Chairmen of the European Research Councils' Chemistry Committees

Young Chemists' Workshop on

Neoteric solvents as reaction media: reality and future.

REPORT

Organized by the Chemistry Department of CNRS in St Malo (France)
April 17th - 21st 2004

Motivation and objectives :

The main objectives of this workshop were :

- to define the state of the art in European efforts to make neoteric solvents a new and superior alternative to conventional solvents,
- to evaluate the impact of neoteric solvents as new reaction media within the objectives of innovation for sustainability in the fields of chemistry and preventive environmental protection,
- to contribute to the structuration and integration of the research efforts within the European Community in this very active but disparate area,
- to encourage and facilitate the formation of European and trans-disciplinary research networks of any kind in this promising area.

A main concern in the development of production processes is their worldwide ecological and economical impacts. How these processes can be improved in view of the economical and ecological use of resources and wastes management ? The development of new chemistries through new media which should allow for improvement of single steps will be of major interest.

New solvent systems such as ionic liquids, fluorous phases and supercritical fluids have recently been added to the arsenal of chemists. For example, ionic liquids offer a wide range of significant improvements upon conventional volatile organic solvents (VOS). Currently the primary researchers in this domain are mainly synthetic chemists. There are many more application fields for ionic liquids and other neoteric solvents, including biotechnologies, catalysis, extraction technologies, batteries, fuel cells, nuclear waste treatment, material science, electrochemistry etc… Efficient development of these fields require integrated efforts based on a wide inter-disciplinarity including synthetic process and physical chemists, electrochemists, spectroscopists, chemical engineers, biochemists, biologists, theoretical chemists, and physicists. It has been the aim of this CERC3 meeting to bring together young scientists involved in these different areas in order to confront results and ideas and therefore cross-fertilize this new field. A most important issue of this meeting is to prepare for future European collaborations and networks.

Topics:

Synthesis and manufacture of neotericsolvents
Green organic synthesis
Biotechnologies in neoteric solvents
Homogeneous catalysis
Electrochemistry
Extraction and processing technologies
Physical, structural, spectroscopic and thermodynamic properties.
New reactor systems

Organization:

Professor Marc Ledoux
Director of the Chemistry Department
CNRS
3, rue Michel Ange
75794 Paris Cedex 16
FRANCE

Annie Dalbéra
European Affairs
Co-secretary of CERC3 "Chairmen of the European
Councils' Chemistry Committees" at
CNRS- Chemistry Department
3, rue Michel Ange
75794 Paris Cedex 16
FRANCE
Tel : + 33 1 44. 96.40.87 (direct)
Fax : + 33 1 44. 96.53.70
E-mail: annie.dalbera@cnrs-dir.fr

Local Workshop Organizer *:*
Dr Michel Vaultier
Université de Rennes 1,
Institut de Chimie, Bât. 10A,
UMR 6510, Avenue du Général Leclerc,
35042 Rennes Cedex. France.
Tel. : + 33 (0)2 23 23 62 74.
Fax : + 33 (0)2 23 23 69 55
E-mail: Michel.Vaultier@univ-rennes1.fr

Junior correspondant
Dr Martinus Werts
Université de Rennes 1,
Institut de Chimie, Bât. 10A,
UMR 6510, Avenue du Général Leclerc,
35042 Rennes Cedex. France.
Tel. : + 33 (0)2 23 23 59 54
Fax : + 33 (0)2 23 23 69 55
E-mail: Martinus.werts@univ-rennes1.fr

Secretary *:*
Mrs A. Delahaie.
Université de Rennes 1,
Institut de Chimie, Bât. 10C,
UMR 6510,Avenue du Général Leclerc,
35042 Rennes Cedex. France
Tel. : 33 (0) 2 23 23 67 97.
Fax : 33 (0) 2 23 23 62 92
Annie.Delahaie@univ-rennes1.fr

Introduction

This workshop was held in St Malo from the 17th to the 21st of April. A tour to Mt St Michel and a guided visit of the abbey has been organized on monday afternoon the 19th followed by a banquet at the “Mère Poulard restaurant” which will probably remain present in memories for a while.

