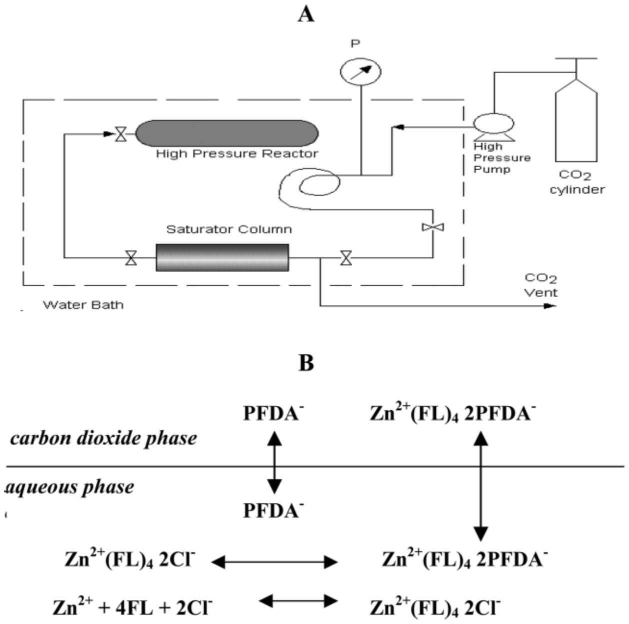

Fig. 1 Schematic representation of the low cost environmentally responsible CO_2 based hydrometallurgical process. **(A)** Carbon dioxide at the desired pressure and room temperature is presaturated with Fluorolink extractant and PFDA counterion. Next the saturated carbon dioxide phase flows into a 25 ml stainless steel bomb reactor containing a metal laden solution, **(B)** resulting in formation of the metal complex; dissociation of PFDA; substitution of PFDA for chloride anion; and partitioning of the material into the carbon dioxide phase. After the reaction system reached equilibrium, phase separation was induced. Depressurization of the system was followed by sampling of the aqueous phase and analysis for residual metal concentration using inductively coupled plasma emission spectroscopy. Use of the CO_2 soluble counterion or perfluorodecanoic acid yielded an optimum zinc recovery of 97% at a low CO_2 temperature and pressure of 25 °C and 860 psi, thereby indicating very favorable commercial scale economics. FL, Fluorolink extractant; PFDA, perfluorodecanoic acid.

odecanoic acid at a temperature and pressure of 25 °C and 1050 psi, a zinc extraction efficiency of 98% was obtained. Clearly low recoveries using only Fluorolink can be attributed to the unfavorable CO_2-chloride anion interactions but also the calculated solubility parameter data of zinc alkylamines (Table 1) shows that the presence of the chloride anion results in a higher solubility parameter than that for perfluorodecanoic acid. Subsequently, it seems that addition of the perfluorodecanoic acid increases the free volume contribution (entropy of mixing) while enhancing dissolution in carbon dioxide (enthalpic contribution). Secondly and most astoundingly, using PFDA and Fluorolink at a low CO_2 temperature and pressure of 25 °C and 860 psi, an optimum zinc recovery of 97% was obtained. Again striking a balance between cohesional energy and free volume contributions seems to account for this observed increase in zinc recovery. Lastly, the recovery of zinc using Fluorolink and PFDA showed little pressure dependence while the effect of pressure on extraction of zinc with only Fluorolink seemed to be appreciable.

In order to elucidate the mechanism responsible for extraction, the effect of the perfluorodecanoic acid concentration on the recovery of zinc was explored (Fig. 2b). Experimental evidence demonstrated that the zinc recovery increased with increasing concentration of the CO_2-soluble counterion and reached a separation efficiency of 99% using a metal : ligand : PFDA ratio of 1 : 4 : 15 at system conditions of 25 °C and 1200 psi. Results seem to confirm the extraction mechanism which involves formation of a metal complex between the zinc cation, fluorinated ligand, and chloride anion; dissociation of PFDA; and substitution of the CO_2-soluble counterion for the chloride anion.

To validate the argument that a CO_2 soluble counterion would increase the CO_2 solubility of the zinc alkylamine complex, the solubility of the zinc metal chelates were determined. UV-vis spectroscopy was employed as a analytical tool to determine the solubility of the metal complex in the carbon dioxide phase.[2] The solubility of the metal complex in CO_2 represents an important process variable since exceeding the solubility limit could mask the performance of the CO_2 based hydrometallurgical process. Assuming the path length and extinction coefficient in the non-polar solvent were constant, the optimal concentration in carbon dioxide was determined using Beer's Law. Calculations showed that the CO_2 solubility of the Zinc-Fluorolink–PFDA complex was 3 times larger than the Zinc-Fluorolink-Chloride complex (125 mM *vs.* 40 mM). Further these solubilities are much higher than those achieved in past research work.[11]

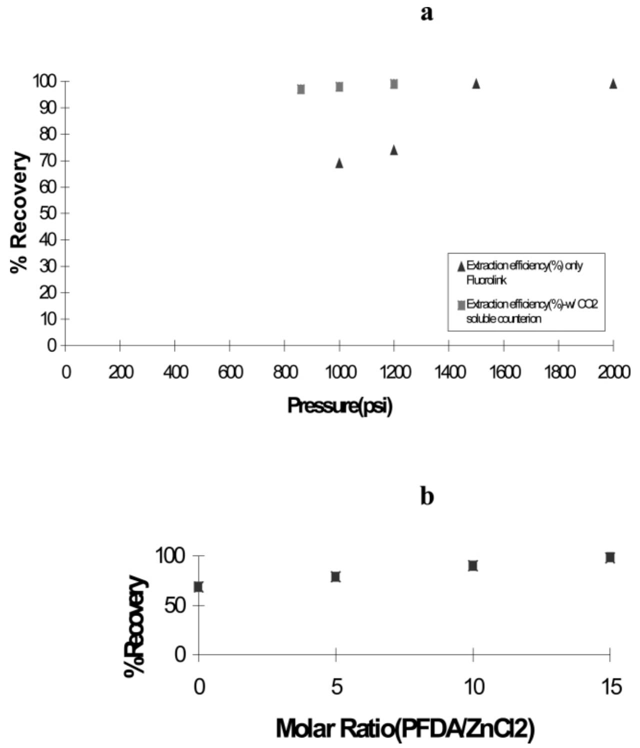

Fig. 2 (**a** and **b**) Extraction results showing the effect of addition of perfluorodecanoic acid (PFDA) on zinc recovery, as well as the effect of PFDA concentration on performance of the CO_2 based hydrometallurgical process. **(a)** Effect of PFDA addition on zinc recovery with pressure at process conditions: $T = 25$ °C, metal/ligand/PFDA ratio = 1 : 4 : 15. **(b)** Variation of zinc recovery w/ molar ratio of PFDA to metal using ligand modified CO_2, system conditions: $T = 25$ °C and $P = 1200$ psi.

Looking ahead, implementation of our process on a commercial scale seems feasible. In a recent study, our research group reported that a CO_2 based hydrometallurgical process operating at pressures close to the vapor pressure of carbon dioxide exhibits very favorable commercial scale economics.[4] Comparison of operating costs of a conventional electrowinning operation to the CO_2 based process shows that zinc can be manufactured for pennies a pound using a liquid carbon dioxide extraction system, whereas using the conventional process zinc can be produced at $0.43 per pound. Implementation of this CO_2 based technology is also facilitated by further simplification of the process scheme depicted in Fig. 1A. Since we are able to achieve substantial recoveries of zinc at low CO_2 pressures of 860 psi, elimination of the high pressure pump is possible. The complications inherent with the conventional electrowinning operation (*i.e.* multi-stage processing; removal of zinc from cathodes; and use and handling of acidic solutions) are also eliminated. Further, development of a low cost environmentally benign hydrometallurgical process has provided a technology platform, enabling the advancement and scaleup of commercially viable metal recovery processes.

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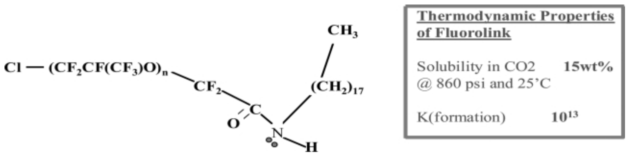
30 Chemical structure of Fluorolink and its thermodynamic properties.



31 Extraction experiments were performed using a custom built 25 ml bomb reactor constructed from 1 inch outside diameter stainless steel tubing sealed at one end and an inlet at the opposite end. High pressure tubing used in the experiment was $\frac{1}{4}$ inch outside diameter stainless steel tubing. A presaturator column having an outside diameter of 1 inch was employed to saturate carbon dioxide with both the Fluorolink complexing agent and perfluorodecanoic acid prior to sending the solution into the reactor. Temperature control of the reactor, presaturator, and process lines was achieved using a water bath and an immersion type heater. Carbon dioxide at the desired pressure and temperature conditions was allowed to flow into a presaturator column containing a known amount of Fluorolink and perfluorodecanoic acid. After allowing the system to come to equilibrium for 1 hour, the saturated carbon dioxide phase was allowed to flow into a 25 ml stainless steel bomb reactor containing an aqueous solution having a high zinc metal loading of 5000 ppm. The reactor contents were mixed using a magnetic mixer to ensure formation of the metal complex and partitioning of the material into the carbon dioxide phase. The final pressure of the reactor was then adjusted to attain the desired pressure and the reaction system was allowed time to come to equilibrium. Once the reaction system had come to equilibrium, the magnetic mixer was shutoff allowing phase separation to occur. The reactor was then depressurized to 1 atm and three 1.25 ml samples of the aqueous phase were taken and analyzed for the residual metal concentration using inductively coupled plasma emission spectroscopy. From the three measurements an average metal concentration is calculated. Finally, knowing the initial and final metal concentration in the aqueous phase the % zinc recovered was determined.
32 Prior to depressurizing the reactor, a sample of the CO_2 phase was taken using a six way switching valve. The six way switching valve was placed in position A, which allowed the 0.250 ml sampling line to be filled with the CO_2 phase. After filling the sampling line, the valve was placed into position B, which allowed the CO_2 phase to expand and bubble through a known volume of hexane. To collect any residual complex that may have precipitated, the sampling line was flushed with 1 ml of hexane. The solvent mixture is then analyzed for the concentration of complex using UV-vis spectroscopy. Zinc mass balance closures were better than 95%.

PAPER

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Quaternary ammonium decatungstate catalyst for oxidation of alcohols

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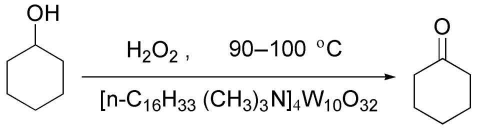
This work describes the use of hydrogen peroxide as oxidant for the selective oxidation of some alcohols in the presence of hexadecyl trimethyl ammonium decatungstate catalyst under simple reaction conditions. It includes the oxidation of cyclohexanol to cyclohexanone in the temperature range of 90 to 100 °C for 2 hours with 89.1% yield and 92.3% cyclohexanol conversion and the oxidation of hexanol and octanol at a temperature of 90 °C or reflux for 12–17 hours with 86.2–93.7% yields and 93.5–98.8% carboxylic acid selectivity.

Introduction

The use of hydrogen peroxide as oxidant has attracted considerable attention in recent years[1–9] There have been a number of procedures[6–9] for alcohol oxidation using H_2O_2 and *in situ*-generated or preformed metal complexes, however, some of them remain in need of improvement for application to practical organic synthesis. Recently, the author found that quaternary ammonium decatungstate could be used as catalyst to promote oxygen transfer from H_2O_2 to the reaction substrates, and used it first for oxidation of cyclohexene.[5,10] The results show that it is effective in canalization of oxidation of cyclohexene, it can efficiently utilize H_2O_2, and can easily be recycled. This catalyst is insoluble in water, but it can be dissolved in a mixture system of organic substrate and H_2O_2. When the H_2O_2 is used up, the catalyst self-precipitates in water. Thus, the advantages of combining homogeneous and heterogeneous catalysis in one system are obvious. The present work explores the application of the catalyst to activation of H_2O_2 for oxidation of cyclohexanol. A more practical organic synthesis to oxidize cyclohexanol and some long chain alcohols is reported herein.

Results and discussion

In this work, cyclohexanol is oxidized directly to cyclohexanone with H_2O_2 using hexadecyl trimethyl ammonium decatungstate as catalyst in a short time with excellent yield and selectivity (eqn. 1). When a mixture of cyclohexanol (50 g), 35% H_2O_2 (53 g), and hexadecyl trimethyl ammonium decatungstate catalyst (2 g) was stirred in air at a temperature of 90 to 100 °C for 2 hours, H_2O_2 was utilized efficiently and cyclohexanone was formed in 89.1% yield. The conversion of cyclohexanol is 92.3%, and the selectivity for cyclohexanone is 96.6% [as determined by gas chromatographic (GC) analysis].[11]



(1)

Cyclohexanol reacts with H_2O_2 to readily form many other compounds such as cyclohexanone, caprolactone, 6-hydroxyhexanoic acids, adipic acid and so on. The experimental results show that using this catalyst system has a highly efficient and high selectivity, and it does not induce the unproductive decomposition of H_2O_2 to any great extent and enables the economic use of the oxidant, namely, 1.1 mol of H_2O_2 per 1 mol of cyclohexanol for the oxidation step. With a higher molar ratio of H_2O_2, the product yield is decreased to some extent.

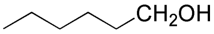
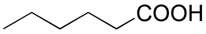
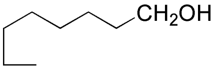
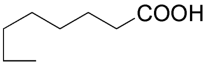
When the system was heated up to 90 °C, it released large quantities of heat spontaneously, maintained over 30 minutes. The total reaction time is normally 2 hours. The catalyst is not soluble in water, but it can dissolve in the reaction mixture and form an emulsifying solution. These phenomena indicate that some active species may form in the process and the tungsten-containing catalyst activates H_2O_2.

The efficiency of this selective oxidation procedure compares favourably with that of the method of Indira *et al.*[6], in which 30% H_2O_2 and tetrabutylammonium salts of divalent transition metal mono-substituted dodecatungstophosphates were used. The reaction time of the process is also shorter than that of the sodium tungstate and oxalic acid catalyst system of Wei *et al.*[7]

The results of the oxidation of hexanol and octanol are listed in Table 1. They show that using hexadecyl trimethyl ammonium decatungstate as catalyst, hydrogen peroxide could efficiently oxidize hexanol or octanol to carboxylic acids with excellent yields and selectivity (eqn. 2).

$$RCH_2OH \xrightarrow[{[n\text{-}C_{16}H_{33}(CH_3)_3N]_4W_{10}O_{32}}]{H_2O_2,\ 90\text{–}100\ °C} RCOOH \qquad (2)$$

Table 1 The oxidation of hexanol or octanol to acids by hydrogen peroxide using a quaternary ammonium decatungstate catalyst[a]

Entry	Substrates	Products	Reaction time/h	GC yield (%)	Conversion (%)	Selectivity (%)
1			13	88.8	91.4	97.2
2			12	86.2	92.2	93.5

[a] Reaction conditions: 0.2 mol of alcohol, 43.5 g (0.44 mol) of aqueous 35% H_2O_2, reflux. The GC yield is the yield of corresponding acids, which is based on amount of the product and its purity [as determined by gas chromatographic (GC) analysis].[11] Amount of $[n\text{-}C_{16}H_{33}(CH_3)_3N]_4W_{10}O_{32}$ is 1.0 g. The conversion of alcohols was based on the content of alcohols in the product, and the selectivity for acids was based on its transformation from the corresponding alcohols.

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Although the oxidation time of long chain primary alcohols is 6 times greater than that of cyclohexanol, even 12 or 13 hours under reflux reaction conditions does not induce the unproductive decomposition of H_2O_2 to any great extent, as observed in the case of cyclohexanol, therefore, it enables the economic use of the oxidant; namely, 2.2 mol of H_2O_2 per 1 mol of hexanol or octanol.

Using Deng's peroxytungstate–organic complex catalyst system[4] could rapidly bring about the unproductive decomposition of H_2O_2. As a result, the oxidation of hexanol and octanol could not be performed and carboxylic acids could not be obtained. In the current work, the yield, the selectivity for acids, and the utilization efficiency of H_2O_2 are also better than those of Zhou's work, where quaternary ammonium peroxyphosphotungstates were used as catalysts.[9]

To identify the reaction profile of the oxidation of long chain alcohols, the reaction products of the mixture of 0.4 mol of octanol, 82.0 g (0.84 mol) of aqueous 35% H_2O_2, and 1 g of $[n\text{-}C_{16}H_{33}(CH_3)_3N]_4W_{10}O_{32}$ catalyst at 90 °C for 17 hours were determined by gas chromatographic (GC) analysis.[11] The analytic results are shown in Fig. 1. The results indicate that initial oxidation obviously proceeds by way of octanal, whereas the second oxidation *via* its hydrate is fast as a result of the acid formation. Octanyl octanoate is also produced in the procedure; however, when H_2O_2 is used up, the final product (after 17 hours) from the reaction system is mainly octanoic acid in 93.7% yield. The conversion of octanol is 94.8%, and the selectivity for octanoic acid is 98.8%.

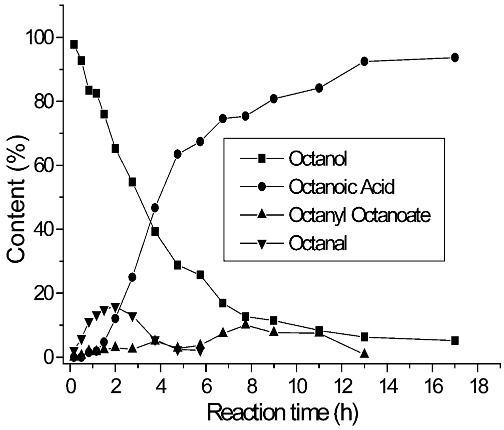

Fig. 1 Reaction profile of the oxidation of octanol over hexadecyl trimethyl ammonium decatungstate.

On considering that the pH value of the mixture of H_2O_2 and the catalyst was lower than that of an aqueous solution of H_2O_2 and that in the process of the oxidation reaction H_2O_2 probably coordinated to the W catalyst to form some kind of peroxypolytungstate active complex, in previous work, the author compared the infrared and ultraviolet absorption spectra of the fresh and recovered catalyst.[10] The result showed that their structures are different. Now, relevant work on the recovered catalyst structure is in progress.

In summary, hexadecyl trimethyl ammonium decatungstate as catalyst enables the economic use of H_2O_2 and can promote active oxygen transfer from H_2O_2 to the reaction substrates. The preparation of the catalyst is simple and it can be easily obtained. This method is high-yield, clean, safe, operationally simple, and cost-effective and therefore meets with the requirements of contemporary organic synthesis.

Experimental

Hexadecyl trimethyl ammonium decatungstate

According to the method reported by Chemseddine and co-workers,[12] the preparation procedure of hexadecyl trimethyl ammonium decatungstate is given as follows:

The hexadecyl trimethyl ammonium decatungstate was prepared by mixing boiling solutions of 16 g of $Na_2WO_4{\cdot}2H_2O$ in 100 ml of water and 33.5 ml of 3 M HCl. After boiling for a few minutes, the clear yellow solution was precipitated by addition of an aqueous solution of hexadecyl trimethyl ammonium bromide (7.3 g/70 ml). The white precipitate was filtered, washed with boiling water, and dried at room temperature to give a colorless powder: yield 13.5 g. IR (cm^{-1}):[13] 995.3 (vw), 956.8 (vs), 891.2 (s), 800.5 (vs) 586.4 (vw), 437.9 (m), 405.1 (m).

The oxidation of cyclohexanol

The typical procedure for oxidation of cyclohexanol and reuse of the catalyst is given as follows. In the first run, a 250 ml three-neck flask equipped with a power-driven stirring bar and a reflux condenser was charged with 2.0 g of the catalyst, 50 g (0.5 mol, purity in 97.35%) of cyclohexanol, and 53 g (0.55 mol) of aqueous 35% H_2O_2. The mixture was stirred and heated to 90 °C. The mixture system releases a quantity of heat spontaneously, maintained over 30 minutes. It is necessary to cool it when the reaction temperature is more than 100 °C. After this procedure had finished, the reaction mixture was heated and stirred in air at reflux temperature (about 98 °C) for 1.5 hours. By this point, the H_2O_2 was used up (as determined by starch iodine paper), and the catalyst was principally dissolved in the organic phase. A dropping funnel with pressure-equalization arm was inserted between the flask and reflux condenser. The mixture was stirred and heated. The stopcock of the funnel was closed; as the azeotrope of cyclohexanol, cyclohexanone and water was distilled, the condensed liquid (two layers) was collected in the dropping funnel. From time to time, the stopcock was opened to drop water back into the flask until the crude product was distilled off. By this point, the catalyst had precipitated in the remaining aqueous phase and could be easily recycled. The remaining solution was poured off from the flask and the self-precipitated catalyst was left behind. In the second run and third run, only the alcohol and H_2O_2 were added. The catalyst that was left in the flask from the previous run dissolved in the mixture again when it was stirred at a temperature of 90 to 100 °C. The phenomena and operation are the same as first run.

The distillate collected in the dropping funnel was separated. Its water phase was saturated with salt and the layer of cyclohexanone was separated in a separatory funnel. The two organic phases were combined. The anhydrous layer was obtained by distillation. The cyclohexanol and cyclohexanone contents were determined by gas chromatographic (GC) analysis.[11] In the second run and third run, the yields of cyclohexanone and the conversion of cyclohexanol are almost the same as with the fresh catalyst.

The oxidation of long chain alcohols

The typical procedure for oxidation of octanol is given as follows. A 250 ml three-neck flask equipped with a power-driven stirring bar and a reflux condenser was charged with 1.0 g of the catalyst, 26 g (0.2 mol) of octanol, and 43 g (0.44 mol) of aqueous 35% H_2O_2. The mixture was stirred, heated and kept at reflux for 12 hours. H_2O_2 was used up (as determined by starch iodine paper) then, the catalyst self-precipitated in water from the reaction system. The oily product was separated by distillation. The precipitated catalyst could be recycled by filtration and washed with ethanol.

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Combining alkylation and transalkylation for alkylaromatic production

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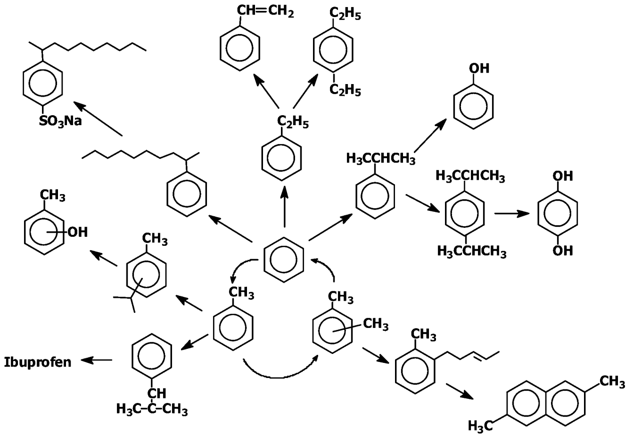
The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry. The efficiency of these productions is highly improved performing alkylation combined with transalkylation, the latter allowing conversion of some low valued by-products such as polyalkylbenzenes into their monosubstituted homologues. The aim of this contribution is to summarize some examples of novel industrial processes, based on new catalysts that are environmentally friendly, for the production of ethylbenzene and cumene, two of the most important chemicals produced by alkylation/transalkylation.