37 participants and 3 representatives of CNRS and CERC3 attended the workshop from the following countries :

- Finland: 1
- France: 6
- Germany: 5
- Italy: 1
- Portugal:2
- Slovenia: 1
- Spain: 1
- Sweden: 2
- Switzerland: 2
- The Netherlands: 2
- United Kingdom: 2
- USA: 3

3 representatives from CNRS attended the workshop. Pr P.Vigny, vice-director of the chemistry department at CNRS made the welcome and the opening of the meeting. Mrs Annie Dalbera co-secretary of CERC3 at CNRS, made an excellent presentation of what is CERC3 and its role. Dr J. Muzart participated to the workshop both as a scientist and a representative of the chemistry department at CNRS.

The organisation of the meeting has been as follows :

8 plenary lectures given by experienced scientists have constituted the spinal of the meeting and introduced the different topics: 2 from Germany, 2 from UK, 1 from Spain and 3 from France).

26 presentations of 20 minutes (15’ talk + 5' discussion) have been given by the young participants. One should mention the very high scientific level and quality of these talks which opened the way to excellent and numerous discussions and scientific exchanges making that meeting very entertaining and exciting. This was followed by a round table held on wednesday morning which conclusions are presented below.

Executive summary

It clearly appeared through the prism of the 8 plenary lectures and the 26 oral communications given at this workshop that the chemistry of neoteric solvents is a new, fast developing and highly innovative field of research with tremendous potential to influence the future development of chemical synthesis. It also appeared very clearly that this chemistry is at the interface of several topics (theory, simulation, understanding of chemical reactivity, synthesis, material sciences, solid phase chemistry, catalysis, biotechnologies, reactors design …) and that an important feature for the future of this scientific area within the European community is the development of strong collaborations. This is most probably a "*sine qua non*" condition to stay at the forefront in the worldwide competition and keep the leading position that we hold at the moment in this area well ahead from the US and South-east Asia.

Besides the now well-known aspects of chemistry of and in ionic liquids and supercritical fluids, in particular $scCO_2$, quite a number of new topics have shown up :

- Apart from the special aspects that each of the solvent concepts provides, a highly important common feature of all these approaches is that they deal with reaction systems that mostly contain at least two phases. Often liquid-liquid (eg ionic liquid/organic solvent or water) or liquid-fluid (eg ionic liquid/-$scCO_2$) processes are used but solid-fluid (eg supported ionic liquid on solid phase/$scCO_2$ or other supercritical phases) and solid-liquid (e.g functionalised surfaces/ fluorinated solvents or molecular solvents) systems are of increasing importance.

- Task specific ionic liquids specially design for catalysis, biocatalysis, supported synthesis, combinatorial chemistry, extraction techniques, material sciences etc…constitute an very important emerging area particularly well suited for the multidisciplinary cooperations.

- The use of freons and water in the supercritical state appeared to be also a very promising area, where much remains to be done. Crossing of this topic with chemistry in ionic liquids should lead to fascinating collaborative developments.

- The study of physical properties and modelisation of all these systems, in close relationship with mechanistic studies should bring tremendous amounts of new information useful for the synthetic chemists and the engineers.

- We can also easily foresee exciting developments in the field of flow-through and micro reactors,. In this respect, the talks by Prs S. Haswell (Hull)on microfluidics and of A.

Kirschning (Hannover) on flow-through reactors have revealed to every participants that coupling technology and new concepts in chemistry could be very fruitful and promising.

- Ionic liquids are entering industrial plans. This has been beautifully shown by Pr P. Wasserscheid. The design of new reactors and chemical processes based on these technologies is a fascinating endeavour.

It also appeared from the discussions that the research efforts in France in the area of ionic liquids should be structured in order to increase efficiency, avoid duplication of research and favoured crossing of competences and knowledge. But this not only true for France and this structuration should be envisioned at the European level, may be in the frame of bilateral research networks like the GDRI French structures. This really worth it to seriously consider this possibility. My personal discussions with several participants show that this is a strong will and motivation for everybody. CNRS and DFG should play a central role in this.