1 Introduction

Ethylbenzene (EB), cumene, *p*-diethylbenzene, *p*-diisopropylbenzene, C_{10}–C_{14} linear alkylbenzenes (LAB) and cymene are some of the chemical intermediates obtained by acid catalyzed alkylation on the aromatic ring of benzene or toluene.[1]

Scheme 1 summarizes several aromatic alkylations industrially applied for the preparation of important chemical intermediates. These reactions include the most important aromatic substrates, benzene, toluene and xylene, and different olefins. They also include two different kinds of alkylation: the electrophilic alkylation on the aromatic ring catalyzed by acids and the side-chain alkylation catalyzed by bases.



Scheme 1 Industrial aromatic alkylations.

From the point of view of production volume, the acid catalyzed alkylations are by far the most important. In 2002 the world overall demand for benzene was around 33 million tons. Alkylbenzene derivatives account for about 75% of the total benzene production (Fig. 1).

Transalkylation is often combined with alkylation in order to convert low valued by-products such as polyalkylbenzenes into their monosubstituted homologues, globally improving the efficiency of the process.

The oldest technologies available to perform these alkylations/transalkylations are based on catalysts which have drawbacks. Often such catalysts are strong mineral acids or Lewis acids (*e.g.*: HF, H_2SO_4, $AlCl_3$). These acids are highly toxic and corrosive. They are dangerous to handle and to transport as they corrode storage and disposal containers. Besides, because the reaction products are mixed with acids, the separation at the end of the reaction is often a difficult and energy consuming process. Very frequently at the end of the reaction these acids are neutralized and therefore the corresponding salts have to be disposed of.

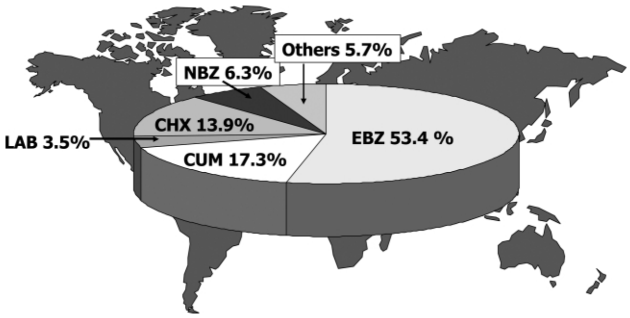


Fig. 1 Breakdown of benzene uses in the chemical industry (EBZ: ethylbenzene; CUM: cumene; LAB: Linear alkylbenzene; CHX: cyclohexane; NBZ: nitrobenzene).

In order to avoid these problems many efforts have been devoted to the search for solid acids that are more selective, safe and environmentally friendly. Among the different solid acids, zeolites have been extensively evaluated for such a purpose,[2] and here we review the main results obtained in this field.

2 Alkylation of benzene to produce ethylbenzene (EB)

The alkylation of benzene with ethylene is an electrophilic substitution on the aromatic ring. Alkylation reactions are commonly considered as proceeding *via* carbenium-ion-type mechanisms. On a Brønsted acid site ethylene is protonated to form the active species. The latter can follow two major routes (Scheme 2):

- it can react with benzene producing EB which can later undergo other reactions producing mainly diethyl- and triethylbenzene (DEB and TEB).
- it can react with another ethylene molecule producing a C4 species which can further transform by alkylation, oligomerization, isomerization or cracking giving other alkylbenzenes and olefins.

To a very small extent EB undergoes alkylation to diphenylethane. It must be remarked that DEB and TEB can be easily recovered by transalkylation with benzene to EB, so they can be considered useful products. On the contrary the formation of olefins and other alkylbenzenes heavily affects the efficiency of the process by increasing the specific consumption of ethylene and benzene and reducing the EB quality.

In the traditional process, developed since the 1930s, the alkylation is performed by reacting benzene and ethylene in the

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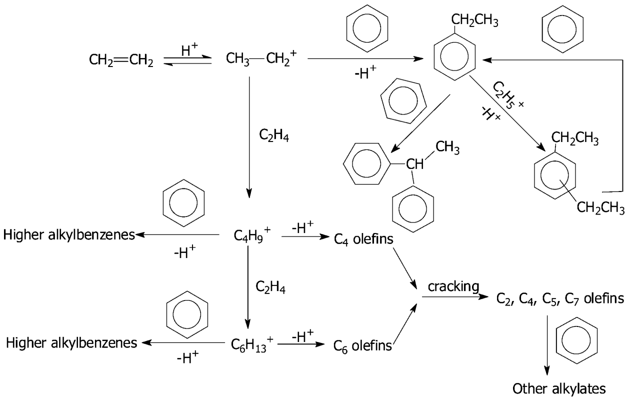

Scheme 2 Reaction pathway of benzene alkylation with ethylene.

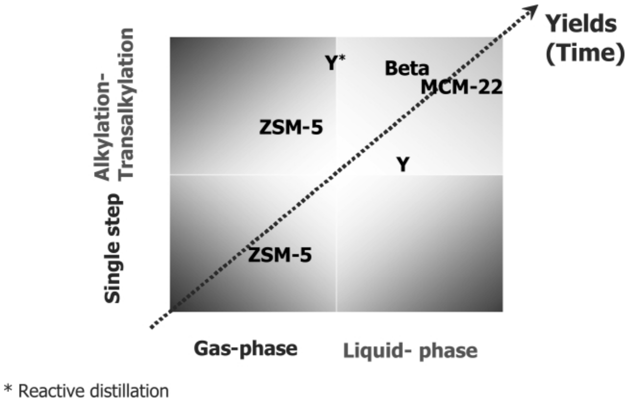

Fig. 3 Yield progress in ethylbenzene production.

presence of a Friedel–Crafts catalyst (*i.e.* $AlCl_3$–HCl) under mild conditions (Fig. 2).

+
- **single step (alkylation + transalkylation)**
- **low benzene/ethylene**
- **mild conditions (160 °C; 0.7 MPa)**

−
- **corrosion**
- **acidic waste**
- **chlorinated impurities**

Fig. 2 Pros and cons in the alkylation of benzene with ethylene catalyzed by $AlCl_3$.

Starting from the mid-1960s different zeolite-based catalysts were extensively evaluated in the alkylation. In 1966 Venuto *et al.* reported that X and Y zeolites are more effective catalysts for benzene alkylation with olefins than amorphous silica-alumina gels.[3]

In spite of the big effort, it still took ten years to accomplish the first industrial alkylation process based on a zeolite catalyst, which in fact occurred in 1976. This process, developed by Mobil and Badger for the production of EB in the gas-phase, was based on a ZSM-5 type zeolite.[4]

Later improvements were obtained introducing

(a) the liquid-phase alkylation and

(b) a separate step of transalkylation.

The liquid-phase has the advantage of better thermal control and longer catalyst life, which allows off site catalyst regeneration and therefore easier control of pollution. To do this it was necessary to move from medium pore zeolites like ZSM-5 to large pore zeolites such as Beta and Y. The introduction of new zeolite catalysts together with process up-grading produced significant yield improvements (Fig. 3).

Therefore, starting from 1980 the Mobil–Badger process has been extensively applied in the alkylation units. The main feature of ZSM-5, the zeolite used, is its tridimensional pore structure with 10MR openings suitable for gas-phase operation.

The next achievement was then represented by the development of a liquid-phase process by UOP/Lummus/Unocal,[5] first commercialized in Japan in 1990, with a catalyst based on zeolite Y. In this case the zeolite has a tridimensional pore system too, but with large openings. A drawback of this structure is represented by the supercages at the interconnection of the pores as they favor the formation of bulky by-products. To overcome this problem, two companies claimed independently the use of zeolite Beta for EB production: Chevron patented it in the USA and EniChem in Europe.[6,7] In fact, zeolite Beta has a tridimensional pore system like Y, but without cages.

More recently the better performance of zeolite Beta with respect to Y type zeolites was also reported by Mobil researchers who confirmed that USY (ultra-stable Y zeolite) is also affected by rapid decay. However in the same paper,[8] a new zeolite MCM-22 was reported to have a catalytic activity comparable (*i.e.* comparable kinetic constants) to USY and around 2.4 times less than zeolite Beta. On the other hand, MCM-22 was much more selective, the formation of DEB and TEB being significantly lower than with USY or Beta. This results in a larger ethylation selectivity (Fig. 4).

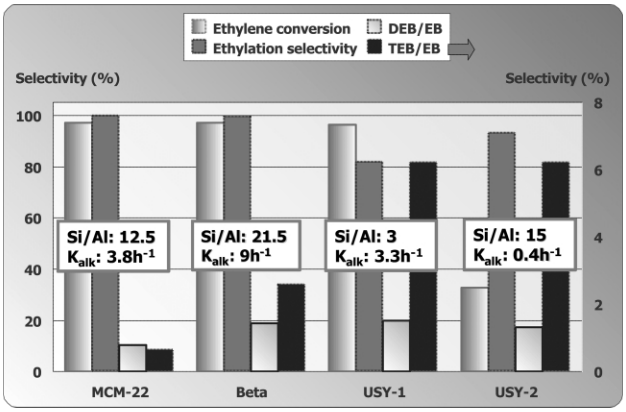

Fig. 4 Liquid-phase alkylation of benzene with ethylene (T = 220 °C; P = 3.44 MPa; B/E = 4). k_{alk} is the pseudo first order kinetic constant of the reaction.

However, the zeolites compared in this paper[8] are characterized by different Si/Al ratios and in particular the Beta sample has a lower Al content than MCM-22. In Fig. 5 the comparison is extended including the data reported by Bellussi *et al.*[9] and Corma *et al.*[10] Though the operating conditions are different, there seems reasonable evidence of an increase of performance while decreasing the Si/Al ratio, *i.e.* increasing the Al content. Additionally, when the Si/Al is similar, zeolite Beta performs a bit better than MCM-22.[10]

By evaluating these data, a straightforward conclusion cannot be drawn. It is only possible to underline that, besides the structure, the composition must also be selected with care in order to develop a good alkylation catalyst.

MCM-22 is characterized by a complex porous structure, formed by two non-interconnected pore systems, both having 10MR openings. One pore system is constituted by large supercages (a sort of cylinder 18 Å long and 7.1 Å wide) interconnected by slightly elliptical openings, the other by sinusoidal channels also with a slightly elliptical section. To account for the interesting performances of MCM-22 in EB synthesis it is assumed that a sensible number of the large cavities that characterize its structure are opened to the exterior at the termination of crystallites. Following this model, it is assumed that on the [001] surface of the platelet-like crystallites are present emisupercages, having a free diameter of *ca.* 0.71 nm. In this case the EB formation should occur in these cavities, practically without diffusion barriers.[8,10]

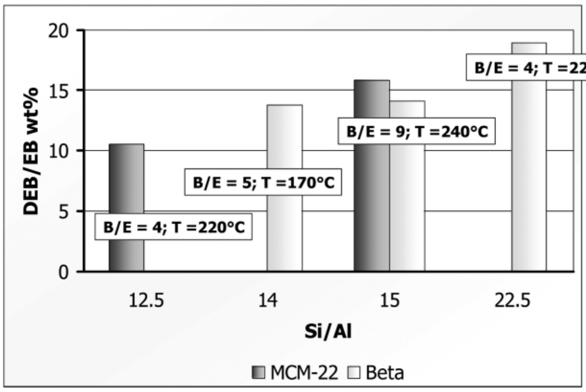

Fig. 5 Effect of Si/Al on zeolite performance.

To further increase the number of these emisupercages, Corma suggested delamination of the MCM-22 precursors, and so obtained a new material called ITQ-2, still preserving the channel system but with the cavities more accessible.[11] The new material was claimed to behave better than MCM-22 in the EB production (Fig. 6).[12]

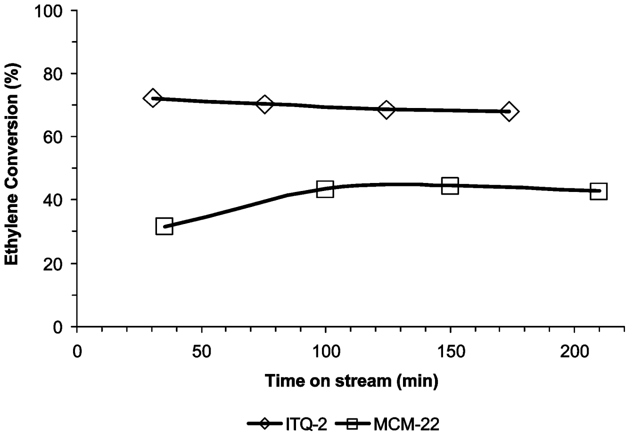

Fig. 6 The catalytic comparison of ITQ-2 and MCM-22 (T = 240 °C; P = 3.5 MPa; B/E = 8).

A useful corollary to the EB synthesis is the transalkylation of polyethylbenzenes (DEB, TEB) with benzene to form EB. The facility of the zeolite-catalyzed transalkylation was already remarked by Venuto *et al.* in contrast to the higher temperatures required for such a reaction with amorphous silica-alumina.[3]

Two different approaches were reported in order to improve the selectivity for monoalkylbenzene. The polyethylbenzene fraction can either be recycled to the alkylation reactor in a proportion over the equilibrium one or it can be transalkylated in a proper reactor. With $AlCl_3$ the first solution is adopted and a composition close to the thermodynamic equilibrium is reached, therefore depending on the ethylene/benzene overall ratio.[13] As reported above, the first generation Mobil–Badger process was characterized by a single reactor where alkylation and transalkylation were performed simultaneously under gas-phase conditions. A separate transalkylation step has since been proposed using either gas-phase with ZSM-5 as catalyst or liquid-phase with Y, Beta and MCM-22 zeolites as catalysts.[13]

An extensive study on the transalkylation of DEB catalyzed by zeolite Beta has been reported by Cavani *et al.*[14] The transalkylation of DEB with benzene goes through an ethyl-1,1-diphenylethane intermediate and in this way EB is formed. Several byreactions affect the selectivity of transalkylation and some of them are favored by temperature, as reported in the reaction pathway proposed in ref. 14 (Fig. 7):

1. cracking of EB to toluene
2. condensation of *ortho*-DEB to tetraline and naphthalene
3. cracking of butylbenzenes to cumene and NPB

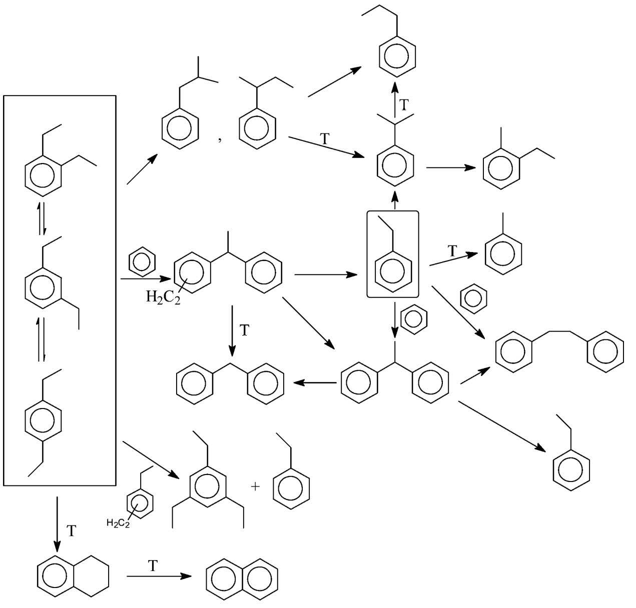

Fig. 7 Reaction scheme for DEB transalkylation with benzene (T = reactions favored at higher temperatures).

4. alkylation of EB on B to 1,1- and 1,2-diphenylethane.

Several industrial units have been recently revamped or realized with new zeolite catalysts operating in the liquid-phase. MCM-22 has been successfully applied in a new process called EBMax^{SM} and licensed by Mobil/Raytheon[15] since 1995. Zeolite Beta has been successfully employed by Polimeri Europa (formerly EniChem) in the revamping of an existing EB unit in 2002. Besides, since 1990 UOP/Lummus have been improving the process based on zeolite Y. Currently, the commercialized process is named EB*One*.[16] A zeolite catalyst has been also applied in the catalytic distillation technology by CDTECH, a partnership between ABB Lummus and Chemical Research and Licensing.[17] CDTECH offers its energy-saving catalytic distillation process for EB production, recommended particularly for dilute ethylene streams. Both EB*One* and CDTECH EB® use a modified zeolite Beta as catalyst.[16,17]

Of around 70 EB units operating in the world, 24% are still based on $AlCl_3$–HCl. The rest are based on zeolite catalysts: 40% in the gas-phase and 36% in the liquid-phase.[13]

3 Alkylation of benzene to produce cumene

The manufacture of cumene as a blending agent for high-octane gasoline was carried out during the Second World War on a very large scale. The alkylation catalyst used was H_2SO_4. The problems related to the use of free mineral acids were later overcome by using supported phosphoric acid (SPA) on Kieselguhr. This catalyst is still largely used for the production of cumene. However, due to the release of the acid, corrosion problems frequently arise. Besides, because of the decay also due to the formation of organic residues on the catalyst surface, at the end of the life cycle this catalyst cannot be regenerated.

The evolution of the catalytic systems for cumene production is somewhat similar to that described for EB. However, differently from EB, the research efforts took longer time to reach an industrial application. This time lag probably depended on the inability of ZSM-5, the first catalyst of EB Mobil–Badger process, to satisfactorily catalyze the cumene synthesis in the gas-phase. ZSM-5, in fact, produces an elevated cumene isomerization to *n*-propylbenzene, possibly due to the high temperature necessary to overcome the diffusion constraints in its 10MR pores. Besides, a quite rapid decay was observed due to the higher tendency of propylene to produce oligomers with respect to ethylene. On the other hand, ZSM-5 shows poor catalytic activity in liquid-phase alkylation, probably because of diffusion constraints.[9]

As a matter of fact, the important steps toward applicable results were

(a) the move to the liquid-phase operation and

(b) the use of zeolites with 12MR pore openings (*e.g.* Y, mordenite, ZSM-12, Omega, Beta and MCM-22†).

Based on these zeolites, new commercial processes or industrial test runs were announced in the 1990s by Dow-Kellogg, Mobil-Raytheon, CDTech, EniChem and UOP.[18]

The reaction pathway of the benzene alkylation with propylene catalyzed by acids is very similar to that already reported for EB. The main difference is represented by the tendency of cumene to isomerize to *n*-propylbenzene, which is thermodynamically more stable at increased temperature.[19] Also, cumene can later undergo further alkylation to diisopropylbenzene (DIPB). Again DIPB can be easily recovered by transalkylation with benzene to cumene, so they can be considered useful by-products.

The isopropylation of cumene is an electrophilic substitution. Isopropyl is an *ortho–para* orienting group. So first *ortho* and *para* isomers are formed, followed by isomerization to *meta*, which is thermodynamically more stable as evidenced by the composition at equilibrium (Fig. 8). Under kinetic control, on a simply statistical basis the distribution would be in favor of *ortho*, but we know that the charge distribution of the corresponding arenium ion will drive the isomer formation: 50% of *ortho*, 30% of *para* and 20% of *meta*. This would be true in the absence of other factors. However, the influence of the steric hindrance of the alkyl group in position 1 on the attack is well known in *ortho*. For instance the *o*/*p* ratio decreases from 1.57 for toluene, through 0.93 for ethylbenzene to 0.48 for cumene in the case of nitration.[20] The catalytic data for SPA, which is a solid acid with an open structure, are in good agreement: the *o*/*p* ratio is around 0.45.

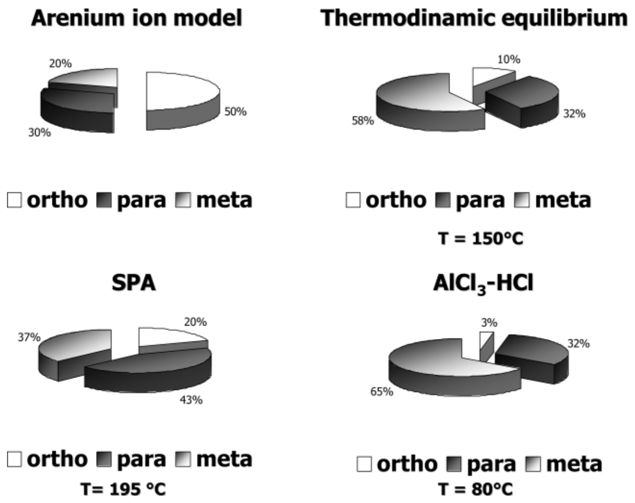

Fig. 8 Isopropylation of cumene catalyzed by acids.

If the catalyst is also strong enough to catalyze the isomerization, the reaction can proceed to approach thermodynamic equilibrium. This is not the case with SPA but is the case with $AlCl_3$.

When zeolites are used another factor plays an important role: the shape selectivity. Fig. 9 compares *meta*/*para* for the different zeolites, as reported in[21,22], with the values of the thermodynamic equilibrium. A high *meta*/*para* ratio, close to the equilibrium value, indicates high isomerization of zeolite Beta and mordenite. In the case of USY, because of the presence of supercages, the shape selectivity should be excluded; so the low *meta*/*para* ratio indicates low isomerization activity. On the contrary, the low *meta*/*para* ratio obtained with ZSM-5 and ZSM-12 seems to be due to the shape selectivity. As a matter of fact, the *para* selectivity of ZSM-5 and ZSM-12 in the isopropylation of cumene has already been reported.[19,23] MCM-22 behaves in the middle.

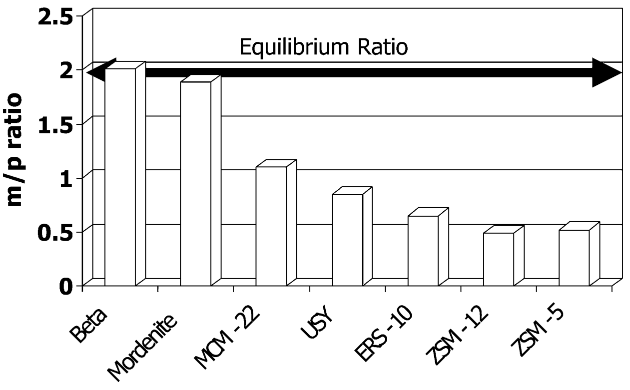

Fig. 9 Alkylation of benzene with propylene (T = 150 °C; P = 3.5 MPa; B/P = 7; WHSV = 3 h^{-1}): *meta*/*para* diisopropylbenzene ratio.

For cumene, the transalkylation also plays an important role. The transalkylation reaction requires a higher temperature than the related alkylation. Besides, not all the alkylation catalysts are suitable for transalkylation. It is known that the SPA is not able to transalkylate DIPB,[1] similar to free sulfuric acid and amorphous silica-alumina gels, under alkylation conditions.[3] On the contrary $AlCl_3$ is able to do it. As a matter of fact, in the 1980s Monsanto introduced a technology based on $AlCl_3$–HCl, similar to that in use for EB production, with the aim of improving cumene yield by polyisopropylbenzene transalkylation,. However, only a few plants were realized using this technology.

The catalytic ability of zeolites (*e.g.* Y) in the transalkylation of DIPB has been claimed in the patent literature since the 1960s.[24] Later, Harper *et al.* showed that during the alkylation of benzene with propylene catalyzed by a rare earth exchanged Y zeolite (REY), the transalkylation reaction also took place.[25] Conversion profiles, obtained by varying the residence time in the alkylator, showed that the DIPBs reach a maximum and then decay, just before the complete conversion of propylene. According to this, the selectivity for cumene increased, approaching the equilibrium value. Therefore two different approaches were suggested in order to improve the selectivity for cumene. The DIPBs fraction can either be recycled to the alkylation reactor in a proportion over the equilibrium one[25] or it can be transalkylated in a proper reactor.[24]

However around 25 years later, a transalkylation zeolite catalyst was industrially applied for the first time by Dow Kellog. In 1992 the cumene plant of Terneuzen (The Netherlands), based on SPA, was modified with the addition of a transalkylation reactor with a dealuminated mordenite catalyst.[26] Nowadays the new cumene technologies include a transalkylation step, based on a zeolite catalyst, the same or similar to the alkylation one.