Finally, we would like to point out that one should be extremely careful in handling the concept of green chemistry. So much chemistry is just chemistry painted in green as I like to say!. We prefer from far the statement that all our efforts are directed towards a cleaner, less material and energy consuming, safer and more performing chemistry. The ultimate goal is of course to end up with a green chemistry but the way is still very long and difficult.

Round table discussions : report.

The Chemistry of Neoteric solvents is a field of multiple-competences, knowledges and technologies. This chemistry is at the interface of several topics (theory, simulation, understanding of chemical reactivity, synthesis, material sciences, solid phase chemistry, catalysis, biotechnologies, reactors design …). Practical aspects show that specific equipment is required to perform for example experiments with supercritical fluids. Therefore, the participants of this CERC3 workshop have agreed upon building up a close European network for the exchange of scientists, technology and knowledge as a collective effort :

- to gain insight into the basic properties of such different reaction media as ionic liquids, $scCO_2$, scH_2O, or fluourous phases.
- to give opportunities in using costly equipment such as sCO_2 reactors or others by several groups.
- to propose and develop innovations in synthesis, catalysis, biocatalysis, material sciences etc…
-to advance design of interfacial processes to improve chemical reactions
-to design new reactors and chemical processes.

To that end, an integrated effort of synthetic, theoretical, and physical chemists is highly aspired.

The following items are of major importance:

- Measuring, Calculating, Understanding

Neoteric solvents have received major interest in the chemistry community over the past few years. But apart from the vast number of new applications that have been (and surely will be) developed, the *basic understanding* of physico-chemical processes on a microscopic level in these media is very low. Surely, this comes as no surprise, since even the microscopic description of liquid water is still very incomplete. Nonetheless, this basic understanding is substantial for the rational *design* of new solvent systems that meet the special properties needed for modern synthetic and industrial chemistry.

. *Our principle goal* is to provide a basic set of data for the variety of media, thus providing *generic information* to be able to *quantify* certain properties. This will then result in a much higher *predictive power* for the design of new media.

To achieve this goal, a group of very simple chemical processes (e.g. tautomerization or simple bimolecular reactions, such as acid-base reactions, redox reactions, proton transfer, electron transfer, S_N2,...) are going to be studied comparatively in the variety of very different media – experimentally as well as theoretically. One focus will be on *interactions* – interactions of the reacting molecules with the medium, interactions of the molecules with each other, interactions at the interphases (e.g. for multiphasic systems). The research will consist of determining the kinetics and thermodynamics for the given reaction in molecular, including fluorous phase and supercritical, and ionic solvents, and relating the parameters determined to the solvent-solute interactions described by molecular dynamics and *ab-initio* methods and experimentally by diffraction techniques. By understanding the impact of the interactions of the solvent species, hydrogen bonding, Van der Waals, Coulombic *etc*., on the fundamental processes, i.e. do they affect the equilibrium or simply the transition state, it will be possible to predict which solvent, neoteric or otherwise, will be best for a given process.

The results of these studies will be highly relevant to the synthetic and the engineering groups of our network and thus have a direct impact on the design of (a) new reaction media, (b) new reactivities and (c) new technical processes. These groups, in return, will help to define "important" properties (e.g. solubilities, separations, reaction rates, equilibria, heat flow, densities,...) to be studied by us with respect to the application.

- **Synthesis and Neoteric Solvents**
-

New media with combination of neoteric solvents:

High viscosity of ionic liquids, which prevents efficient stirring in many processes, could be reduced by the combination of this solvent with $scCO_2$. The later can also modify the melting point of neoteric solvent; this can give opportunities to expand the range of usable ionic liquids. Mixing water and ionic liquids may also lead to new and original media.