According to Pradhan and Rao,[27] zeolite Beta is more stable in the transalkyaltion of DIPB, with respect to LaY and mordenite (Fig. 10).

The first industrial demonstrations of cumene technologies based on zeolite catalysts were started-up in 1996 by Mobil-Raytheon, EniChem and UOP, independently. In all cases, existing SPA cumene plants were revamped by substituting the old SPA catalyst with new zeolite catalysts. According to Degnan *et al.*[28] in 2001 14 cumene units in the world were already operating with zeolite catalysts.

4 Conclusion

For the production of alkylaromatics new solid catalysts and new processes have recently been introduced conforming to the environmental and safety concerns. Various solid catalysts based on different zeolites have been developed for both the alkylation and transalkylation steps. In particular for EB and cumene, which

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† MCM-22, while being characterized by 10MR pore openings, behaves like a large pore zeolite as previously reported for EB.

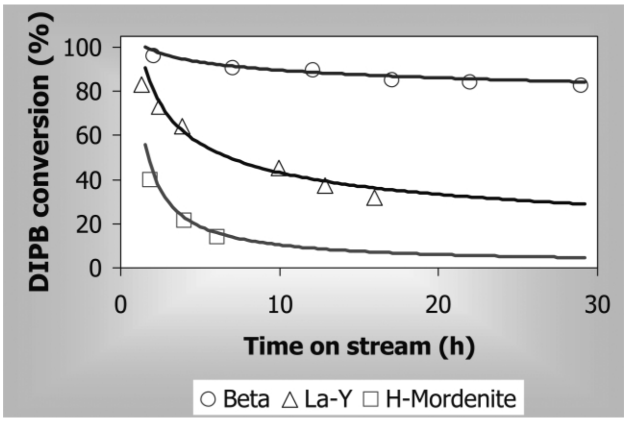

Fig. 10 DIBP transalkylation (T = 170 °C, P = atmospheric, benzene/DIPB = 17, WHSV = 3.5 h^{-1}).

account for the largest alkylaromatic productions, new zeolite catalysts are currently available.

Of around 70 EB units operating in the world, 24% are still based on $AlCl_3$–HCl. The others are based on zeolite catalysts: 40% in the gas-phase and 36% in the liquid-phase.

For cumene production, among 40 units in the world, 14 cumene plants are in operation with zeolite catalysts.

The most promising zeolites for liquid-phase production of both EB and cumene are MCM-22 and Beta.

Appendix 1

Capacity and uses

In 2001 the global production for ethylbenzene was almost 24 million metric tons and its demand will increase at an average annual rate of 4.6% from 2001 to 2006. Almost all of the ethylbenzene produced in the world is used in the manufacture of styrene, the building block for plastics and elastomers. Therefore the demand for ethylbenzene is determined primarily by styrene production. Consumption of ethylbenzene for uses other than the production of styrene is estimated to be less than 1% of total ethylbenzene production. It is used as a solvent and, on occasion, in the production of diethylbenzene, acetophenone and ethyl anthraquinone.

As far as cumene is concerned, the world production in 2001 accounted for 8.5 millions metric tons. Essentially all global cumene is consumed for the production of phenol and acetone. New bisphenol A capacity and increased demand for bisphenol A will result in a strong demand for phenol. As a result, consumption of cumene for phenol is forecast to show annual growth rates of 5.4% from 2001 to 2006 (Chemical Economics Handbook – SRI International 2002).

Appendix 2

Ethylbenzene production by recovery of aromatic mixtures

Ethylbenzene is present in the C8 aromatic streams coming from catalytic reforming or from steam cracking in quantities ranging from 10 up to 40%. Due to the low relative volatility of the ethylbenzene/xylenes system, the separation of ethylbenzene from the aromatic C8 requires a large number of trays and a high reflux ratio (390 real trays with reflux ratios up to 80 to 90). These conditions are highly costly which makes this superfractionation quite expensive. Besides, the quality of ethylbenzene from C8 cuts is usually lower than that from alkylation because of the large contamination from xylenes (some hundreds ppm *vs.* less than 50 ppm). However, the separation of ethylbenzene from the aromatic C8 cut improves the efficiency of the following xylene isomerization and separation process.[29] As a matter of fact, the ethylbenzene from superfractionation of C8 cuts accounts for about 5% of the overall ethylbenzene production.

Questions and answers

Will acetone co-production negatively affect the cumene process?

The oxidative conversion of cumene into phenol implies the co-production of an equimolar quantity of acetone. The fact that acetone demand is totally unrelated to phenol demand may cause concerns about the success of phenol production *via* cumene. In fact, phenol production *via* cumene would not be viable if phenol demand was much higher than acetone demand. A possible solution to these problems is the re-use of acetone in the benzene alkylation prior to acetone hydrogenation to isopropanol. The alkylation of benzene with isopropanol has been extensively studied: in one of the most interesting studies it has been shown that a catalyst based on zeolite Beta is highly adequate for the reaction, producing results comparable to those performed in an industrial plant using propylene[30]

Alternative methods for phenol production which fully overcome the possible problems associated with the cumene process are:

Direct benzene oxidation by N_2O catalyzed by iron zeolite. This process has been tested at a pilot plant by Solutia and is called AlphOx. It provides benzene conversion up to 30% with phenol selectivity of 99% but the process seems to be cost effective only if N_2O can be obtained cheaply as a by-product from adipic acid production.[31]

Direct benzene oxidation by H_2O_2 catalyzed by a modified titanium silicalite. This method has been developed by Polimeri Europa and researchers have demonstrated that it is possible to obtain benzene conversion higher than 8% with phenol selectivity up to 94%.[32]

Direct benzene oxidation by oxygen activated by dissociated hydrogen obtained from a palladium membrane. An efficient one step conversion of benzene to phenol has been reported performing the oxidation by means of oxygen and hydrogen catalyzed by a palladium membrane. The results are still at the laboratory scale and show that it is possible to obtain phenol with a selectivity higher than 90% at a benzene conversion lower than 3%.[33]

These last two procedures are very interesting although much has still to be done to arrive at an industrial process.

Will benzene continue to be the raw material for styrene production?

According to Dow and DSM, butadiene could be the raw material for styrene production. The new process implies:

Catalytic cyclodimerization of butadiene to 4-vinylcyclohexene.

Oxidative dehydrogenation of 4-vinylcyclohexene.

Although all the steps have been fully demonstrated and optimized, the butadiene based process will hardly be competitive with the traditional process, specially due to the limited feedstock availability which imposes a small plant capacity and therefore a diseconomy of scale.

A second alternative to the use of benzene as raw material is based on methanol alkylation of toluene: it is an old technology, developed by Monsanto in the 70’s which has not had significant improvements in recent years. Despite the fact that selectivities based on methanol are low (about 50%), this chemistry suggests an interesting process that may utilize toluene and synthesis gas which very likely costs lower than the conventional raw material.[34]

Will the use of alkanes in the benzene alkylation processes be possible?

Light paraffins are very abundant and much less expensive than the corresponding olefins; therefore employing alkanes as raw material for the synthesis of bulk chemicals is certainly one of the challenges for this century. Among others, interesting results have been reported on benzene alkylation with propane over a Pt-modified MFI zeolite, for which the yield of propylbenzenes reached 96% with respect to equilibrium and selectivity for propylbenzenes was about 60%. On these bi-functional catalysts, propane dehydrogenation and protonation may take place on a metal-acidic center, which results in direct benzene alkylation.[35] At present these results are meaningful only as far as the scientific point of view is concerned, however, if they ever led to an industrial success, they would represent a real breakthrough in alkylbenzenes production.

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PAPER

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Microwave promoted Heck reactions using an oligo(ethylene glycol)-bound SCS palladacycle under thermomorphic conditions

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Palladium catalyzed Heck couplings utilizing an air-stable, water-soluble oligo(ethylene glycol)-bound SCS palladacycle catalyst and microwave irradiation lead to formation of several cinnamic acid derivatives with reaction times of less than 1 hour. Such couplings of various aryl halides with alkene acceptors occur in an air atmosphere with aqueous and organic solvents are described. Recycling of the catalyst was accomplished using a 10% aqueous DMA–heptane thermomorphic system that was advantageously homogeneous during these microwave promoted reactions and biphasic during the catalyst recovery step.

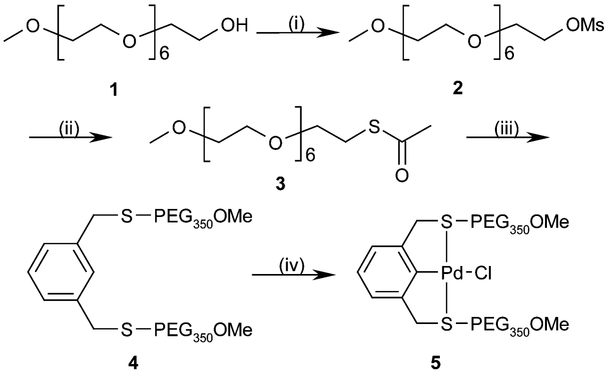
Introduction

The development of new ways to use catalysts and the use of alternative greener solvents for catalytic reactions are areas that continue to attract attention. We have recently described the utility of transition metal complexes or organic catalysts that can be attached to soluble polymer supports and used in fluorous solvents, water, or monophasic/biphasic mixtures.[1] Palladium complexes containing pincer-type sulfur–carbon–sulfur (SCS)-ligated Pd(II) species are among those species we and others have studied as catalysts or catalyst precursors for Heck and Suzuki reactions.[2–7] Such complexes are much more stable to oxygen than simpler $(Ph_3P)_4Pd$ species often used for these reactions and they have high thermal stability too. Moreover, previous results showed no Pd leaching in preparative scale Heck and Suzuki coupling reactions with a polymer-bound catalyst based on ICP analyses.[3,8] Similar low molecular weight Pd complexes have also been explored by other groups in organic solvents. Recently a report appeared that described the use of pH responsive SCS–Pd(II) pincer complexes in aqueous media.[9–13] Here we describe our recent work with SCS-ligated Pd(II) complexes in Heck catalysis in polar-organic, aqueous, or thermomorphic[7] solvent systems promoted by microwave irradiation where relatively low molecular weight oligo(ethylene glycol)s are sufficient to furnish aqueous or polar-organic solubility.

Poly(ethylene glycol) is one of the most common soluble polymers used to support catalysts, reagents and substrates.[14,15] In addition to its ready recoverability by solvent precipitation, this polymer has the advantage of having a simple spectroscopic signature and compatibility with a variety of reagents. This polymer is soluble in water as well as many organic solvents. The relatively benign nature of this material has led to its use as a drug conjugate. Thus, this polymer could also be considered a green polymer support.[16,17] Since these PEG supports are end-functionalized, high molecular weight forms of this polymer have relatively low loading. However, PEG analogs can be prepared that have higher capacity. PEG or other poly(alkene oxide) supports also have temperature regulated phase selective solubility.[18,19] Smaller oligo(ethylene glycol) groups are also widely available. Such materials are commercially available with various end group functionality because of the widespread use of such oligomers and polymers in preparation of forming bioavailable drug conjugates.[20,21] Such oligomers have water solubility that is similar to larger PEG analogs and these oligomers have the same chemistry as the larger PEG polymers in many applications. However, PEG oligomers are not easily recovered as solids as are their higher molecular weight analogs. Thus, to explore the utility of PEG-like polymers as solubility control elements for SCS–Pd complexes, we have used these smaller oligomers to prepare oligo(ethylene glycol)-bound SCS complexes and used them both in aqueous and in mixed phase aqueous systems. The results presented in this paper illustrate how these complexes behave like the previously described SCS complexes. In addition, these polar Pd-complexes' reactivity is conveniently accelerated by microwave irradiation and these Pd-catalysts are recyclable when used in thermomorphic solvent mixtures.[22–25]

Results and discussion

Our synthesis of an oligo(ethylene glycol)-bound SCS–Pd(II) complex is shown in Scheme 1. The products of this synthesis were characterized by ^1H and ^{13}C NMR spectroscopy. There was no visual sign of decomposition of the final SCS–Pd(II) compound on heating this compound in air in organic solvents or water to temperatures as high as 200 °C. This result is consistent with our prior reports and other TGA studies of other similar SCS–Pd(II) complexes.[3,8,26]



Scheme 1 (i) MsCl, TEA, CH_2Cl_2, 25 °C, 24 h; (ii) $KSCOCH_3$, DMF, 75 °C, 24 h; (iii) 1) NaOMe, MeOH, N_2, 2) α,α′-dichloro-*m*-xylene, 60 °C, 24 h; (iv) 1) $Pd(PhCN)_2Cl_2$, CH_3CN, 25 °C, 24 h 2) 80 °C, 24 h.

While the synthesis of the SCS–Pd(II) complex **5** is straightforward, **5** does exhibit interesting dynamic behavior in NMR spectroscopy. Specifically, while the ^1H and ^{13}C NMR spectrum of **5** had peaks at the expected chemical shifts (including the *ipso* carbon at δ 150 ppm in the ^{13}C NMR spectrum), the peak corresponding to the benzylic protons in **5**'s ^1H NMR spectrum was broadened. We had noted this before in other SCS–Pd(II) complexes and interpreted this as being a result of the C_2 chirality

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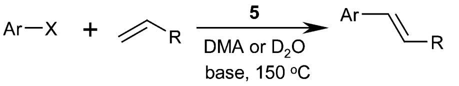
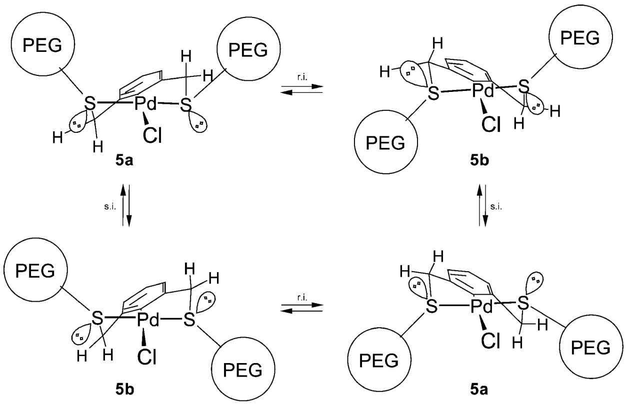
of these complexes seen in crystal structures of low molecular weight SCS–Pd(II) complexes.[3] While our explanation of dynamic behavior in the ^{1}H NMR spectrum in terms of dynamic chirality at sulfur was a plausible explanation for this spectroscopic observation, earlier work by DuPont where the similar complex **6** was studied had invoked a more complex explanation including *cis*- and *trans*-diastereomers of the pincer complex.[27] More extensive spectroscopic analyses of the dynamic behavior of **5** in $CDCl_3$ as studied by ^{1}H NMR spectroscopy agree with this more complex interpretation. Cooling a sample of **5** in $CDCl_3$ separated a high temperature singlet for the Ar–CH_2–S– protons not into the double of doublets expected for a simple diastereotopic methylene group but rather into a pair of doublets of doublets as shown in the spectra in Fig. 1. This behavior is consistent with the oligo(ethylene glycol) groups interconverting between isomers **5a** (*cis*) and **5b** (*trans*) (Scheme 2) through sulfur or ring inversions as described originally by DuPont.[27] Such behavior and the presence of multiple stereoisomers of these complexes may account for the inability of complexes like **5** to effect asymmetric catalysis.[28]

The catalytic activity of **5** in the Heck coupling of several aryl halides and alkene acceptors in a polar aprotic solvent like *N,N*-dimethylacetamide (DMA) or *N,N*-dimethylformamide (DMF) as well as water were investigated [eqn. (1)]. No special precautions such as purified reagents/solvents or inert atmosphere were necessary due to the stability of the SCS palladacycles. While no decomposition to Pd black was seen, the formation of undetectable amounts of a very active colloidal catalyst cannot be excluded.[8,29,30] Indeed, some evidence that these SCS–Pd(II) complexes are precursors for an extremely active Pd-catalyst is the induction period observed in the plot in Fig. 2.

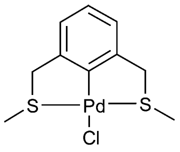


(1)

The use of microwave irradiation to enhance reaction rates and shorten process times is an area of growing interest.[22–25] We thought that might be particularly true with these catalysts since microwave radiation should be effective whether these polar complexes themselves are catalyst or if unspecified so-called homeopathic colloids[29] were the actual active species. The evaluation of microwave heating was carried out by running identical reactions in either an oil bath or microwave reactor at 150 °C. The data in Table 1 clearly show an enhancement in rate with microwave heating. While this could reflect non-thermal “microwave effects”[31], at this time it is premature to conclude that the microwave radiation itself is causing the rate acceleration since we have not fully elucidated how SCS–Pd(II) catalysts function (*i.e.* in a Pd(II) → Pd(IV) cycle or as precursors of a very active Pd(0) species).



Scheme 2 Representation of the two enantiomers of **5a** (*cis* diastereomer) and **5b** (*trans* diastereomer) that can interconvert through ring inversions (r.i.) or sulfur inversions (s.i.).



6

Catalytic reactions of **5** with several aryl halides and alkenes were carried out in DMA at 150 °C employing microwave irradiation (Table 2). Since these catalysts are active in DMA and

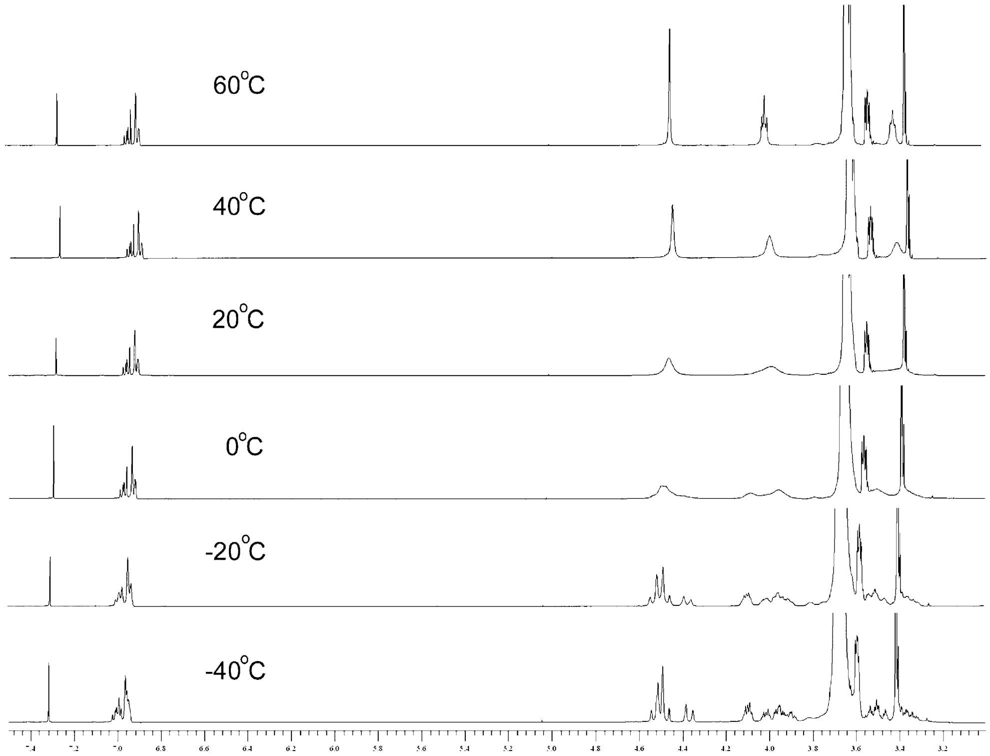


Fig. 1 ^{1}H NMR spectra of complex **5** in $CDCl_3$ showing dynamic changes in the peaks in the δ 3.8–4.6 region of the spectrum. Smaller concomitant changes are seen in the δ 3.4–3.6 region.

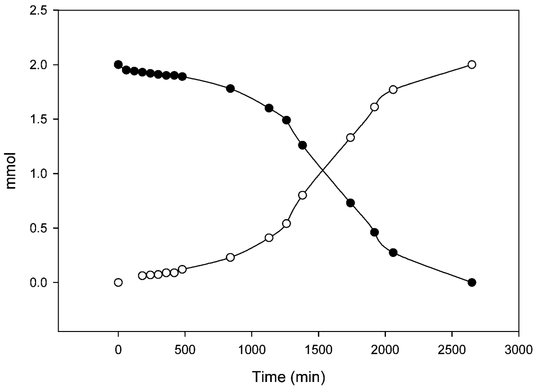
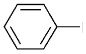
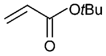
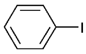
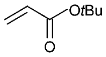
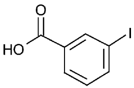
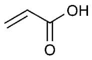
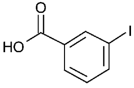
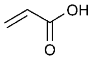


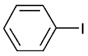
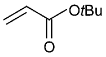
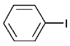
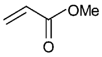
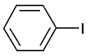
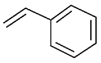
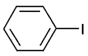
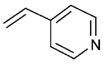
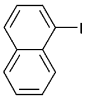
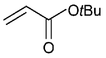
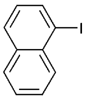
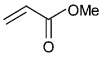
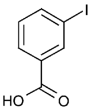
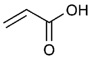
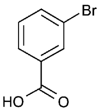
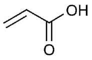
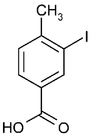
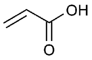
Fig. 2 Changes in concentration for iodobenzene (●) or methyl cinnamate (○) in a Heck reaction in DMF with conventional heating at 100 °C. Pseudo first-order conditions were used with 0.5 mmol of PhI and 20 mmol of both methyl acrylate and Et_3N in 10 mL of DMF.

Table 1 Comparison of conventional and microwave heating of Heck couplings employing **5** as a catalyst[a]

Entry	Aryl iodide	Alkene	Heating method[d]	Time/ min
1[b]			C	70[e]
2[b]			M	20[e]
3[c]			C	220[f]
4[c]			M	20[f]

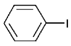
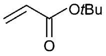
[a] These reactions used ArI (0.5 mmol), alkene (1.0 mmol) at 150 °C with varying amounts of base and catalyst. [b] Et_3N (2.0 mmol) and **5** (0.01 mol%) in DMA (2.5 mL) were used. [c] K_2CO_3 (1.5 mmol) and **5** (0.1 mol%) in D_2O (2.5 mL) were used. [d] Heating used a conventional oil bath (C) or microwave (M) reactor. [e] This is the time to reach 100% conversion based on PhI and cinnamate determined by GC using *n*-dodecane as internal standard. [f] This is the time to reach 100% conversion of ArX based on ^1H NMR spectroscopic analysis of the reaction mixture looking for peaks for the $IC_6H_4CO_2H$ and product.

Table 2 Heck couplings of various organic-soluble aryl halides and alkenes promoted by microwave irradiation employing **5** as a catalyst[a]

Entry	Aryl halide	Alkene	Product	Time/ min	Yield[c] (%)
5			**7**	10	69
6			**8**	10	74
7			**9**	40	33
8			**10**	60	54
9			**11**	15	79
10			**12**	10	75
11[b]			**13**	10	63
12[b]			**13**	10	63
13[b]			**14**	10	97

[a] These reactions used ArX (0.5 mmol), alkene (1.0 mmol), TEA (2.0 mmol), **5** (0.1 mol%) in DMA (2.5 mL) at 150 °C with microwave irradiation at 30 W. [b] K_2CO_3 (1.5 mmol) was used as the base. [c] This is an isolated yield. All the reactions' conversions of ArX were quantitative based on GC analysis using *n*-dodecane as an internal standard to follow the disappearance of the ArX.

Table 3 Recycling of **5** under thermomorphic conditions[a]

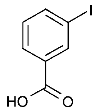
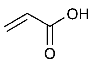
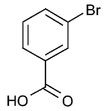
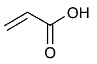
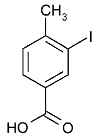
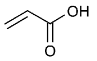
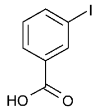
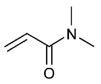
Entry	Aryl iodide	Alkene	Product	1st cycle (%)	2nd cycle (%)	3rd cycle (%)	4th cycle (%)
14			**7**	49	98	88	78

[a] These reactions used ArI (0.50 mmol), alkene (0.60 mmol), TEA (0.75 mmol), **5** (0.2 mol%) in 1 : 2 (v/v) 10% aqueous DMA–heptane (3.0 mL) at 150 °C with microwave irradiation. The reactions were monitored by GC (following disappearance of ArI) and were complete within 20 min. All yields are from products isolated from the heptane phase.

since DMA mixed with other solvents is an established thermomorphic system,[7] we decided to try recycling the catalyst using a thermomorphic solvent mixture consisting of a 1 : 2 v/v mixture of 10% aqueous DMA and heptane. The results of these studies are summarized in Table 3 and show that catalyst recycling with thermomorphic solvent mixtures and microwave heating is an efficient and effective procedure. No added solvent is required for product and catalyst isolation in such systems and catalyst recycling just requires addition of a fresh substrate solution to the mixed aqueous solution of catalyst. Inductively coupled plasma emission-mass spectrometry (ICP-MS) was used to analyze the heptane phase for each cycle to investigate leaching of Pd from the polar phase. The amount of Pd detected in an aliquot of the heptane phase for cycles 1, 2, 3, and 4 suggested that the heptane phase of each of these cycles could have had as much as 0.133 ppm, 0.075 ppm, 0.080 ppm, and 0.064 ppm Pd respectively. A similar volume heptane blank had 0.021 ppm Pd. In each case, these values were determined by taking a *ca.* 0.6 g aliquot of the heptane phase after the reaction and concentrating it to dryness. The residue was digested with HNO_3 and the digested sample was diluted to 25 mL of volume with distilled water for ICP-MS analysis. These ICP-MS samples had *ca.* 4 ppb Pd in the case of the first cycle and *ca.* 2–3 ppb Pd in cycles 2, 3, and 4. A blank had *ca.* 1 ppb Pd. These values are at the limit of detection for Pd in cycles 2–4. These numbers indicate that there is a trace of Pd lost in cycle 1 (*ca.* a 0.3% loss of the 5×10^{-5} M Pd catalyst). The loss of Pd in cycles 2, 3, and 4 is barely detectable. Together these results show that recovery of the Pd was excellent. Moreover, they show that if **5** is a precatalyst and if the catalysis is due to a decomposition product that does not reform **5**, that decomposition product must be a very active Heck catalyst.

Water is an ideal solvent since it is cheap, abundant, and benign.[32,33] Water is also very polar making it highly microwave active so it is an attractive solvent for transition-metal catalyzed coupling reactions too.[34] Traditionally transition-metal catalysts have been made water soluble by trying to find a catalytically active metal salt or by making more traditional catalysts soluble with organic ligands that contain ionic or ionizable groups.[32] However, transition metal salts are not always as soluble or active as desired. Modification of ligands can also have undesirable effects on the electronic nature of a ligand or can make catalysts acid or base sensitive. The oligo(ethylene glycol) ligands used here are less invasive. Solubility is controlled by the nonionic oligomer which is relatively inert in all other chemistry. Microwave irradiation was used to promote coupling reactions between several water-soluble aryl halides with water-soluble alkenes employing **5** as a catalyst (Table 4). These *meta*-substituted aryl halo acids were chosen for their water solubility as well as the convenience of monitoring reaction progress by ^1H NMR spectroscopy in D_2O.[35,36]

Table 4 Heck couplings of water-soluble aryl halides and alkenes promoted by microwave irradiation employing **5** as a catalyst[a]

Entry	Aryl halide	Alkene	Product	Time/ min	Yield[b] (%)
15			**13**	20	42
16			**13**	30	42
17			**14**	30	58
18[c]			**15**	20	82

[a] *Reaction conditions*: ArX (0.5 mmol), alkene (1.0 mmol), K_2CO_3 (1.5 mmol), **5** (0.1 mol%) in D_2O (2.5 mL) at 150 °C with microwave irradiation at 30 W. [b] This is an isolated yield. All reactions had a quantitative conversion of the aryl halide to product based on ^1H NMR spectroscopic analysis of the reaction mixture and the disappearance of peaks for the ArX and the appearance of product peaks. [c] K_2CO_3 (0.5 mmol) was used as the base.

Conclusion

In summary, oligo(ethylene glycol) ligands are sufficient to engender water or polar phase solubility into SCS–Pd(II) catalysts for Heck reactions. Catalytic reactions using such complexes exhibit no visual evidence for complex decomposition and the speed of the catalytic reactions is significantly increased with microwave radiation. Water is a viable solvent for these types of coupling reactions provided that the substrates are water soluble. Recycling of the catalyst using a thermomorphic system was possible even with small oligo(ethylene glycol) groups and microwave irradiation of these thermomorphic mixtures of palladium complexes and substrates is a viable scheme to significantly shorten reaction times for simple Heck reactions of aryl iodides.

Experimental

General

All reagents and solvents were obtained from commercial sources (Aldrich) and used without further purification unless specified. ^1H NMR spectra were obtained on Varian Inova 300, Mercury 300, or Inova 500 spectrometers at 300 or 500 MHz. ^{13}C NMR spectra were obtained on Varian Inova 300, Mercury 300, or Inova 500 spectrometers at 75 or 125 MHz. ^1H and ^{13}C NMR spectroscopy chemical shifts are reported in ppm referenced to tetramethylsilane, or residual solvent peaks respectively. Gas chromatography was performed on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector using a SUPELCO 15 m long, 0.53 mm ID fused silica capillary column with a 3.0 μm thick film bonded poly(5% diphenyl/95% dimethylsiloxane) stationary phase. The microwave reactions were either carried out using a CEM Discover™ model reactor or using a Personal Chemistry Emrys™ Creator model microwave reactor. Elemental analysis was carried out on a Perkin Elmer DRCII ICP-MS.

Synthesis of MeOPEG$_{350}$-OMs (2). Triethylamine (62 mL, 0.46 mol) was added to a solution of poly(ethylene glycol) monomethyl ether MW ≈ 350 g mol^{-1} (100 mL, 0.31 mol) in 500 mL of CH_2Cl_2. This solution was cooled to 0 °C and methanesulfonyl chloride (36 mL, 0.46 mol) was slowly added to the reaction mixture. The thick yellow slurry so formed was then stirred at room temperature for 24 h. The slurry was allowed to settle for several minutes and the resulting clear brown solution was separated from the less dense, white, crystalline solid by decantation. This organic phase was washed with 3 M HCl (3 × 125 mL), saturated $NaHCO_3$ (2 × 125 mL), and brine (1 × 125 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the thick brown oil isolated was dried under vacuum yielding 127.3 g (96%) of the pure product **2**. ^1H NMR ($CDCl_3$) δ 3.09 (3H, s), 3.38 (3H, s), 3.55–3.78 (26H, PEG), 4.38 (2H, t, $^3J_{HH}$ = 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 37.49, 52.56, 53.59, 58.81, 68.82–71.73 (PEG).

Synthesis of MeOPEG$_{350}$SCOCH$_3$ (3). A mixture of **2** (20.0 g, 47 mmol) and potassium thioacetate (10.0 g, 87 mmol) in 500 mL of DMF was mechanically stirred at 75 °C for 24 h. The thick, dark-red suspension that formed was filtered hot and the supernatant was allowed to cool to room temperature. This solution was filtered again and most of the solvent (~75 mL remaining) was removed with gentle heat *in vacuo*. The resulting thin, dark-red oil was then taken up into 800 mL of water and this aqueous phase was extracted with CH_2Cl_2 (4 × 100 mL). A small amount of brine was added to break up any emulsion. The organic phase was in turn washed with water (5 × 100 mL), brine (2 × 100 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a reddish-brown oil that was further dried under vacuum to yield 16.85 g (84%) of **3**. ^1H NMR ($CDCl_3$) δ 2.31 (3H, s), 3.09 (2H, t, $^3J_{HH}$ = 6.5 Hz), 3.38 (3H, s), 3.55–3.78 (26H, PEG); ^{13}C NMR ($CDCl_3$) δ 29.06, 30.80, 59.27, 69.97–72.16 (PEG), 195.73.

1,3-Bis(MeOPEG$_{350}$thiomethyl)benzene (4) synthesis. Clean, dry sodium metal (563 mg, 25 mmol) was dissolved in 150 mL of dry MeOH. Once all of the sodium had dissolved the flask was sealed and N_2 was bubbled through the system. During this time α,α'-dichloro-*m*-xylene (1.07 g, 6 mmol) and **3** (5.00 g, 12 mmol) were added to a 250 mL two-necked, round-bottomed flask equipped with a condenser and the system was flushed with N_2 for 2 h. The base solution was transferred by forced siphon to this reaction flask and the resulting reaction mixture was protected from light while it was stirred at 60 °C under N_2 for 12 h. Then the reaction solution was allowed to cool to room temperature under N_2 and was acidified to a pH ≈ 7 (pH paper) with 1 M H_2SO_4. The majority of the solvent was removed under reduced pressure and the resulting oil was taken up into 450 mL of water. The aqueous solution that formed was extracted with CH_2Cl_2 (5 × 100 mL). A small amount of brine was added to break up any emulsion. The organic phase was washed with brine (2 × 100 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was dried under vacuum to yield 4.6 g (92%) of **4**. ^1H NMR ($CDCl_3$) δ 2.61 (4H, t, $^3J_{HH}$ = 6.7 Hz), 3.38 (6H, s), 3.55–3.70 (52H, PEG), 3.75 (4H, s), 7.2 (4H, m); ^{13}C NMR ($CDCl_3$) δ30.99, 36.75, 59.15, 70.49–72.14 (PEG), 127.80, 128.75, 129.59, 138.93.

1,3-Bis(MeOPEG$_{350}$thiomethyl)benzene palladium chloride (5) synthesis. A solution of **4** (1.40 g, 1.7 mmol) in 100 mL of CH_3CN was added to a solution of $Pd(PhCN)_2Cl_2$ (644 mg, 1.7 mmol) in 100 mL of CH_3CN. The clear solution so formed was stirred at room temperature for 12 h and then refluxed for 24 h. The solvent was removed under reduced pressure and the resulting brown oil was taken up into 300 mL of water. The aqueous solution was washed with Et_2O (4 × 50 mL), and the product was extracted into CH_2Cl_2 (4 × 100 mL). Brine was added as needed to enhance separation of layers. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting oil was dried *in vacuo* to yield 1.13 g (76%) of the product **5**. ^{1}H NMR ($CDCl_3$) δ 2.61 (4H, t, $^3J_{HH}$ = 4.9 Hz), 3.38 (6H, s), 3.55–3.70 (52H, PEG), 4.00 (4H, bs), 4.45 (4H, bs), 6.85 (3H, m); ^{13}C NMR ($CDCl_3$) δ 38.55, 48.22, 59.06, 70.46–71.97 (PEG), 122.17, 124.82, 149.42.

General procedure for use of 5 in homogeneous Heck reactions in DMA. An aryl halide (0.5 mmol), an alkene acceptor (1.0 mmol), and either TEA (2.0 mmol), K_2CO_3 (1.5 mmol with halobenzoic acids) or K_2CO_3 (0.5 mmol with acrylamide) as a base were added to 2.5 mL of DMA in a 10 mL microwave vial. Then either 42 μL of a 12 mM (5×10^{-7} mol, 0.1 mol%) solution of **5** in DMA or 42 μL of a 1.2 mM (5×10^{-8} mol, 0.01 mol%) solution of **5** in DMA were added. A $t = 0$ sample was taken and the vial was sealed with a Teflon septum using an aluminium crimp. The reaction solution was then either placed in a silicone oil bath at 150 °C or irradiated at 30 W using a microwave reactor (with the maximum temperature set to 150 °C). In kinetic studies of the conventional oil bath heated reaction, a sample was removed every 10 min using a syringe. In the microwave reactor samples were also taken every 10 minutes. However, in this case the microwave tube was quickly cooled using the cooling gas (N_2) feature on the microwave and then a sample was removed using a syringe. The remaining reaction solution was simply placed back into the reactor and further irradiated. All samples were analyzed by gas chromatography following disappearance of the PhX starting material and appearance of cinnamate product (n-$C_{12}H_{26}$ was used as an internal standard). When the reaction was complete, the product was isolated by pouring the reaction mixture into 20 mL of water and either collecting the precipitate or washing the aqueous phase several times with diethyl ether. The structures of the isolated products were confirmed by ^{1}H and ^{13}C NMR spectroscopy.

General procedure for recycling 5 in homogeneous Heck reactions under thermomorphic conditions. A 9.7 mM (104 μL, 1×10^{-6} mol, 0.2 mol%) solution of **5** in DMA was added to 1 mL of 10% aqueous DMA in a 10 mL microwave vial. The aryl iodide (0.50 mmol), the alkene acceptor (0.60 mmol), and TEA (0.75 mmol) were dissolved in 2 mL of heptane. This heptane solution was added to the catalyst solution and the vessel was sealed and microwaved at 150 °C for 20 minutes. The mixture was allowed to cool and the heptane phase was removed. Fresh reactants in heptane were then added to the catalyst solution for each additional cycle. Each cycle proceeded to greater than 96% conversion by GC analysis. The products were isolated by taking the heptane phase after each cycle and removing the solvent under reduced pressure. The isolated products' structures were confirmed by ^{1}H NMR spectroscopy.

General procedure for using 5 in homogeneous Heck reactions in D_2O. A halobenzoic acid (0.5 mmol), acrylic acid or *N*,*N*-dimethylacrylamide (1.0 mmol), and K_2CO_3 (1.5 mmol for acrylic acid or 0.5 mmol for dimethylacrylamide) were added to 2.5 mL of D_2O in a 10 mL microwave vial. Then 60 μL of a 8.4 mM (5×10^{-7} mol, 0.1 mol%) solution of **5** in D_2O were added. A ^{1}H NMR spectrum was obtained for $t = 0$. Then the NMR spectroscopy sample was poured back into the reaction mixture and the vial was sealed with a Teflon septum using an aluminium crimp. The sample was then irradiated at 30 W with the maximum temperature set to 150 °C. After 10 min, the sample was quickly cooled using the cooling gas (N_2) feature on the microwave. The percent conversion was determined by ^{1}H NMR spectroscopy of reaction mixture monitoring the disappearance of ArX and the appearance of product peaks. When the reaction was complete, the solution was neutralized with 6 M H_2SO_4 and the precipitate was collected and washed with water. The product was then dried and the structures of the isolated products were confirmed by ^{1}H and ^{13}C NMR spectroscopy.

NMR spectral data for Heck coupling products

***tert*-Butyl cinnamate (7)**. ^{1}H NMR ($CDCl_3$) δ 1.55 (9H, s), 6.39 (1H, d, $^3J_{HH}$ = 16 Hz), 7.38 (3H, m), 7.50 (2H, m), 7.59 (1H, d, $^3J_{HH}$ = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 28.41, 80.67, 120.40, 128.15, 129.02, 130.15, 134.87, 143.75, 166.51.

Methyl cinnamate (8). ^{1}H NMR ($CDCl_3$) δ 3.60 (3H, s), 6.45 (1H, d, $^3J_{HH}$ = 16 Hz), 7.39 (3H, m), 7.52 (2H, m), 7.70 (1H, d, $^3J_{HH}$ = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 51.96, 118.02, 128.32, 129.13, 130.55, 134.60, 145.12, 167.68.

Stilbene (9). ^{1}H NMR ($CDCl_3$) δ 7.12 (2H, s), 7.25 (2H, m), 7.35 (4H, m), 7.52 (4H, m); ^{13}C NMR ($CDCl_3$) δ 126.77, 127.88, 128.94, 137.57.

4-Stilbazole (10). ^{1}H NMR ($CDCl_3$) δ 7.00 (1H, d, $^3J_{HH}$ = 16 Hz), 7.31 (1H, d, $^3J_{HH}$ = 16 Hz), 7.38 (5H, m), 7.55 (2H, m), 8.59 (2H, m); ^{13}C NMR ($CDCl_3$) δ 121.09, 126.23, 127.25, 129.00, 129.09, 133.38, 136.37, 144.81, 150.47.

***tert*-Butyl β-(1-naphthyl)acrylate (11)**. ^{1}H NMR ($CDCl_3$) δ 1.49 (9H, s), 6.42 (1H, d, $^3J_{HH}$ = 16 Hz), 7.50 (3H, m), 7.72 (1H, d, $^3J_{HH}$ = 7 Hz), 7.85 (2H, $^3J_{HH}$ = 8.5), 8.19 (1H, d, $^3J_{HH}$ = 8.5 Hz), 8.41 (1H, d, $^3J_{HH}$ = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 28.51, 88.88, 123.07, 123.70, 125.14, 125.71, 126.40, 126.99, 128.93, 130.46, 131.66, 132.26, 133.90, 140.83, 166.50.

Methyl β-(1-naphthyl)acrylate (12). ^{1}H NMR ($CDCl_3$) δ 3.82 (3H, s), 6.51 (1H, d, $^3J_{HH}$ = 16 Hz), 7.50 (3H, m), 7.72 (1H, d, $^3J_{HH}$ = 7.08 Hz), 7.85 (2H, t, $^3J_{HH}$ = 7.9 Hz), 8.19 (1H, d, $^3J_{HH}$ = 7.8 Hz), 8.51 (1H, d, $^3J_{HH}$ = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 52.06, 120.66, 123.61, 125.23, 125.71, 126.49, 127.14, 128.99, 130.81, 131.65, 131.95, 133.91, 142.13, 167.58.

***m*-Carboxycinnamic acid (13)**. ^{1}H NMR (DMSO-d_6) δ 6.60 (1H, d, $^3J_{HH}$ = 16 Hz), 7.58 (1H, t, $^3J_{HH}$ = 7.7 Hz), 7.65 (1H, d, $^3J_{HH}$ = 16 Hz), 7.98 (2H, d, $^3J_{HH}$ = 7.7 Hz), 8.19 (1H, s), 12.82 (1H, bs); ^{13}C NMR (DMSO-d_6) δ 121.12, 129.66, 129.92, 131.42, 132.21, 132.66, 135.34, 143.61, 167.57, 168.03.

2-Methyl-5-carboxycinnamic acid (14). ^{1}H NMR (DMSO-d_6) δ 2.22 (3H, s), 6.41 (1H, d, $^3J_{HH}$ = 16 Hz), 7.41 (1H, d, $^3J_{HH}$ = 8 Hz), 7.83 (1H, d, $^3J_{HH}$ = 16 Hz), 7.86 (1H, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.17 (1H, d, $^4J_{HH}$ = 2 Hz), 12.82 (1H, bs); ^{13}C NMR (DMSO-d_6) δ 20.17, 122.10, 127.85, 129.78, 131.03, 131.78, 133.98, 141.18, 142.96, 167.61, 167.93.

***N*,*N*-Dimethyl-3-carboxycinnamamide (15)**. ^{1}H NMR (DMSO-d_6) δ 2.95 (3H, s), 3.19 (3H, s), 7.29 (1H, d, $^3J_{HH}$ = 16 Hz), 7.51 (1H, d, $^3J_{HH}$ = 16 Hz), 7.54 (1H, t, $^3J_{HH}$ = 7.7 Hz), 7.93 (1H, d, $^3J_{HH}$ = 7.7 Hz), 7.97 (1H, d, $^3J_{HH}$ = 7.7 Hz), 8.21 (1H, s); ^{13}C NMR (DMSO-d_6) δ 35.35, 36.90, 119.90, 128.48, 129.09, 130.04, 131.44, 132.15, 135.61, 139.89, 165.34, 167.06.

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PAPER

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Effects of ionic liquids on the acetylcholinesterase – a structure–activity relationship consideration

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Ionic liquids are discussed as sustainable green solvents, but toxicity and ecotoxicity data are rare. In this paper we present our results for different ionic liquids with the acetylcholinesterase inhibition assay. The results show that the acetylcholinesterase can be inhibited by ionic liquids containing a cation with a positively charged nitrogen and a certain lipophilicity. We tested imidazolium ionic liquids with different alkyl chains at R_1 and R_2 as well as with different anions and compared these results with our findings for other cation structures such as pyridinium ionic liquids and phosphonium ionic liquids. According to our results imidazolium and pyridinium ionic liquids inhibit the purified enzyme with EC_{50} values as low as 13 μM. The bulky phosphonium ionic liquids were less inhibitory. These results can be rationalized by structure–activity relationship considerations.

Introduction

Ionic liquids are a group of chemicals which have gained increasing attention in recent years as alternative solvents.[1,2] They are salts with a melting point below 100 °C. A variety of possible structural modifications allows a wide range of technical applications. Due to their low vapour pressure ionic liquids are discussed in the context of green and sustainable chemistry.[1,3,4]

Although these chemicals have a high technical and possibly commercial potential, toxicity and ecotoxicity data are rare and even basic information for risk analysis is missing.[1,4] We therefore developed a strategy to overcome this drawback[3] and started to assess biological and biochemical data of ionic liquids with a set of toxicity and ecotoxicity test systems.[5] These data can be included in our multidimensional risk analysis.[6] Our aim is to gain information about the overall toxicity of ionic liquids and the influence of structural modifications on toxicity in order to analyse the potential risk of ionic liquids to the environment.[3] Here we present our first results on molecular toxicity of ionic liquids with an acetylcholinesterase inhibition assay using the purified enzyme from electric eel (*Electrophorus electricus*). The active centre of this enzyme is very well known[7] which allows detailed structure–activity relationship considerations. The acetylcholinesterase inhibition assay was chosen because the enzyme is an essential part of the nervous system of nearly all higher organisms including humans[8,9] The active centre of the enzyme is very conservative among organisms[8–10] allowing for extrapolation of structure–activity relationships between organisms.

The enzyme has been the main target for the design of insecticides including organophosphorus and carbamate pesticides which resulted in a very good knowledge of structure–activity relationships for different chemical entities. Acetylcholinesterase catalyses the degradation of the neurotransmitter acetylcholine. Inhibition of acetylcholinesterase results in a variety of effects including heart diseases and amyosthenia.[11] Brain acetylcholinesterase inhibition in estuarine fish of more than 70% is well correlated with mortality.[8,9,12] Acetylcholinesterase is used as a biomarker detecting two classes of pesticides: organophosphates and carbamates,[8,13] but several studies showed that acetylcholinesterase is also inhibited by other different classes of chemicals including metals and surfactants.[14,15] Recently the enzyme has become a target for drug design for the treatment of diseases of the nervous system.[16] Structure–activity relationship comparisons clarified that these pharmaceuticals inhibit the enzyme because of a positively charged nitrogen combined with a certain lipophilicity.[16] Some of the most common ionic liquids with imidazolium or pyridinium as the core structure of the cation fulfil these criteria. Therefore this paper aims to test if ionic liquids inhibit the acetylcholinesterase. This will be achieved by focussing on the following questions:

- Are imidazolium and pyridinium ionic liquids inhibitors of the acetylcholinesterase due to their positively charged nitrogen combined with a lipophilic alkyl side chain?
- Is there a dependency of inhibitory potency on the chain length?
- Does the nature of the anion influence the inhibitory potency?
- Is the inhibitory potency reduced if different cationic core structures are used?