Combining solid phase synthesis with neoteric solvents:

Functionalized surfaces (functionalized reactors, flow-through reactors, ionic polymers, fluorinated polymers…) or specific devices (micro fluidic reactors) can be combined with the use of ionic liquids, supercritical fluids and fluorinated solvents (for extraction and better diffusion). Many competences and collaborations are required in that field, such as chemists with experiences in solid phase synthesis, neoteric solvents, simulation of reactors etc….

Catalysis: Biotechnology can be connected with neoteric solvents for immobilization of biocatalysts, this field is growing up. Neoteric solvents can be used to recycle well known or original catalysts and to decrease the price of a process, but problems still remain and loss of activity of catalyst is often observed, better understanding in interaction between catalysts and neoteric solvent is required. Nanoparticules as catalysts can be obtained in neoteric solvents, this field is growing up, since these materials are more often present than we think in many processes. We need lots of competences (characterization, heterogeneous and homogeneous chemistry, physical organic chemists, simulation) and collaborations could be engaged. These materials are of interest in synthesis since they can lead to more active catalysts (the size of particules can be controlled) and better selectivities (protecting shell i,e stabilizing agents of nanoparticules can induce selectivities).

Biocatalysis in neoteric solvents:

The ability of enzymes to catalyze synthetic organic chemical reactions with high level of activity, enantioselectivity and stability have been clearly demonstrated in neoteric solvents, even under very harch reaction conditions (i.e. 100 bars of pressure and 150 ºC). Indeed, biphasic reaction systems, formed by an ionic liquid phase containing enzymes and a supercritical phase i,e $scCO_2$ which transports substrates and products in a continuous reactor were shown to be able to produce in only one step without using molecular solvents enantiopure products. The activity, stability and the important role of mass-transfer phenomena were analyzed. These very nice findings open the way to very large developments in this area.

Synthesis of new ionic liquids, in particular task specific ionic liquids or how to make a solvent which can be more than a solvent:

Chiral ionic liquids for enantioselective processes are in progress, results are not good at that time but efforts are worthwhile and must be pursued. Ionic liquids can be used to immobilize catalysts and therefore allowing for their recycling. Purification and recycling of ionic liquids is an important problem which concerns the all community. The conception and synthesis of task specific ionic liquids specially designed for special purposes (bases, acids, scavengers, organic functions, ligands, fluorescent probes etc…) is probably a major topic for innovation in the near future in connection with other important topics including solution phase supported synthesis, combinatorial chemistry, material sciences, biotechnologies etc… .

Chemistry in water:

Supercritical water can also be used as a new reaction media. A very interesting talk showing how to gasify biomass by using supercritical water has been presented. This might be of large interest for the future. Water itself as a reaction media is not new but it seems that revisitation of this reaction media could be of broad interest when looking at new selectivities and reactivities.

- **Technical Applications**
-

With respect to technical applications it became clear during discussions that the understanding and optimization of interface processes between neoteric solvents and between neoteric solvents and functionalized surfaces are of the highest importance

"Advanced design of interfacial processes can improve chemical reactions by combinations of neoteric reaction media and functionalised surfaces for new reactivities and reactors (micro-reactors, flow-through reactors…) and advanced analytic and processing tools

In-between this broad bracket we see space for a whole range of highly innovative project ideas that will be subject of bilateral proposals submitted by the individual teams to CERC3. Just to illustrate the scope of such concrete projects we want to give here some examples that were already discussed among the partners :

1) The application of ultrasounds to improve mass transfer between an ionic catalyst layer and supercritical CO_2. Future joint research should therefore target these fundamental aspects. This effort could result in the design of interfacial processes directed to improve selectivity To achieve this deeper understanding of the interfacial process, importance of new analytical and processing tools especially adapted to work in / with neoteric solvents has been emphasized during the discussions.
2) Catalytic systems consisting of an ionic liquids and a supercritical medium other than CO_2 (e.g. sc CH_2F_2, scNH_3 etc);
3) The application of electrical and magnetic fields to create special interface effects in systems of ionic liquids and scCO_2
4) Adjustable functionalized surfaces by means of pressure dependent swelling processes using compressed CO_2.