To answer these questions, chemicals were selected according to the "test-kit concept" first described for nucleotide analogues[17] and recently successfully applied in a first description of the toxicological potential of ionic liquids.[5]

To test the influence of the alkyl chain the imidazolium cation was selected with varying alkyl chains at position R_2 and a methyl group at R_1 as shown in Fig. 1. The anion tested was tetrafluoroborate. Additionally the influence of an aromatic ring at the end of R_2 (1-methyl-3-(phenylmethyl)-1H-imidazolium tetrafluoroborate (BnMIM BF_4) and 1-methyl-3-(2-phenylethyl)-1H-imidazolium tetrafluoroborate (PhEtMIM BF_4)) was tested to analyse the influence of aromatic substituents. The influence of a variation of the group at position R_1 was tested comparing 1-butyl-3-methyl-1H-imidazolium tetrafluoroborate (C_4MIM BF_4) and 1-butyl-3-ethyl-1H-imidazolium tetrafluoroborate (C_4EIM BF_4) and the influence of varying anions was tested using C_4MIM with different anions. Commercially available imidazolium ionic liquids have a high variety of different anions and the number of anions used for ionic liquid synthesis are increasing constantly. We first focussed on small anions representing different classes of commonly used ionic liquids: chloride and bromide, tetrafluoroborate and hexafluorophosphate. In addition we tested some more complex anions. They are not representative for the variety of anions available but their different chemical structures and different complexity provide initial hints about the influence of the chemical structure of the anions on acetylcholinesterase inhibition in general. To investigate whether the influence of the anions differs between the different

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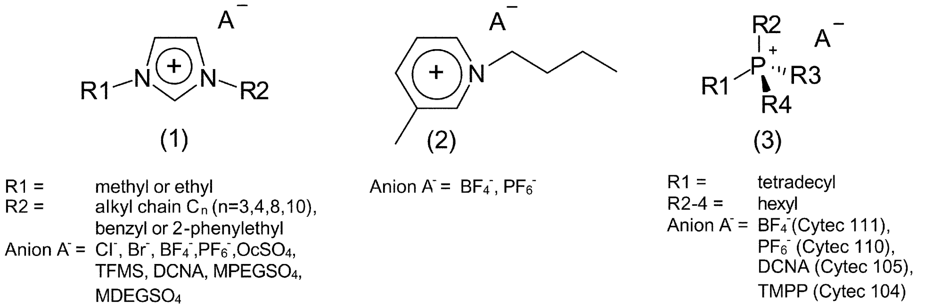

Fig. 1 Chemical structures of ionic liquids tested. (1) Imidazolium ionic liquids abbreviated C_nMIM [A$^-$] for R_1 = methyl and C_nEIM [A$^-$] for R_1 = ethyl, where C_n is the number of C atoms at R_2. R_2 = benzyl is abbreviated BnMIM and R_2 = 2-phenylethyl is abbreviated PhEtMIM. (2) Pyridinium ionic liquids abbreviated C_4MPy [A$^-$] (3) Phosphonium ionic liquid trihexyl(tetradecyl)phosphonium (Cytec) with different anions. $OcSO_4$ = octyl sulfate, TFMS = trifluoromethyl sulfonate, DCNA = dicyanamidate, $MPEGSO_4$ = α-methyl[poly(oxy-1,2-ethanediyl)] sulfate, $MDEGSO_4$ = 2-(2-methoxyethoxy)ethyl sulfate, TMPP = bis(2,4,4-trimethylpentyl)phosphinate.

cationic structures 1-butyl-3-methylpyridinium (C_4MPy) was tested with BF_4^- and PF_6^- and the trihexyl(tetradecyl)phosphonium cation was tested with BF_4^- (Cytec 111), PF_6^- (Cytec 110), dicyanamidate (DCNA) (Cytec 105) and bis(2,4,4-trimethylpentyl)phosphinate (TMPP) (Cytec 104). Wherever available the corresponding sodium salts of the anions (NaCl, NaBr, $NaBF_4$, $NaPF_6$, sodium trifluoromethyl sulfonate and sodium octyl sulfate) were also tested as a control. The impact of the cationic core structure was tested using the following ionic liquids: 1-butyl-3-methyl-1H-imidazolium tetrafluoroborate (C_4MIM BF_4), 1-butyl-3-methylpyridinium tetrafluoroborate (C_4MPy BF_4) and trihexyl(tetradecyl)phosphonium tetrafluoroborate (Cytec 111).

Results of this test-kit are discussed according to the T-SAR approach as recently published by Jastorff *et al.*[18]

Results and discussion

For all substances tested concentration–response curves were obtained and EC_{50} values were calculated. For substances with a calculated EC_{50} value higher than the highest concentration tested, EC_{50} values were indicated as > 2000 μM. EC_{50} values and confidence intervals (α = 0.05) for all substances are summarised in Table 1. Depending on the chemical structure, EC_{50} values vary between 13 μM and > 2000 μM. The EC_{50} value for aldicarb, a carbamate-type specific inhibitor of acetylcholinesterase, was 5 μM in this assay.

Results indicate that imidazolium and pyridinium ionic liquids inhibit the enzyme at relatively low concentrations and that inhibitory potency depends on the alkyl chain length at position R_2. These results will be discussed in two steps. First the influence of structural modifications on inhibitory potency will be presented, and second the importance of the results for an environmental risk assessment will be discussed.

Influence of structural modifications

Influence of alkyl chain length. All imidazolium ionic liquids showed acetylcholinesterase inhibition with EC_{50} values between 13 and 189 μM. A correlation between alkyl chain length of R_2 and inhibitory potency was observable. A longer chain length resulted in a stronger inhibition of the enzyme (Fig. 2).

This relationship can be quantified by a linear regression on the logarithms of the EC_{50} values *versus* the number of carbon atoms at R_2 (nR_2). The equation is $\log_{10}(EC_{50}) = -0.15(nR_2) + 2.70$. The residual standard error is 0.145 at 2 degrees of freedom.

In order to understand the influence of structural modifications on the inhibition of the enzyme a brief look at the molecular structure of the active centre of the acetylcholinesterase is necessary.

The entrance to the active centre of the acetylcholinesterase of electric eel is a narrow gorge, lined with lipophilic aromatic amino residues. The active centre of the enzyme consists of a catalytic site catalysing the hydrolysis of the acetylcholine and an anionic site,

Table 1 EC_{50} values and confidence interval (α = 0.05) for all ionic liquids tested. *b* = slope parameter of the lognormal regression, *n* = number of replicates

Substance	Log EC_{50}/μM	*b*	EC_{50}/μM	Interval	*n*
C_3MIM BF_4	2.28 ± 0.03	0.73	189	178–201	4
C_4MIM BF_4	2.02 ± 0.02	0.78	105	101–109	6
C_8MIM BF_4	1.66 ± 0.03	0.88	46	43–48	6
C_{10}MIM BF_4	1.10 ± 0.04	0.79	13	12–14	4
BnMIM BF_4	1.97 ± 0.02	0.73	93	89–97	4
PhEtMIM BF_4	1.89 ± 0.02	0.76	77	73–81	4
C_4EIM BF_4	2.03 ± 0.01	0.78	107	105–110	4
C_4MIM PF_6	2.15 ± 0.05	0.76	140	126–157	6
C_4MIM Cl	1.92 ± 0.05	0.83	84	75–94	4
C_4MIM Br	1.90 ± 0.02	0.77	80	76–83	4
C_4MIM $OcSO_4$	1.98 ± 0.01	0.8	97	93–100	6
C_4MIM TFMS	1.94 ± 0.06	0.84	88	77–101	4
C_4MIM DCNA	1.95 ± 0.07	0.88	89	75–105	4
C_4MIM $MDEGSO_4$	2.06 ± 0.08	0.87	114	96–136	4
C_4MIM $MPEGSO_4$	2.03 ± 0.06	0.83	106	93–121	4
C_4MPy BF_4	1.53 ± 0.02	0.72	34	32–36	4
C_4MPy PF_6	1.45 ± 0.02	0.76	28	27–30	4
Cytec 104[a]	> 3.30	3.20	> 2000	> 2000	4
Cytec 105[a]	3.40 ± 0.2	1.20	> 2000	> 2000	4
Cytec 110[a]	> 3.30	1.10	> 2000	> 2000	4
Cytec 111[a]	3.47 ± 0.08	0.89	> 2000	> 2000	4
Aldicarb	0.69 ± 0.06	0.61	5	4–6	4

[a] Calculated EC_{50} value higher than the highest concentration tested.

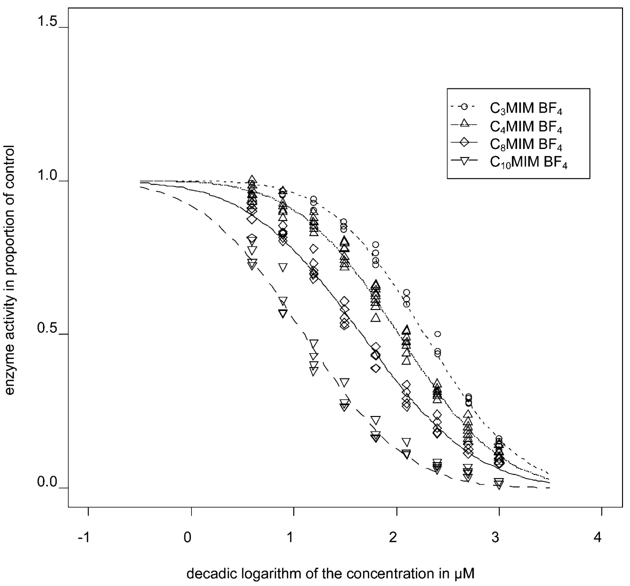

Fig. 2 Concentration–response curves for imidazolium ionic liquids with different alkyl chain length at R_2 (R_1 = methyl, anion = BF_4).

surrounded by lipophilic amino residues with a tryptophan which binds the choline part of the substrate *via* charge-transfer interactions.[11]

In contrast to the natural substrate acetylcholine and to inhibitors such as carbamates and organophosphates, the ionic liquids investigated here are missing the molecular interaction potential of the ester group which enables binding of the substance to the catalytic site.[11] However, regarding the positive charged nitrogen, imidazolium and pyridinium ionic liquids resemble the choline part of the substrate which binds to the anionic site of the enzyme. Therefore the inhibitory potency of these ionic liquids is likely to be due to binding to the anionic site of the enzyme. This is in concordance with quantitative structure–activity relationship (QSAR) calculations in pharmacological studies where a positively charged nitrogen is one of the most important descriptors for the inhibition of the enzyme.[16] The hypothesis is supported by the results of Palin *et al.*[19] with piperidinium and pyridinium salts.

The increase of inhibition with increasing alkyl chain length seems to be a result of a higher flux into the gorge and a better fit to the anionic site. For several pharmaceutical products quantitative structure–activity relationship calculations (QSARs) showed that lipophilicity or lipophilic properties are important descriptors for toxicity of chemicals that inhibit the enzyme by binding to the anionic site.[16] Results obtained in this study therefore correspond well with results from other studies.

No influence of an elongation of R_1 ($C_4EIM\ BF_4$ compared to $C_4MIM\ BF_4$) was observable (Table 1). This indicates that not only the lipophilic properties but also the steric position of the lipophilic side chains influences toxicity. This was also found to be true for other chemical classes.[16] However results are only based on the comparison of two substances and further tests would be necessary to support this hypothesis.

Substitution of the alkyl chain with an aromatic residue at the end (BnMIM and PhEtMIM BF_4) resulted in EC_{50} values only slightly lower than for $C_4MIM\ BF_4$ (Table 1). As the fragment constants describing the lipophilicity of a benzyl moiety sum up to a value which is just slightly higher than the sum of the fragment constants for a butyl moiety, the different EC_{50} values can be explained by substituent lipophilicity. We therefore conclude that there is no further specific interaction of the aromatic ring within the active centre of the enzyme. This hypothesis is supported by QSAR results of many different chemical classes with different substituents.[16]

Influence of cation structure. Results for different cation structures are displayed in Fig. 3.

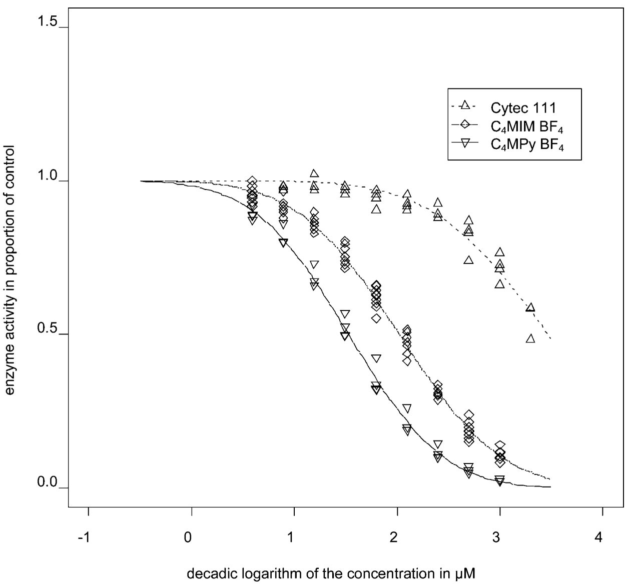

Fig. 3 Concentration–response curves for ionic liquids with different core structures of the cation. The anion is BF_4. Data for $C_4MIM\ BF_4$ *cf.* Fig. 2.

The results clearly show a dependency of inhibitory potency on the core structural elements of the ionic liquids.

The strongest inhibition was obtained with ionic liquids containing a positively charged nitrogen (pyridinium and imidazolium). The ionic liquid with pyridinium as the cationic core structure inhibited the enzyme slightly stronger than the imidazolium analogue. The ionic liquid based on phosphonium was less inhibitory (Fig. 3).

The higher inhibitory effect of pyridinium ionic liquids compared to the imidazolium ionic liquids may be due to a better binding to the tryptophan moiety of the anionic site. This hypothesis is supported by preliminary calculations with MOPAC 2000 (PM3 method)[20] of the binding enthalpies for C_4MIM and C_4MPy to the 3-methyl-1H-indole (as a model of the tryptophan moiety). Calculated heats of formation indicate that both structures bind to tryptophan, with a slightly better binding of C_4MPy compared to C_4MIM.

The phosphonium ionic liquids tested here are less potent inhibitors of acetylcholinesterase. They are lacking the charge-transfer potential and the positively charged moiety is shielded much stronger by the long alkyl chains. Phosphonium ionic liquids have a large van der Waals radius. This makes entry into the narrow gorge of the enzyme difficult. None of the inhibitors described in the literature have a phosphonium substructure. Nevertheless phosphonium compounds were slightly inhibiting the enzyme at high concentrations. This might be due to a disturbance of the tertiary structure of the enzyme at high concentrations as postulated for some surfactants.[15]

Influence of anions. The influence of the anions of the ionic liquids on inhibition of acetylcholinesterase was tested with C_4MIM combined with several anions. The EC_{50} values varied between 80 (C_4MIM Br) and 140 µM ($C_4MIM\ PF_6$) (Table 1). For the pyridinium type cation the influence of the anion was different than for the C_4MIM cation. While $C_4MIM\ PF_6$ was less inhibitory than $C_4MIM\ BF_4$, the corresponding results with C_4MPy were inverted (Table 1). EC_{50} values for the phosphonium ionic liquids with different anions (Cytec 104, 105, 110 and 111) were higher than the highest concentration tested with a high variation of parallels.

These differences in inhibition can not be rationalised by structure–activity relationship considerations. The tested anions alone did not inhibit the enzyme with the exception of $NaPF_6$ which produced an EC_{50} value of 190 µM (data not shown). The molecular size of the anions seems not to play a major role. C_4MIM with comparatively small anions such as chloride and bromide showed a stronger inhibition than C_4MIM BF_4, whereas C_4MIM with the bulky anions $MPEGSO_4$ and $MDEGSO_4$ showed a similar inhibitory potency as C_4MIM with the small anion BF_4^-. Low inhibitory potency was obtained for C_4MIM with the small anion PF_6^-. In the literature it is shown that salts can influence the inhibition of acetylcholinesterase by salting out effects.[21] Thus different electrostatic interactions could be an explanation for the different inhibitory potency of varying anions. But to support this hypothesis more data, especially about the speciation of ionic liquids in aqueous solutions, are necessary.

Importance for man and environment

To evaluate the importance of the findings to man and environment an extrapolation from *in vitro* to *in vivo* is necessary.

Results obtained with *in vitro* assays can only give indications about the hazard potential of chemicals, but an inhibition of the enzyme does not necessarily mean that an effect in whole organisms will occur. To cause an effect in organisms the chemical needs to reach the target site. Unfortunately no experimental data about the uptake and bioaccumulation of ionic liquids are available. If the chemicals are able to reach the enzyme the potential of some of the ionic liquids to cause an effect on the whole organism must be judged as high because the enzyme catalyses an essential process in many organisms. Several studies with other chemicals revealed that already a 70% inhibition of the enzyme is followed by death of the organisms.[8–10] The inhibition concentration of C_{10}MIM BF_4 (13 μM) is almost as low as for aldicarb (5 μM), an insecticide designed to cause death of insects *via* inhibition of the acetylcholinesterase. Thus, if the ionic liquid can enter the organism and reach the enzyme the potential to inhibit the enzyme and thereby cause death is high.

The active centre of the enzyme is highly conservative among organisms.[8–10] An inhibition of the enzyme of electric eel is therefore an indicator that enzymes of other organisms can also be inhibited. But again the ability to reach the enzyme is crucial to cause an effect in organisms and might be very different between organisms.

Conclusion

The simple and cost effective tests with acetylcholinesterase showed that ionic liquids with imidazolium and pyridinium cations as core structures have a toxic potential for the environment because of the inhibition of acetylcholinesterase. Inhibitory potency depends on the type of the cationic structure and the alkyl side chains. To evaluate the risk of these chemicals for the environment further experiments about bioaccumulation and behaviour in the environment (persistence and long transport range) are highly recommended. Beside this uncertainty about exposure some recommendations can be given:

As far as technically possible, ionic liquids with short alkyl chains should be preferred. These results are consistent with results obtained with *Vibrio fischeri* and leukaemia cells[5] and with our first risk analysis.[3] If only data from acetylcholinesterase inhibition assay are taken into account imidazolium ionic liquids should be preferred in comparison to pyridinium ionic liquids, and if possible phosphonium ionic liquids should be used.

Results presented in this study indicate that the influence of the anion does not dominate the toxicity of the ionic liquids. This is important because the anion used in ionic liquids has a high influence on the industrial applicability of the substances. But further research should be done to better understand the influence of anions on the toxicity of ionic liquids.

In summary it can be stated that some of the ionic liquids tested do show a hazard potential due to their ability to inhibit the acetylcholinesterase. But as long as data about biouptake and metabolism are lacking no prediction of the toxicity of ionic liquids *in vivo* can be done.

Experimental

Ionic liquids

Imidazolium ionic liquids with R_1 representing a methyl or ethyl group and R_2 representing a straight chain alkyl group C_4 to C_{10} and the anions BF_4^-, PF_6^-, Cl^-, as well as C_4EIM BF_4 were prepared at the ITUC Jena. For details see Ranke *et al.*[5] BnMIM BF_4 and PhEtMIM BF_4 were prepared in the same way but at room temperature. These substances were also synthesised at the ITUC Jena. C_4MIM TFMS, C_4MIM DCNA, C_4MPy BF_4 and C_4MPy PF_6 were donated by Merck GmbH (Darmstadt, Germany). Cytec 104, Cytec 105, Cytec 110 and Cytec 111 were provided by Cytec GmbH (Welland, Canada), C_4MIM $OcSO_4$ (ECOENG™ 418), C_4MIM $MDEGSO_4$ (ECOENG™ 41M) and C_4MIM $MPEGSO_4$ were donated by Solvent Innovation (Köln, Germany). Sodium salts of the anions were purchased from the following companies: sodium chloride and sodium trifluoromethyl sulfonate from Fluka (Buchs, Switzerland) and sodium tetrafluoroborate and sodium hexafluorophosphate from Lancaster (Frankfurt, Germany). Sodium octylsulfate ($NaOcSO_4$), was donated by Solvent Innovation (Köln, Germany).

Further chemicals

Sodium hydrogen carbonate was purchased from GIBCO BRL Life technologies (Eggenstein, Germany), sodium hydrogen phosphate and methanol were obtained from Merck-Schuchardt (Hohenbrunn, Germany) and Carl Roth GmbH (Karlsruhe, Germany) respectively, bovine serum albumin and 5,5′-dithio-bis-(2-nitrobenzoic acid) (DTNB) were purchased from Sigma Aldrich GmbH (Steinheim, Germany) and acetylcholine iodide was provided by Fluka (Buchs, Switzerland).

Acetylcholinesterase

Acetylcholinesterase (EC 3.1.1.7) from the electric organ of the electric eel (*Electrophorus electricus*) Type VI-S was purchased from Sigma (Steinheim, Germany). The activity was 301 U mg solid^{-1} (463 U mg Protein^{-1}).

Acetylcholinesterase inhibition assay

Inhibition of acetylcholinesterase was measured using a colorimetric assay based on the reduction of 5,5′-dithio-bis-(2-nitrobenzoic acid) (DTNB) as previously described by Ellman *et al.*[22] The test procedure in a 96 multiwell plate was adapted from Fisher *et al.*[23] On each plate four substances with two replicates, eight wells with blank and 16 controls were tested. Briefly, a dilution series of the substances in phosphate buffer (0.02 M, pH 8.0) with max. 1% methanol was prepared directly in the wells, DTNB (2 mM, 0.185 mg ml^{-1} $NaHCO_3$ in phosphate buffer) and the enzyme (0.2 U ml^{-1}, 0.25 mg ml^{-1} bovine serum albumin in phosphate buffer) was added and the reaction was started by adding acetylcholine iodide (2 mM in phosphate buffer). Final concentrations in the test were 0.5 mM of DTNB and acetylcholine iodide and 0.05 U ml^{-1} acetylcholinesterase. For some compounds the highest concentration tested was above the solubility of the substance. Nevertheless results were considered valid because independent tests with different stock solutions and at least two replicates yielded similar results.

Enzyme kinetics were measured in 30 second intervals in a microplate-reader (MRX Dynatech) for 5 minutes at 405 nm. Enzyme activity was expressed as OD min^{-1} from the linear regression. To ensure that inhibitory effects are not due to pH variations the pH of every substance in solution was monitored. The pH varied between 7.9 and 8.3. The activity of the enzyme was found to be constant in this pH range.

Effect data modelling

Concentration–response curves were fitted to the multinomial data with the R language and environment for statistic computing version 1.6 (see http://www.r-project.org, or Ihaka and Gentleman[24]) using the probit model for the relation of enzyme activity to the decadic logarithm of the tested concentrations. The concentration–response curve is normalised from 0 to 100% activity and is described by the log EC_{50} and the slope of the curve. Confidence intervals ($\alpha = 0.05$) of the log EC_{50} values and linear regressions on the logarithms of the EC_{50} values *versus* the number of carbon atoms in the alkyl chains were calculated with the R language as well.

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Environmentally-friendly physico-chemical rapid ultrasonic recycling of fumed silica-filled poly(dimethyl siloxane) vulcanizate

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Fumed silica-filled PDMS, where quite a strong interaction exists between the filler and matrix *via* hydrogen bonding, was recycled by means of an extruder with high power ultrasound attachment. It was found that the reinforcing filler plays an important role in the devulcanization process. Compared to the precipitated silica-filled PDMS, higher power is consumed during the devulcanization process of fumed silica-filled PDMS due to a strong interaction between the fumed silica particles and PDMS chains. The decrease in crosslink density after the devulcanization process shows that the process is quite dependent on the concentration of fumed silica. Throughout a simulation of scission of chemical bonds during the process, the influence of the concentration of filler on the devulcanization was investigated. The scission of main chains (Si–O) and crosslinks (Si–C and C–C) concurrently occurs during the process. Crosslinks are predominantly severed in the absence of fumed silica while the main chain rupture tends to increase with the filler concentration. The main chain scission leads to the deactivation of filler which reduces gel fraction and crosslink density of the revulcanizates. The mechanical properties of the revulcanizate show that the fumed silica significantly affects the final properties of the recycled PDMS.

1 Introduction

Development of economic and viable processes to recycle used tires and waste rubbers still remains a tremendous problem that scientists/engineers should solve, not only to protect against environmental pollution but also to prevent the depletion of natural resources. Among various mechanical and chemical recycling methods, ultrasonic treatment has been suggested as a promising technique since it possesses various advantages.[1] Ultrasonic recycling is a fast continuous extrusion process with a residence time of a few seconds. The process does not require use of any chemical agent for devulcanization and does not generate by-products. It is an energy efficient environmentally friendly physical process. Another attractive feature of this process is the direct usability of the treated rubber by means of revulcanization which is similar to the vulcanization of virgin material. Various types of elastomers have been studied including ground tire rubber,[2] natural rubber,[3] styrene-butadiene rubber,[4] EPDM,[5] butadiene rubber,[6] and polyurethane.[7] These studies reveal that ultrasonic waves, at a certain level of pressure and moderate temperature, can rapidly break down the three-dimensional rubber network. This is caused by cavitation which is created by high intensity ultrasonic waves in the presence of pressure and heat.[8] Driven by ultrasound, microscopic cavities, typically present in any rubber due to the existence of voids and imperfections, pulsate with amplitude depending upon the ratio between ambient and ultrasonic pressure (acoustic cavitation). This leads to mechanochemical degradation of overstressed bonds around pulsating cavities.

Consumption of poly(dimethyl siloxane) (PDMS), composed of alternating silicone and oxygen atoms in the main chain, is growing very rapidly due to its unique chemical composition and excellent properties. The applications range from consumer products to industrial applications, such as household and personal care products, textile treatments, and antifoams for food processing.[9] The bond energies of the crosslinked PDMS network, consisting of Si–O bonds in the main chains and Si–C and C–C bonds in the crosslinks, are substantially higher than those of other sulfur-cured synthetic rubbers, consisting of C–C in the main chains and C–S and S–S in the crosslinks.[10] Therefore, the breakage of the crosslinks in PDMS is more difficult to achieve than in other rubbers. The traditional recycling of PDMS is classified into three categories: (1) thermal depolymerization in a thermal cracking bed reactor[11] or in a closed vessel,[12] (2) chemical treatment using various chemical agents.[13–15] (3) mechanical grinding waste scraps and compounding with virgin material.[16,17] In addition, high power ultrasound has been successfully used to recycle unfilled[18] and precipitated silica-filled,[10,19] PDMS vulcanizates, where incorporated filler plays a significant role in recyclability of the vulcanizate. For the unfilled system, almost identical physical properties of revulcanized PDMS as those of virgin vulcanizate were achieved, while approximately 80–90% recovery of mechanical properties was obtained for the precipitated silica-filled system. Since PDMS itself is too weak, fumed silica is most frequently used for reinforcing purposes. Therefore, the investigation of the effect of fumed silica on recycling of PDMS was the initiative of this study.

2 Experimental

A polymeric network was prepared by crosslinking PDMS, SE 64 made by General Electric Company with weight-average molecular weight $M_w = 4.14 \times 10^5$ and number-average molecular weight $M_n = 2.34 \times 10^5$ (measured by gel permeation chromatography, GPC). It contained 0.6 mol% vinyl groups. Fumed silica, Aerosil 200® (Degussa Co.), having a surface area of 200 $m^2\ g^{-1}$ was used as a reinforcing filler. Dicumyl peroxide (DCP), LUPEROX® 500R (Pennwalt Corp.), was used as the curative. Various concentrations of silica were incorporated in PDMS by a Moriyama mixer having a chamber capacity of 3 L. Half the amount of filler was added in PDMS and after 3 min the rest was added and mixed for 7 min at room temperature. The silica-filled PDMS compounds were then homogenized by a two-roll mill (Dependable Rubber Machinery Co.). 0.5 phr DCP was added to compounds on the two-roll mill at 25 °C. After mixing, the compounds were pre-cured at 170 °C by a compression molding press (Wabash) into $260 \times 260 \times 12\ mm^3$ slabs and then post-cured in a ventilated oven at 200 °C for 2 hours.

The bound rubber content in uncured PDMS compounds was determined by the Soxhlet extraction method using benzene as a good solvent. Extraction in a cellulose thimble was carried out for

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5 days. The remaining non-extracted part (gel) was dried at 50 °C for 48 hours in a vacuum oven. The amount of bound rubber was determined as the ratio of the amount of rubber in the unextracted gel to the amount of rubber in the compound.

The vulcanized sheets were ground into particles using a Nelmor grinding machine with 5 mm screen. These PDMS particles were then fed into a rubber extruder with an ultrasound die attachment[2a] to achieve devulcanization. The temperature of the extruder barrel was set at 180 °C. The screw speed was 20 rpm and both the die and horn cooling water flow rate were set to be 0.09 m^3 h^{-1}. The gap, δ, between the flat face of the horn and the die exit surface was either 0.35 mm or 0.63 mm. The material flow rate, Q, was 0.32 g s^{-1}. A 3000 W ultrasonic power supply, a converter and a booster were used to provide longitudinal vibrations to the horn at a frequency of 20 kHz. The amplitudes, A, of the ultrasonic wave were 5, 7.5 and 10 μm. The devulcanized silicone rubber exiting from the die was collected for further investigation. The devulcanized rubber was revulcanized with 0.5 phr DCP in slabs of dimensions of 180 × 130 × 3 mm^3 at 170 °C for 10 min. The revulcanizates were also post-cured under the same conditions as virgin compounds.

Gel fractions of the vulcanized and devulcanized samples were measured by Soxhlet extraction, using benzene as the solvent. The extraction time was set at 24 hours. Crosslink densities were determined by the swelling method. The weights of the swollen samples were measured after removing the surface solvent. Then the samples were dried in a vacuum oven at 50 °C for 24 hours and were weighed again. The crosslink density, ξ, was calculated using the Flory–Rehner equation.[20]

The mechanical properties of the virgin vulcanizates and revulcanized samples were measured at an elongation speed of 50 mm min^{-1} by a Instron 5567 tensile test machine with a 500 N load cell following ASTM D 412–92.

3 Results and discussion

3.1 Energy consumption

The power consumption instantaneously monitored by a watt meter was recorded during the devulcanization process and is represented as a function of ultrasonic amplitude at various filler concentrations in Fig. 1. It is seen that the power consumption increases with the filler concentration and ultrasonic amplitude for all concentrations of the filler. Compared to the precipitated silica-filled system,[19] higher energy is consumed in the fumed silica-filled system. This observation is more pronounced at higher ultrasonic amplitudes. For example, 2005 watts were needed for 40 phr fumed silica-filled PDMS at 10 μm, while 1490 watts were consumed for 40 phr precipitated silica-filled PDMS at the same amplitude. The measured ultrasonic power consumption includes the useful power and the losses. One cannot estimate experimentally what portion of the power is used by devulcanization. Also the power expended on heat dissipation in the material and power transmitted by the travelling wave through the rubber cannot be separated. Apparently, ultrasound may break both chemical crosslinks between PDMS chains and physical crosslinks between rubber chains and filler particles. It is thought that more energy is used to break the physical crosslinks in the highly filled system due to the increased amount of bound rubber in fumed silica-filled PDMS compounds, as indicated in Fig. 2. The amount of bound rubber is strongly related to the interaction between the filler and matrix polymer, the surface area of the filler, the solubility of the extraction agent, molecular weight of the matrix polymer, the concentration of filler in the compound and the extraction time and temperature. The bound rubber content is 79.2% at a concentration of fumed silica of 10 phr and it continuously increases up to 94.6% at 40 phr causing an increase of the concentration of physical crosslinks with an increase of the concentration of fumed silica in PDMS vulcanizates. This explains why a higher power consumption for devulcanization of PDMS vulcanizates is required at a higher concentration of filler. The degree of breakage of the chemical and physical crosslinks are estimated in the following simulation.

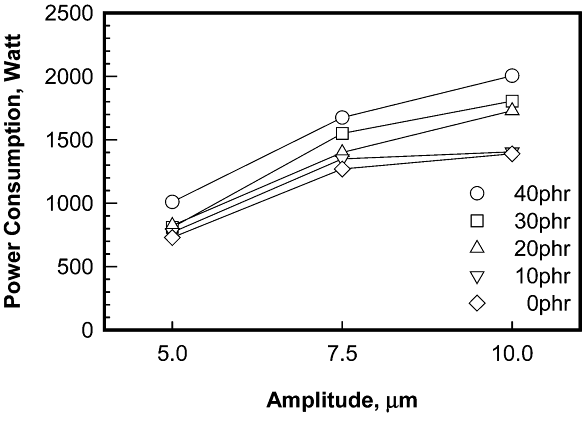

Fig. 1 Power consumption *vs.* amplitude for unfilled and fumed silica-filled PDMS at a flow rate of 0.32 g s^{-1}, a gap size of 0.63 mm, and at 180 °C.

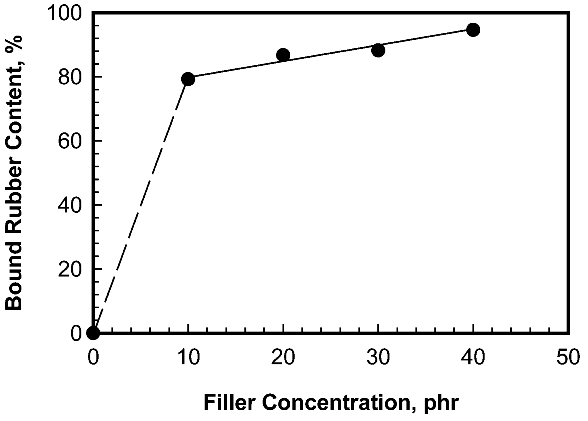

Fig. 2 Bound rubber content *vs.* filler concentration in fumed silica-filled PDMS compounds.

3.2 Breakage of 3-dimensional network

The degree of devulcanization is quantified by the reduction of the crosslink density and gel fraction. In measuring the crosslink density of the filled system, the Kraus correction[21] was employed in order to avoid misleading values due to the presence of filler. Details of the Kraus correction procedure can be found elsewhere.[19] It is noted that the Kraus correction constant of 1.93 was experimentally obtained and used for the calculation. Fig. 3 depicts the normalized crosslink density as a function of ultrasonic amplitude at various filler concentrations. It is clearly seen that the

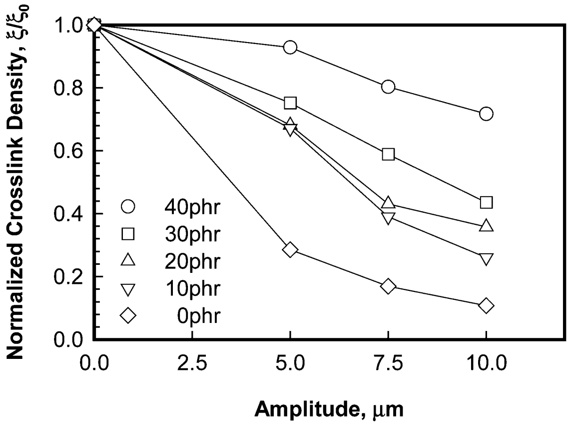

Fig. 3 Normalized crosslink density *vs.* amplitude for PDMS filled with various amounts of fumed silica devulcanized at a flow rate of 0.32 g s^{-1}, a gap of 0.63 mm, and at 180 °C.

decrease in crosslink density is strongly dependent on the filler concentration and the amplitude. For the unfilled system, 89% of crosslinks are broken at 10 μm of ultrasonic amplitude, while only 28% of crosslinks are ruptured in the 40 phr filled system at the same amplitude. However, it is not easy to estimate how many of the main chains and crosslinks are ruptured during the process. In order to investigate the effect of filler on the breakage of the main chains and crosslinks during the devulcanization process, a simulation, based on the classical theory of brached polymers by Dobson and Gordon[22,23] and adopting Flory molecular weight distribution, was conducted for the different filler concentrations.

The breakage of main chain and crosslinks is expressed as a function of the ratio of scission rates, k_p/k_a, which is an adjustable parameter. k_p and k_a denote the rate of main chain and crosslink rupture, respectively.[26] There are two limiting cases. One of them corresponds to $k_p/k_\alpha \rightarrow \infty$ when only rubber main chains are subjected to breakage (line 2 in Fig. 4). In the opposite limiting case $k_p/k_\alpha \rightarrow 0$, only crosslinks rupture and main chains remain intact (line 1 in Fig. 4). It is demonstrated in Fig. 4 that the experimental points lie in between the two limiting cases indicating that both rupture of main chain bonds and breakage of crosslinks occur during devulcanization. It is seen that the $k_p/k_\alpha = 7.40 \times 10^{-4}$ in the case of unfilled PDMS provides a fairly good agreement between the experimental and theoretical data. It should be noted that the model predicts a higher rate of crosslink scission in comparison with that of main chain bond rupture for devulcanization of PDMS. This is quite reasonable because in this case main chain bonds are stronger than crosslink bonds. Moreover, the difference between main chain and crosslink bond energies in peroxide-cured PDMS is higher than in sulfur-cured synthetic rubber. Fig. 4 shows the experimental and calculated results of the normalized gel fraction *vs.* the normalized crosslink density plot for unfilled and fumed silica-filled PDMS. The physical–chemical characteristics of vulcanized PDMS used in the calculations are shown in Table 1. The resulting k_p/k_a values for different filler concentrations from the simulation are given in Table 2. For fumed silica-filled PDMS systems, higher values of k_p/k_a are obtained at 40 phr than at 10 phr, indicating that a greater amount of the main chains are subjected to rupture in highly filled PDMS. In addition, approximately a 100-fold increase in the k_p/k_a ratio is seen for the 40 phr filled compound ($k_p/k_\alpha = 6.91 \times 10^{-2}$) compared to the unfilled system ($k_p/k_\alpha = 7.40 \times 10^{-4}$) indicating the severity of main chain breakage in the filled system.

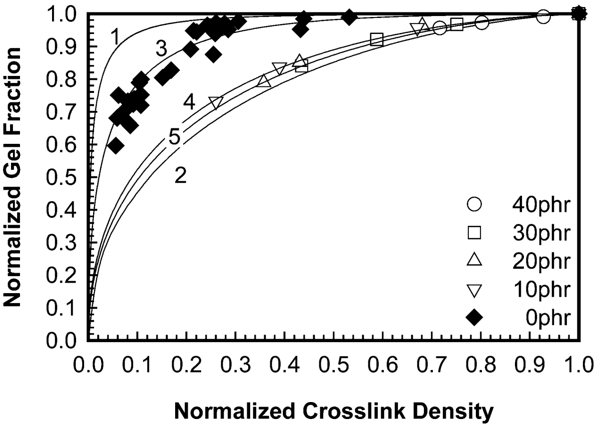

Fig. 4 Normalized gel fraction *vs.* normalized crosslink density of devulcanized unfilled and fumed silica-filled PDMS. Line 1: crosslink rupture, line 2: main chain rupture, line 3: unfilled PDMS, line 4: 10 phr filled PDMS, line 5: 40 phr filled PDMS.

Table 1 Physical–chemical properties of PDMS

Description	Symbol, Unit	PDMS	Reference
Density	ρ, kg m^{-3}	980	24
Molecular weight: number-averaged	M_n, g mol^{-1}	2.34×10^5	18
Molecular weight: weight-averaged	M_w, g mol^{-1}	4.14×10^5	18
Monomeric: molecular weight	M_0, g mol^{-1}	74	25
Crosslink density in gel	$\xi_a^{(g)}$, kmol m^{-3}	0.08	18

Table 2 The k_p/k_a values for unfilled and fumed silica-filled PDMS

		Fumed silica-filled			
	Unfilled	10 phr	20 phr	30 phr	40 phr
k_p/k_a	7.40×10^{-4}	1.97×10^{-2}	4.26×10^{-2}	6.16×10^{-2}	6.91×10^{-2}

3.3 Mechanical properties of recycled PDMS

Fig. 5 represents crosslink densities and gel fractions of virgin vulcanizates, devulcanized and revulcanized rubbers. It is seen that a significant decrease in both crosslink density and gel fraction upon ultrasonic devulcanization is achieved during devulcanization. However, they are not recovered after revulcanization compared to those in virgin vulcanizates although the same amount of curative as in virgin rubber was used. Since a crosslink reaction is achieved through the participation of vinyl groups in methyl vinyl silicone rubber,[27] further crosslinking reaction through the vinyl groups upon revulcanization is limited since vinyl groups are consumed in the first stage of curing. Another reason is a possibility of a partial deactivation of the filler. It is known that rubber molecules are bonded onto the filler surface and penetrated into pores existing in silica filler leading to bound rubber. The mobility of such chains is considerably restricted. This means that the chains of bound rubber can be more easily broken than those of the non-bound rubber during ultrasonic treatment. Accordingly, after ultrasonic treatment a considerable amount of bound rubber chains are broken. This process may lead to a partial deactivation of filler causing the loss of reinforcement. The depletion of vinyl groups and the deactivation of filler may be the reasons for the low crosslink density and gel fraction of revulcanized PDMS. These results may be also related to the mechanical properties of the revulcanized samples.

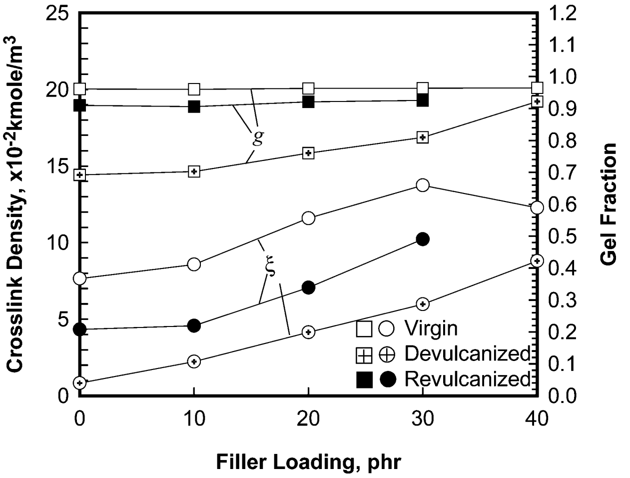

Fig. 5 Crosslink density (ξ) and gel fraction (*g*) of virgin, devulcanized, and revulcanized fumed silica-filled silicone rubber *vs.* filler loading. Rubber was devulcanized at a flow rate of 0.32 g s^{-1}, a gap of 0.63 mm, an amplitude of 10 μm, and 180 °C.

30 phr fumed silica-filled devulcanized rubber was blended with virgin 30 phr fumed filled silicone rubber at various concentrations. Fig. 6 represents the stress-strain behavior of the blend vulcanizates. The ultrasonically treated PDMS was able to be revulcanized (line 5 in Fig. 6), but the mechanical properties were significantly reduced due to the low crosslink density and gel fraction as

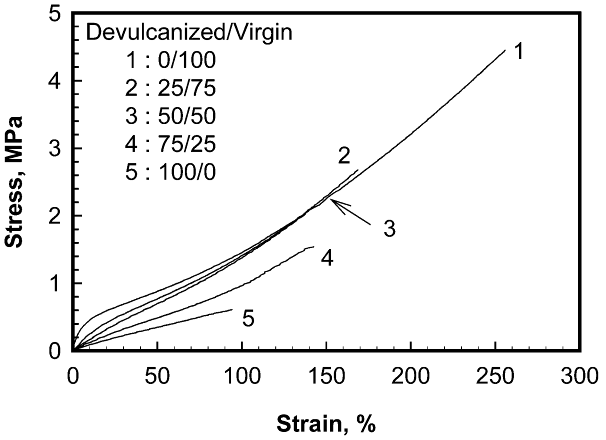

Fig. 6 Strain-stress curves of 30 phr fumed silica-filled devulcanized/virgin silicone rubber blend vulcanizates cured with 0.5 phr DCP at 170 °C. Rubber was devulcanized at a flow rate of 0.32 g s^{-1}, a gap of 0.63 mm, an amplitude of 10 μm, and 180 °C and then cured with 0.5 phr DCP at 170 °C.

mentioned earlier. Varying concentrations of the ultrasonically treated PDMS were blended with virgin material. In the case of 25/75 devulcanized/virgin blend revulcanizate, almost identical 100% modulus was achieved as that of virgin vulcanizate (line 1 in Fig. 6). However, the elongation at break shows a 66% recovery. Compared to our previous work on precipitated silica-filled PDMS,[19] the recovery of the mechanical properties was lower. Considering the stronger interaction of fumed silica than precipitated silica in PDMS, this could be explained by the fact that more bound rubber chains are subject to breakage upon ultrasonic devulcanization in the fumed silica/silicone rubber system.

4 Conclusion

The fumed silica-filled PDMS, where quite a strong interaction exists, such as hydrogen bonding, was devulcanized by an extruder with a high power ultrasound attachment. Compared to traditional recycling methods, this process provides facile reclamation of used rubber products since it is continuous, fast and does not involve any chemical agents. In addition, the recycled rubber obtained by this process can be directly revulcanized similar to vulcanization of virgin material. In this study, it is found that the reinforcing filler plays an important role in the devulcanization process. Compared to precipitated silica-filled PDMS, higher power is consumed during the devulcanizatin process of fumed silica-filled PDMS due to a strong interaction between the fumed silica particles and PDMS chains. The decrease in crosslink density after the devulcanization process shows that the process is quite dependent on the concentration of fumed silica. By means of simulation, the influence of the concentration of filler on the devulcanization process was thoroughly investigated. The scission of main chains and crosslinks concurrently occurs during the process since the experimental data lie between the two extreme cases of main chain breakage and crosslink rupture. Crosslinks are predominantly severed in the absence of fumed silica while the main chain rupture tends to increase with the filler concentration. For example, approximately a 100-fold increase in the k_p/k_a ratio is found for a 40 phr filled compound compared to an unfilled system. The main chain scission leads to the deactivation of filler which reduces the gel fraction and crosslink density of the revulcanizates. The mechanical properties of the revulcanizate show that the fumed silica significantly affects the final properties of the recycled PDMS.

Acknowledgments

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Hydrodechlorination of chlorinated benzenes in a continuous microwave reactor

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An expeditious hydrodechlorination of chlorobenzenes is observed over 0.5% Pd/Al_2O_3 catalyst by conducting the reaction under microwave irradiation conditions. Even though the loss of active metal surface area is substantial and identical in both microwave and conventional heating reactions, the higher rate and sustainability of the microwave reaction may be due to the selective and rapid absorption of microwaves by the polar chlorinated substrates that facilitates their relatively easy removal from the catalyst surface. It is also speculated that the rate of desorption of the products (especially the poisonous HCl) is more critical in sustaining the catalyst activity. The experiments also reveal a significant reduction in power consumption under the microwave reaction than the reaction conducted using conventional heating.

Introduction

Aromatic hydrocarbons containing chlorine are among the most hazardous toxic pollutants with carcinogenic and mutagenic properties besides being primarily responsible for the stratospheric ozone depletion.[1,2] Therefore it is not surprising that the disposal of chlorinated organic wastes has become a major environmental and health concern;[3] the typical mode of disposal is *via* land filling or incineration methods.[4] However, land filling causes further environmental problems due to their poor biodegradability[5] and leaching into the ground water, whereas incineration leads to the formation of highly toxic by-products such as dioxins.[6] Another alternative is their degradation to safer compounds which is, however, a highly energy intensive process.[6] The most attractive and efficient method has been catalytic hydrodechlorination[5] using a variety of catalysts such as Pt, Pd, Ni *etc.*, in presence of either gaseous hydrogen[7–11] or an alcohol as hydrogen donor.[12–15] Most of the studies in hydrodechlorination are conducted in the vapor phase in the temperature range 140–200 °C in a fixed bed reactor at atmospheric pressure.[8,9] One of the main problems of the catalytic hydrodechlorination is the deactivation of catalyst caused by adsorption of chlorine on the catalyst causing a change in the catalyst surface composition and also by poisoning or blocking of the active sites.[16,17] The hydrodechlorination activity is found to be affected by the nature of the support and metal particle size as well as on the presence of promoters.[18–20] Therefore, the development of a suitable reaction procedure where the catalytic activity is maintained for a longer period is very important.

The use of microwaves (MW) in enhancing chemical transformations has been gaining attention in recent years due to their several advantages such as rapid reaction rates and higher yield of pure products.[21–23] This is a consequence of the selective absorption of microwave energy by polar molecules or polar transition states formed during the course of the reaction.[22] Microwave irradiation has also been successfully utilized in the efficient preparation of various types of catalysts and related materials.[23] The in-core homogeneous and rapid heating of microwaves by a dielectric loss mechanism is exploited in the preparation of catalysts with improved microstructures. Subsequently MW irradiation has been efficiently utilized in the preparation of supported metal catalysts with higher residual activity for hydrodechlorination reactions.[24] Nevertheless, microwave irradiation has not been exploited well in the hydrodechlorination reaction. As the feed materials are polar compounds, they are highly microwave absorbing compounds and therefore the reaction is expected to be efficient under microwave conditions. Decomposition of PCBs in soil[25] and dechlorination of chlorinated aromatics adsorbed on fly ash[26] are studied under MW irradiation conditions. There are, however, not many studies reported on the hydrodechlorination of chlorinated benzenes under MW irradiation conditions. Radoiu *et al.*, have studied the microwave-enhanced dechlorination of chlorobenzene over palladium-based catalysts in an aqueous solution of NaOH in 2-propanol at reflux temperature.[27] Herein, we report the hydrodechlorination of chlorobenzenes over Pd/Al_2O_3 catalyst under a continuous phase microwave irradiation method. A comparison has also been made with the corresponding reaction under conventional heating conditions.

Results and discussion

Hydrodechlorination of chlorobenzenes was conducted in a continuous phase microwave reactor equipped with a pressure pump, a stirrer and a fiber optic temperature sensor (Fig. 1). A comparison of hydrodechlorination of chlorobenzene over 0.5% Pd/Al_2O_3 catalyst under continuous microwave irradiation and conventional heating conditions is shown in Fig. 2. It is apparent that the reactions under microwave irradiation conditions afford a relatively higher conversion than the reactions under conventional heating conditions at various temperatures. The figure also shows that the chlorobenzene conversion increases with an increase in temperature from 50 to 100 °C and the rate acceleration by microwave irradiation is more prominent at elevated temperatures.

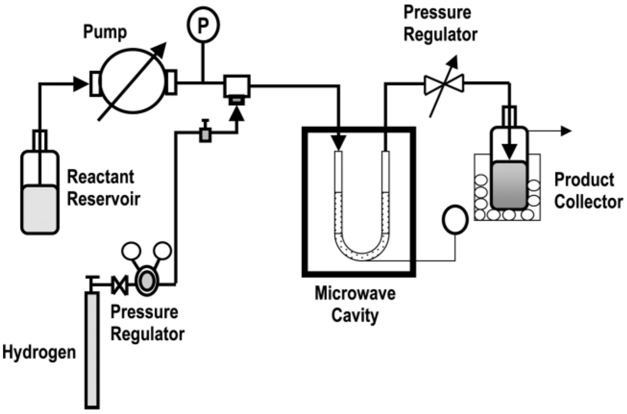

Fig. 1 Schematic of the continuous microwave reactor used for the hydrodechlorination reaction (CEM Corporation, Model-Voyager).

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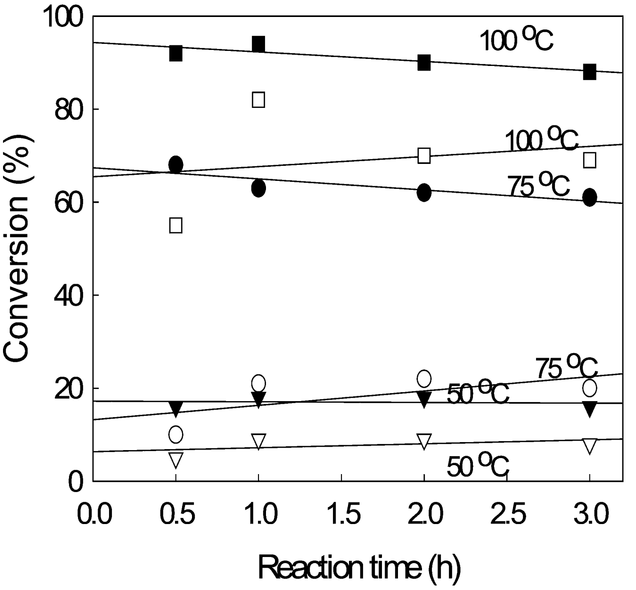

Fig. 2 Comparison of hydrodechlorination of chlorobenzene over 0.5% Pd/Al_2O_3 catalyst under MW (solid symbols) and conventional heating (open symbols) conditions at different temperatures (chlorobenzene = 2.5 mmol min^{-1}, catalyst loading = 3 g, H_2/substrate = 4).

Studies on the effect of reaction time show a decline in the conversion after 2 h of the reaction under both microwave and conventional heating conditions (Fig. 3). The decrease in the conversion is more prominent in the case of the conventional heating reaction (~15%) than the microwave reaction (~6%). Also, the MW reaction shows a higher conversion than the conventional heating reaction throughout the experiment. The loss in activity with reaction time is a very common phenomenon observed for the hydrodechlorination reactions caused by the deactivation of the catalyst due to poisoning by HCl formed during the reaction.[16,17] We have conducted experiments to determine the amount and rate of formation of hydrogen chloride from the dehyrodrochlorination of chlorobenzene. The product streams from both MW and conventional reactors were passed through an alkali trap kept in an ice bath containing 40 ml of 2% KOH solution. After one hour the alkali was back titrated using standard 0.05 N H_2SO_4 solution and subsequently the HCl produced was determined. In this context it is very interesting to see that the MW reaction minimizes the loss of activity due to catalyst deactivation. This may be attributed to the selective and rapid absorption of microwave energy by the highly polar HCl molecules that may lead to its enhanced rate of desorption/removal from the catalyst surface, especially in the presence of flowing hydrogen (reducing environment).

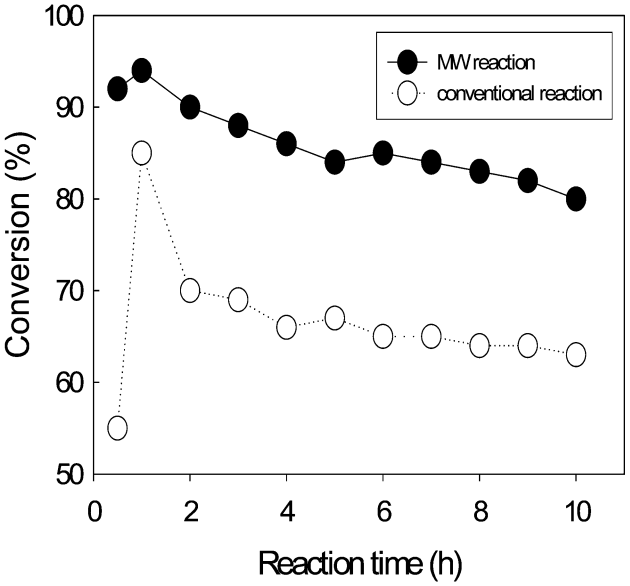

Fig. 3 Comparison of hydrodechlorination of chlorobenzene under microwave and conventional heating conditions over 0.5% Pd/Al_2O_3 catalyst (chlorobenzene = 2.5 mmol min^{-1}, catalyst loading = 3 g, H_2/substrate = 4, temperature = 100 °C).

Another important attribute of the MW-assisted reaction is the improved product selectivity (Fig. 4). A comparison of the product selectivity obtained during the hydrodechlorination of chlorobenzene reveals that MW reaction leads to the formation of benzene selectively whereas the conventional reaction results in the formation of an appreciable amount of cyclohexane besides benzene. This could be explained again due to the accelerated microwave reaction. Being a polar molecule, the substrate (chlorobenzene) absorbs microwave energy relatively easily and forms the hydrodechlorinated product, benzene, before it is desorbed from the catalyst surface. On the other hand, the absorption of energy by the substrate is relatively slow during the conventional heating reaction and this results in the hydrogenation of the hydrodechlorinated product to a certain extent to form some amount of its hydrogenated product *viz.*, cyclohexane.

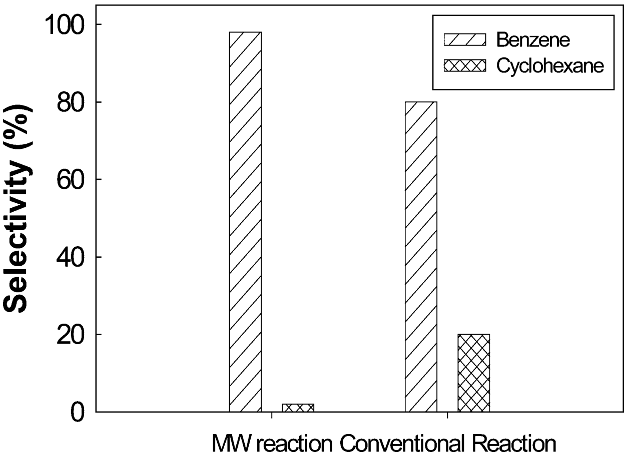

Fig. 4 Comparison of product selectivity of hydrodechlorination of chlorobenzene over 0.5% Pd/Al_2O_3 catalyst under microwave and conventional heating conditions (chlorobenzene = 2.5 mmol min^{-1}, catalyst loading = 3 g, H_2/substrate = 4, temperature = 100 °C).

The microwave absorbing characteristics of a molecule are measured by its ability to store electric charges, which is proportional to the dielectric constant (ε'). The ability of a molecule to convert microwave energy into heat is determined by tan $\delta = \varepsilon''/\varepsilon$, where ε'' is the dielectric loss. The dielectric loss is the amount of input microwave energy that is lost by dissipation as heat. Chlorobenzene can be classified as a low dielectric loss substrate since it has dielectric constant of 2.6, dielectric loss of 0.263 and tan δ equal to 0.1.[28] It is estimated that the energy consumption per mole of the microwave assisted hydrodechlorination reaction is approximately half of what is needed for the conventional reaction. Although, chlorobenzene does not couple to microwave energy very efficiently to generate heat, the mixture serves as a heat sink for highly exothermic reactions. This could be critical for controlling exothermic reactions and avoiding runway conditions, and maintaining high selectivity of the desired products. Also, as the microwaves heat by a dielectric loss mechanism, only the polar substrate (chlorobenzene) absorbs microwave energy in an essentially transparent glass reaction vessel. On the contrary, in the case of conventional heating, the energy is used for heating the substrate, the reaction vessel as well as any other reactor fittings and the heating reaction occurs mainly by a conduction and convection mechanism. This results in a significant reduction in energy consumption in the microwave reaction and the magnitude of the difference in energy consumption between the two types of reaction increases with an increase in the volume or size of the reactor.

The hydrodechlorination reaction of trichlorobenzene shows similar results (Fig. 5). The microwave reaction shows a higher activity and a greater selectivity relative to benzene formation. Reaction under conventional heating conditions affords some hydrogenated product as well as mono- and dichlorobenzenes, whereas the microwave reaction forms only negligible amounts of these secondary reaction products.

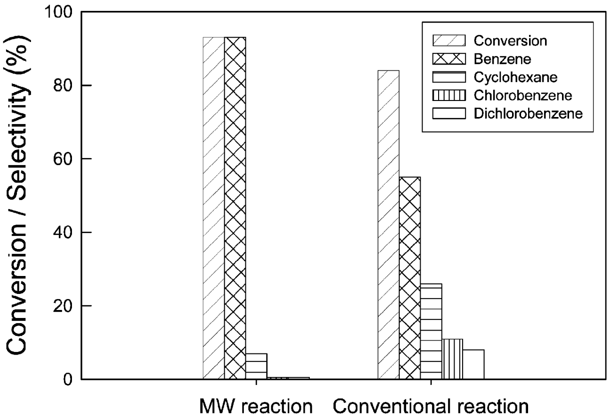

Fig. 5 Comparison of the conversion and product selectivity of hydrodechlorination of 1,2,4-trichlorobenzene over 0.5% Pd/Al_2O_3 catalyst under microwave and conventional heating conditions (trichlorobenzene in acetone = 2.5 mmol min^{-1}, catalyst loading = 3 g, H_2/substrate = 4, temperature = 100 °C).

A comparison of the adsorption properties of the catalysts after the microwave and conventional heating reactions reveals significant and identical loss of metal area in both cases (Table 1).

Table 1 Comparison of the adsorption properties of 0.5% Pd/Al_2O_3 catalyst before and after hydrodechlorination of chlorobenzene under microwave and conventional heating conditions

	Microwave reaction			Conventional reaction		
0.5% Pd/ Al_2O_3	Surface area/m^2 g^{-1} cat	Metal area/m^2 g^{-1} metal	Metal dispersion (%)	Surface area/m^2 g^{-1} cat	Metal area/m^2 g^{-1}metal	Metal dispersion (%)
Fresh	119.5	77.9	17.5	119.5	77.9	17.5
Spent	119.8	14.7	3.3	126.5	14.6	3.3

Nevertheless, the microwave reaction displays a higher activity than the conventional heating reaction throughout the study, thereby suggesting that the loss of metal area is not very crucial in ensuring a good reaction rate. On the other hand, it may be the rate of desorption of the products, especially the poisonous HCl, that could be critical in sustaining the catalyst activity. Microwave irradiation can be very instrumental in the relatively easy removal of the products due to the rapid absorption of microwave energy by the polar HCl, which is primarily responsible for the loss of catalytic activity. It has been shown that the catalytic activity and selectivity of the hydrodechlorination reaction strongly depends on the particle size of the metal and that a higher particle size results in higher activity.[24] This study also corroborates that microwave irradiation leads to agglomeration of palladium particles with the subsequent reduction in metal area and dispersion. This acts synergistically with the high rate of product desorption leading to the advantageous effect of microwaves in the hydrodechlorination reaction.

Conclusions

In summary, it is found that the hydrodechlorination reaction can be significantly improved by conducting the reaction under microwave irradiation conditions rather than conventional heating. The higher rate of the microwave reaction may be attributed to the selective and rapid absorption of microwaves by the polar chlorinated substrates. Moreover, catalyst poisoning by chloride ions may also be minimized under MW irradiation conditions especially at elevated temperature and in a reductive atmosphere due to rapid microwave absorption by the chlorides, which facilitates their relatively easy removal from the surface. Significant and identical loss of active metal surface area is observed in both microwave and conventional heating reactions. Nevertheless, the microwave reaction consistently displays a higher activity than the conventional heating reaction throughout the study suggesting that the rate of desorption of the products, especially the poisonous HCl, may be critical in sustaining the catalyst activity. Microwave heating may ideally facilitate this desorption better than conventional heating reactions. In terms of energy utilization, a significant reduction in the power consumption during the microwave reaction is also observed when compared to the reaction under conventional heating. As the conversion is not 100%, the addition of a recycling unit would be very appropriate for the efficient utilization of the system.

Experimental

The chlorinated benzenes, chlorobenzene and trichlorobenzene, were obtained from Aldrich Chemicals and used as such without any further purification. A 0.5% Pd/Al_2O_3 catalyst obtained from Engelhard Corporation in spherical form was used for the reaction.

Hydrodechlorination of chlorobenzenes was conducted at atmospheric pressure in a continuous phase microwave reactor (CEM, Model-Voyager) equipped with a pressure pump (for feeding the substrate), a stirrer and a fiber optic temperature sensor as shown in Fig. 1. The catalyst was packed in a 15 mL quartz U-tube (1.1 cm i.d, 12.5 cm long) placed in the microwave chamber. Chlorobenzene was fed to the reactor at an adjustable flow rate by the pressure pump along with a controlled flow of hydrogen from a cylinder. In the case of 1,2,4-trichlorobenzene, the solid material was dissolved in acetone (0.5 M) before being pumped through the reactor. The reactor was subjected to microwave irradiation at 100 W power for a given period. The temperature of the system was monitored by a fiber optic temperature sensor attached to the U-tube reactor and was maintained constant at a predetermined value by automatic variation of the MW power. The outlet of the reactor flowed through a pre-cooled collector where the products were collected. The mixture was extracted into diethyl ether, the organic layer was separated and analyzed by a Hewlett-Packard 6890 Gas Chromatograph using a HP-5 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm) and a quadruple mass filter equipped HP 5973 mass selective detector. The product yield reported is the GC yield and the purity of the products was established by TLC as well as the GC-MS analysis of the samples.

The approximate power consumption during the microwave heating method was determined by integrating the average power utilization during the reaction time. The instrument software controls and adjusts the microwave power for a constant reaction temperature. The average power utilization for an isothermal reaction at 100 °C was found to be 92 W for the microwave reactor, whereas the average electrical heating needed for the conventional reactor was more than 200 W.

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PAPER

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pH Measurements of 1-alkyl-3-methylimidazolium chloride in alcohols†

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This paper reports the pH of binary systems containing 1-butyl-3-methylimidazolium chloride, [bmim][Cl], and alcohols [ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol, 2-butanol, 2-methyl-2-propanol (*tert*-butyl alcohol)] in a range of ionic liquid concentrations (c_1) from 0.7×10^{-2} mol dm^{-3} to 3.51×10^{-2} mol dm^{-3} in the temperature range from 290 to 348.15 K. In this work, the pH of solutions of 1-butyl-3-methylimidazolium chloride, [bmim][Cl], or 1-octyl-3-methylimidazolium chloride, [C$_8$mim][Cl], or 1-decyl-3-methylimidazolium chloride, [C$_{10}$mim][Cl], or 1-dodecyl-3-methylimidazolium chloride, [C$_{12}$mim][Cl] + ethanol are also presented, which allows us to show the effect of the alkyl chain length of the cation in the investigated ionic liquids on the solutions' pH. Our investigation permits us to find the required range of the pH values from 3.0 to 8.5. It can be noted that the pH value of binary systems consisting of a chloride ionic liquid and an alcohol is dependent on temperature, the nature of the alcohol, the alkyl chain length substituted at the imidazolium ring and the concentration of [alkylmim][Cl]. The investigated ionic liquids also exhibit superacidity properties. The acidity of the solution increases with an increase of the alkyl chain substituted at the imidazolium ring.

Introduction

Imidazolium ionic liquids have become increasingly important as solvents for both organic and inorganic chemistry. During the last few years other kinds of ionic liquids (ILs) have also been found and applied. At this time, imidazolium, pyridinium, ammonium and phosphonium ionic liquids have been used in many fields of chemistry. These ionic liquids are the best solvents for catalysis and synthesis. Room temperature ionic liquids have developed, in less than 20 years, from US 'Star Wars' research on battery electrolytes into an industrial reality as media for catalytic chemical processes.[1] Ionic liquids fulfil one of the goals of Green Chemistry because they create a cleaner and more sustainable chemistry.[2–12] It is an umbrella concept that describes the search for reduction or even elimination of the use of substances in chemical products and reactions which are hazardous to human health and the environment. Green Chemistry searches for alternative, environmentally friendly reaction media (as compared to the traditional organic solvents) and, at the same time, aims for increased reaction rates, lower reaction temperatures as well as higher selectivities (so an overall cost reduction). Ionic liquids, supercritical CO$_2$ and the use of aqueous media in biphasic systems are some of the most promising reaction media in this field. That is why ILs are receiving increasing interest as environmentally-friendly solvents for a range of synthetic and catalytic processes.[1,13–15] ILs represent clean industrial technology that considers the reduction of waste from an industrial chemical process to a minimum: it requires the rethinking and redesign of many current chemical processes. Using ionic liquids as solvents is one of four main strategies in clean industrial technology.[1] The major reason for the interest in ILs is their negligible vapour pressure, which decreases the risk of technological exposure and the loss of solvent to the atmosphere.[12,16] The specific and selectable solvent properties are a key feature of ionic liquids as solvents and have been utilised to develop a range of synthetically important catalytic reactions, some of which are being investigated as economically and environmentally viable alternatives to existing industrial processes. The low temperature ionic liquids, which are used as reaction media in many of the catalytic processes, represent the first generation of ionic liquid processes. The second generation of ionic liquid processes is based on other, more benign ionic liquids, which are currently under investigation and development in a variety of laboratories around the world. There are a lot of advantages of using ionic liquids. The first one is optimization of compound characteristics through a broad choice of anion and cation combination (tailor-made solvents). The second one is reaction rate enhancement and higher selectivities as well as higher yields. The last one is the advantage of using them as a replacement for Volatile Organic Compounds (VOC) in chemical processes or extraction procedures.

This work follows the acidity of modern binary solvent systems containing 1-alkyl-3-methylimidazolium chloride and an alcohol. The alcohol and ionic liquids are often used during chemical processes as potential successful replacements for conventional media and as a catalyst. The synthesis of cyclotriveratrylene is an acid-catalyzed condensation of benzyl alcohol derivatives.[17] In alcoholysis, ammoniolysis and perhydrolysis catalyzed by *C. Antarctica* lipase, ionic liquids and alcohol are used.[18] The distinct type of reaction accompanied by ionic liquids and alcohols includes hydrogenation,[19] polymerization[20] and many others. The success of the reaction depends on the conditions of the process realisation and, among others, upon the acidity of the reaction media. The acidity and the coordination properties of the ionic liquid are essentially determined by the nature of its anion. The investigated ionic liquid consists of the chloride anion and, as is generally known, a chloride ionic liquid exhibits a strongly coordinating character.[5] Two further phenomena in the field of the acid–base chemistry of ionic liquids deserve to be mentioned. These are the so-called latent acidity and superacidity of protons in ionic liquids. The latent acidity of ionic liquids arises when weak bases are added to buffered neutral chloroaluminate melts. Such melts are formed when, for example, excess alkali metal chloride is added to an acidic chloroaluminate melt.[21,22] The superacidity of protons in ionic liquids is also worth mentioning. This has been observed when strong mineral acids were dissolved in acidic chloroaluminate ionic liquids. The superacid properties of protons in acidic chloroaluminate melts have been explained by the reaction between

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† Electronic supplementary information (ESI) available: pH values of binary systems and pure alcohols. See http://www.rsc.org/suppdata/gc/b4/b403757j/

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the dissolved HCl and acidic species in the melt, which releases protons with extremely low solvation and therefore very high reactivity.[23,24] In contrast to normal superacid systems, superacid ionic liquids are much easier and safer to handle.[23] They could, therefore, represent a very promising alternative to the superacids normally used. Moreover, the H atom in the 2-position of an imidazolium cation possesses significant Brønsted acidity.[14]

This work is a study on the pH range of 1-butyl-3-methylimidazolium chloride in alcohols (C_2–C_{10}) over a wide range of temperatures and concentration as well as of other 1-alkyl-3-methylimidazolium chlorides in ethanol at 295.15 K. The background acidity was also measured for all solvents in the same range of temperatures. The work is a continuation of our systematic investigations into the solubilities of 1-alkyl-3-methylimidazolium chloride in alcohols (C_2–C_{12}).[25–30]

Results and discussion

The first step of the research was the measurement of the acidity of binary systems containing 1-butyl-3-methylimidazolium chloride, [bmim][Cl], and alcohols [ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol, 2-butanol, 2-methyl-2-propanol (*tert*-butyl alcohol)] in a range of ionic liquid concentrations (c_1) from 0.7×10^{-2} mol dm^{-3} to 3.51×10^{-2} mol dm^{-3} at temperatures from 290 to 348.15 K. The same measurements were carried out for the pure alcohols in the same range of temperatures as for the binary mixtures.

Our experimental research on the pH range investigated in this work is characterized by the following: (i) the pH values of binary systems [bmim][Cl] and an alcohol decrease with an increase of the alkyl chain length of the alcohol; (ii) for all binary mixtures of [bmim][Cl] + an alcohol, the pH values decrease with increasing the ionic liquid's concentration; (iii) for all systems the pH values decrease with an increase of the temperature; (iv) for similar concentrations of [bmim][Cl] in binary systems with 1-hexanol, or 1-octanol, or 1-decanol, the pH values decrease slower with an increase of the temperature, contrary to other systems with alcohols with shorter carbon chains [Fig. 1 and Fig. 2]; (v) considering the range of pH values for [bmim][Cl] in C_4- alcohols, it can be noted that pH values increase in the following order: 1-butanol > *tert*-butyl alcohol > 2-butanol [Fig. 3 and Fig. 4]; (vi) a binary system containing [bmim][Cl] + an alcohol does not exhibit an alkaline range for systems with 1-decanol and 2-butanol.

The values of pH as a function of temperature for a binary system with [bmim][Cl] + an alcohol at different concentrations of [bmim][Cl] are presented in Table 1 in the Electronic Supplementary Information.†

Another part of our experiment was the measurement of the pH of alcohols from C_2–C_{10}. Our investigation permits us to note that the pH range of pure alcohols decreases with a decrease of the molar weight of 1-alcohol and with an increase of the temperature [Fig. 5]. It is possible to conclude that for primary, secondary and tertiary alcohols, the pH values of the pure alcohol decrease with an increase of the temperature. The pH values of primary, secondary and tertiary butanols increase in the following order: *tert*-butyl alcohol > 1-butanol > 2-butanol.

The pH values of pure alcohols as a function of temperature are presented in Table 2 in the Electronic Supplementary Information.†

It should be emphasised that even a small addition of chloride ionic liquids causes a decrease in the pH value because a chloride ionic liquid is a superacid. 1-Butyl-3-methylimidazolium chloride is also a strongly coordinating agent. We can expect that the proton in the 2-position of the imidazolium ring coordinates to the hydroxy group of the alcohol by a hydrogen bond. It is due to this proton ring that ionic liquids exhibit the strong acidic effect, which is why the acidity increases with an increase of the concentration of [bmim][Cl] in binary mixtures with alcohols.

For comparison, the pH of solutions of [C_8mim][Cl], or [C_{10}mim][Cl], or [C_{12}mim][Cl] in ethanol at 295.15 K at various

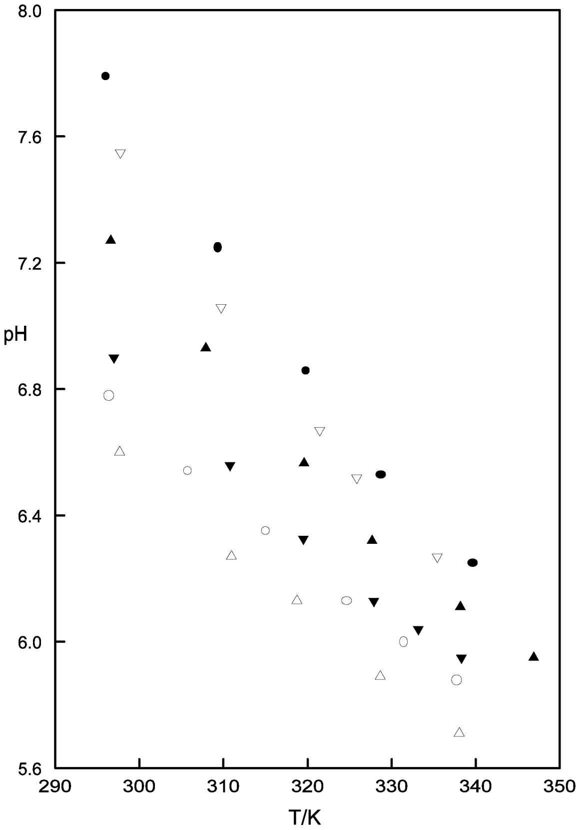

Fig. 1 The pH values for the binary system [bmim][Cl] + 1-butanol as a function of temperature: ● – c_1 = 0.0265 mol dm^{-3}, ▽ – c_1 = 0.0403 mol dm^{-3}, ▲ – c_1 = 0.0458 mol dm^{-3}, ▼ – c_1 = 0.0693 mol dm^{-3}, ○ – c_1 = 0.0736 mol dm^{-3}, △ – c_1 = 0.1297 mol dm^{-3}.

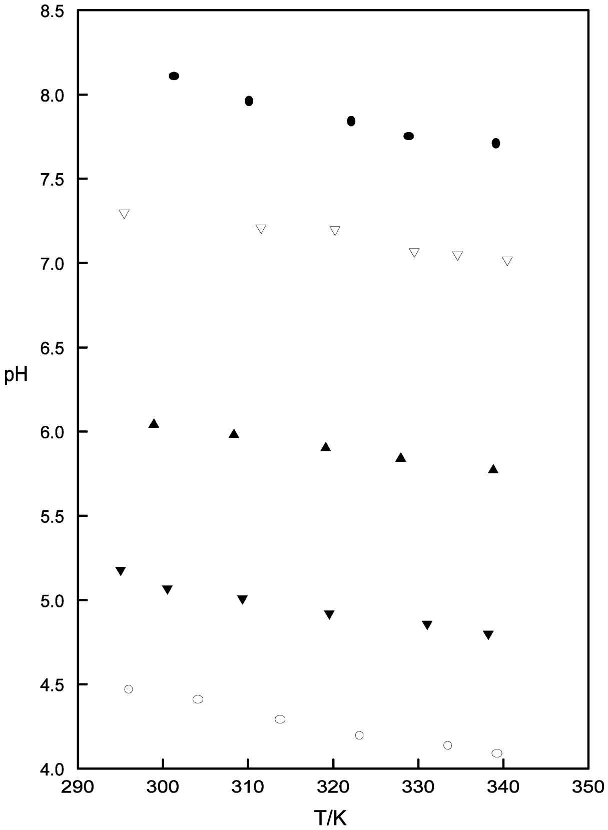

Fig. 2 Dependence of the pH values for the binary system [bmim][Cl] + 1-hexanol on temperature: ● – c_1 = 0.0079 mol dm^{-3}, ▽ – c_1 = 0.0466 mol dm^{-3}, ▲ – c_1 = 0.0892 mol dm^{-3}, ▼ – c_1 = 0.1205 mol dm^{-3}, ○ – c_1 = 0.1529 mol dm^{-3}.

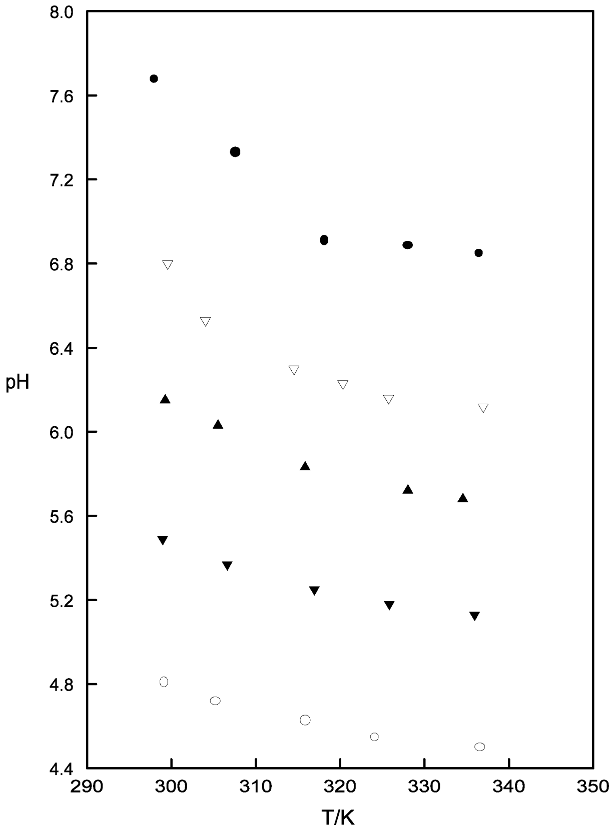

Fig. 3 The pH values for binary system [bmim][Cl] + *tert*-butyl alcohol as a function of temperature: ● – c_1 = 0.0042 mol dm^{-3}, ▽ – c_1 = 0.0256 mol dm^{-3}, ▲ – c_1 = 0.0490 mol dm^{-3}, ▼ – c_1 = 0.0731 mol dm^{-3}, ○ – c_1 = 0.1116 mol dm^{-3}.

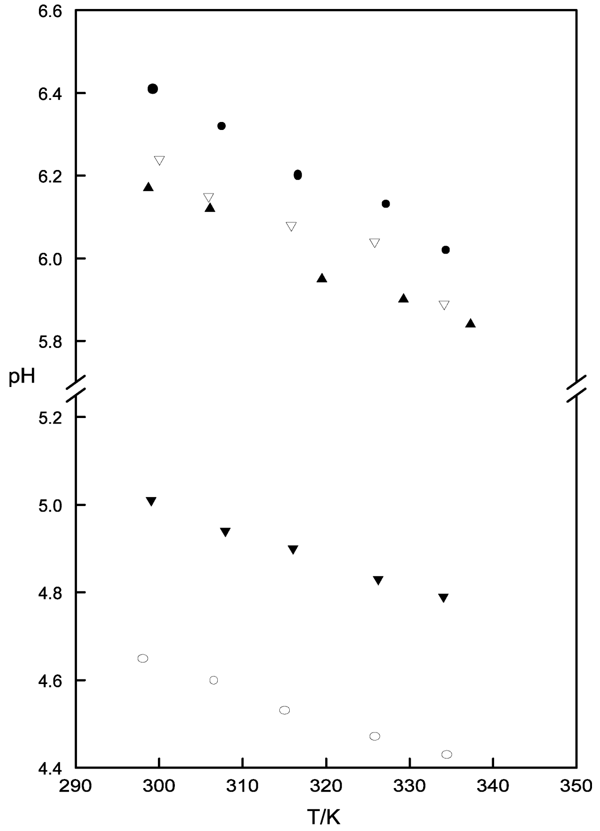

Fig. 4 Dependence of the pH values for binary system: [bmim][Cl] + 2-butanol on temperatures: ● – c_1 = 0.0099 mol dm^{-3}, or ▽ – c_1 = 0.0300 mol dm^{-3}, or ▲ – c_1 = 0.0391 mol dm^{-3}, or ▼ – c_1 = 0.1692 mol dm^{-3}, or ○ – c_1 = 0.3481 mol dm^{-3}.

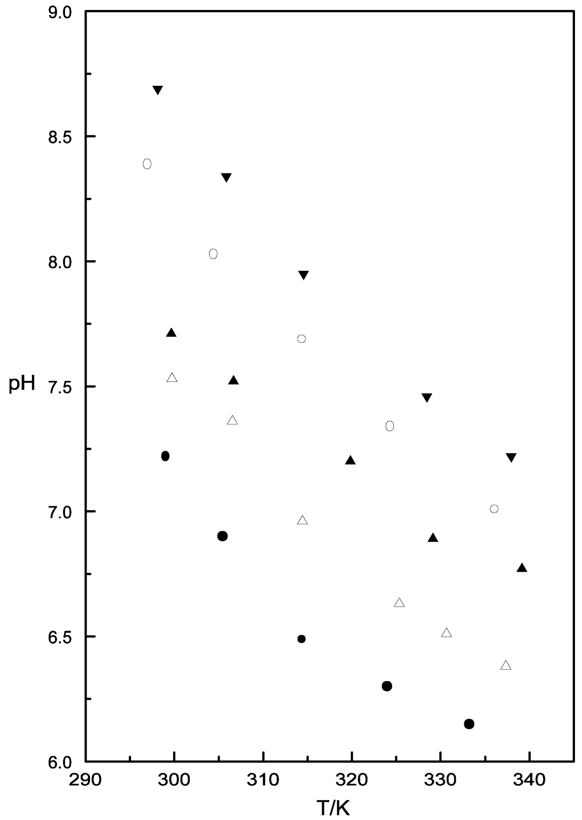

Fig. 5 The pH values for the pure 1-alcohols as a function of temperature: ● – ethanol, △ – 1-butanol, ▲ – 1-hexanol, ○ – 1-octanol, ▼ – 1-decanol.

concentrations of ionic liquid was measured. Analyzing the influence of the alkyl substituted at the imidazolium ring, it can be noted that with an increase of the alkyl chain length in the imidazolium cation, the solutions' pH decreases and the solution is more acidic [Fig. 6]. This feature is opposite to that observed for alcohols, where with an increase of the alkyl chain of an alcohol, the pH increases. However, for solutions of [bmim][Cl] + an alcohol, the pH decreases with an increase of the alkyl chain length of the alcohol.

Moreover, the dependence of ΔpH = pH(alcohol + IL) − pH(alcohol) on temperature was presented. The dependence ΔpH permits us to conclude that for a low concentration of ionic liquids (for example c_1 = 0.0042 mol dm^{-3}), the shape exhibits a characteristic minimum [see Fig. 7] and for a higher concentration of ionic liquids (for example c_1 = 0.0265 mol dm^{-3}), the shape demonstrates a maximum [see Fig. 8]. ΔpH exhibits positive and negative values and strongly depends on the mixtures under study and the temperature. This confirms our previous conclusion that the chloride ionic liquid is a superacid and even a small addition of ionic liquid to the solvent decreases the pH values and the ΔpH has negative values for an average concentration of IL in the solution higher than 0.03 mol dm^{-3}.

Conclusions

In conclusion we can state that the acidity of binary systems containing 1-butyl-3-methylimidazolium chloride, [bmim][Cl], + an alcohol were determined over a wide range of temperatures and molar concentrations of [bmim][Cl]. As we expected, the addition of [bmim][Cl] to the alcohol permits us to find the required range of pH values from 3.0 to 8.5. Thanks to that we can easily modify the range of pH values of the reactions carried out in mixtures of 1-butyl-3-methylimidazolium chloride and an alcohol. Moreover, analyzing the influence of the alkyl substituted at the imidazolium ring, it can be noted that with an increase of the alkyl chain length in the imidazolium cation, the solutions' pH decreases and the

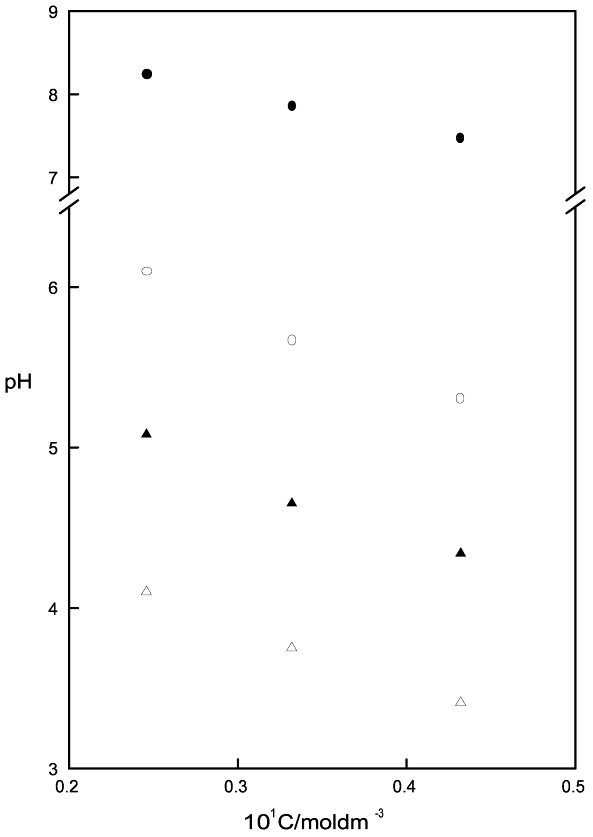

Fig. 6 The pH values for binary system: {● – [bmim][Cl], or ○ – [C_8mim][Cl], or ▲ – [C_{10}mim][Cl], or △ – [C_{12}mim][Cl]} + ethanol at 295.15 K.

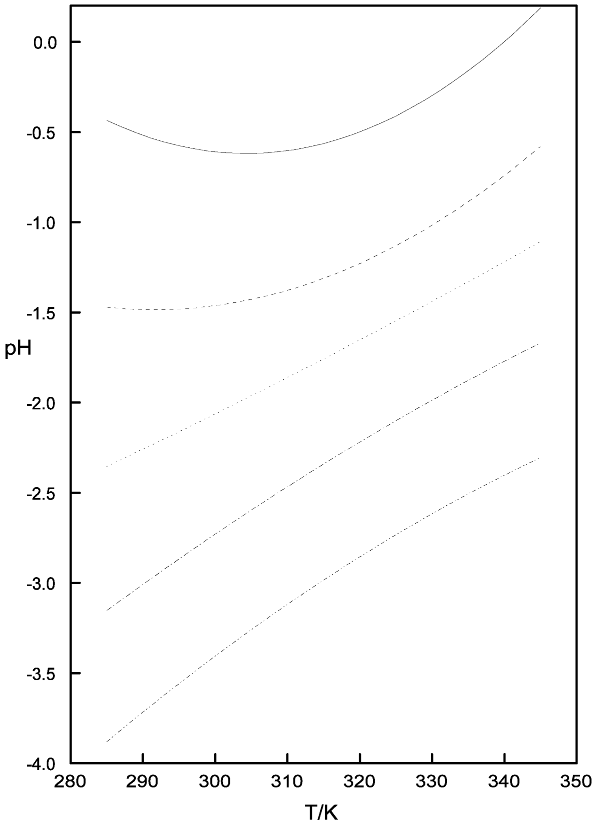

Fig. 7 The ΔpH values for the binary system [bmim][Cl] + *tert*-butyl alcohol as a function of temperature: solid line – $c_1 = 0.0042$ mol dm^{-3}, dashed line – $c_1 = 0.0256$ mol dm^{-3}, dotted line – $c_1 = 0.0490$ mol dm^{-3}, dashed-dotted line – $c_1 = 0.0731$ mol dm^{-3}, dashed-dotted-dotted line – $c_1 = 0.1116$ mol dm^{-3}.

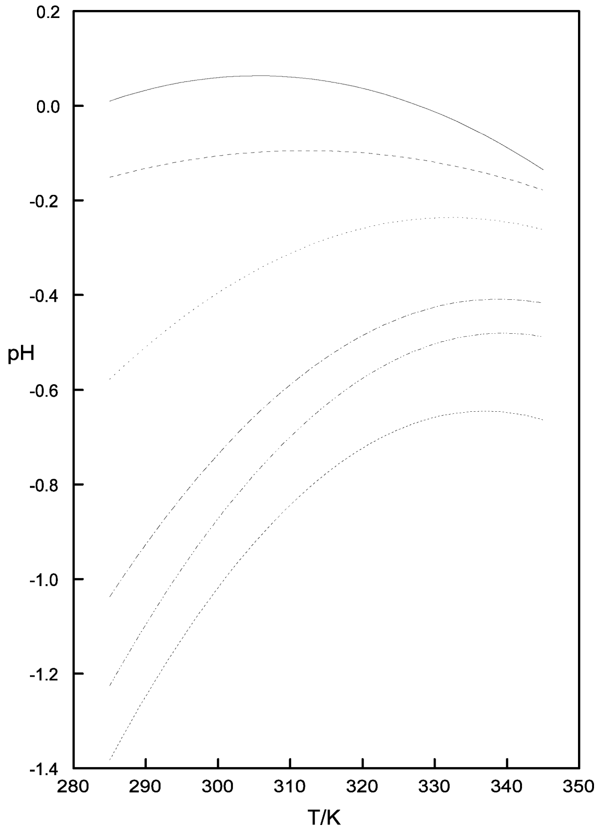

Fig. 8 The ΔpH values for the binary system [bmim][Cl] + 1-butanol as a function of temperature: solid line – $c_1 = 0.0265$ mol dm^{-3}, dashed line – $c_1 = 0.0403$ mol dm^{-3}, dotted line – $c_1 = 0.0458$ mol dm^{-3}, dashed-dotted line – $c_1 = 0.0693$ mol dm^{-3}, dashed-dotted-dotted line – $c_1 = 0.0736$ mol dm^{-3}, short dashed line – $c_1 = 0.1297$ mol dm^{-3}.

solution is more acidic. Generally, the results of our research permit us to conclude that the pH value of binary systems consisting of a chloride ionic liquid and an alcohol depends on the temperature, the nature of the alcohol, the alkyl chain length substituted at the imidazolium ring and the concentration of the ionic liquid.

[Alkylmim][Cl] is one of the most common types of IL presented in the literature. Good knowledge of [alkylmim][Cl] and its solutions promises that chemical processes could, in the future, be friendlier to the environment.

Experimental

The 1-alkyl-3-methylimidazolium chloride sample was obtained from Solvent Innovation GmbH, Köln, Germany. The sample purities were ≥98 mass percent and they were used without any chemical purification. The purification and first drying were made by the private producer (Solvent Innovation). Before every experiment the investigated ionic liquids were dried by high vacuum line and the water contamination was determined using the Karl–Fischer technique. The water content was < 0.02 mol percent. Moreover, the purities were also checked by DSC measurements.[26] All alcohols were delivered from Sigma–Aldrich Chemie GmbH, Stenheim, Germany. Before direct use they were fractionally distilled over different drying reagents to the mass fraction purity ≥99.8 mass percent. The solvents were stored over freshly activated molecular sieves of type 4 Å (Union Carbide). The analysis for water contamination using the Karl–Fischer technique for the alcohols showed that the impurity in each of the solvents was < 0.02 mol percent. Three kinds of pH standard buffer solution delivered from POCh S.A., Gliwice, Poland with pH values equal to 3 ± 0.02, 7 ± 0.02 and 10 ± 0.02 were used for calibration of the pH apparatus. The solutions for measurements were prepared under the nitrogen in a dry-box.

The acidity measurements were carried out with an Elmetron pH/conductivity meter CPC-401 using a combination pH electrode EPS-1 (a glass electrode and a reference electrode) delivered from Hydromet, Gliwice, Poland. The accuracy of acidity measurements was ±0.01 pH unit. The pH measurements cell was thermostated and the temperature was controlled using a calibrated GALLENKAMP AUTOTHERM II thermometer. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The accuracy of temperature measurements was ±0.01 K. The investigations were carried out in the cell over a wide range of concentrations of ionic liquid and in the range of temperatures from ambient to 348.15 K. The mixtures of solute and solvent were prepared by weighing the pure components to within 1×10^{-4} g. Before every pH reading, three types of pH buffer solution were used to check the measurements of the electrode.

Acknowledgements

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