



IONIC LIQUIDS MATERIAL AS MODERN CONTEXT OF CHEMISTRY IN SCHOOL

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ABSTRACT

One way to improve students' chemistry literacy which is demanded in the modernization of modern technology-based chemistry learning is by studying ionic liquids. Low level of scientific literacy of students in Indonesia as revealed in the PISA in 2012 was the main reason of the research. Ionic liquids-based technology are necessary to be applied as a context for learning chemistry because: (1) the attention of the scientific and technology community in the use of ionic liquids as a new generation of green solvent, electrolyte material and fluidic engineering in recent years becomes larger, in line with the strong demands of the industry for the provision of new materials that are reliable, safe, and friendly for various purposes; (2) scientific explanations related to the context of the ionic liquid contains a lot of facts, concepts, principles, laws, models and theories can be used to reinforce the learning content as a media to develop thinking skill (process/competence) as demanded by PISA; (3) The modern technology-based ionic liquid can also be used as a discourse to strengthen scientific attitude. The process of synthesis of ionic liquid involves fairly simple organic reagents, so it deserves to be included in the chemistry subject in school.

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Keywords: chemistry literacy, chemistry content, ionic liquids material

INTRODUCTION

One result of the Programme of International Student Assessment studies (PISA) in 2012 about the ability of science literacy, showed that only a few (6.9%) of Indonesian students can clearly identify scientific issues in various contexts (OECD, 2013). According to the Firman (2007), Hayat & Yusuf (2010) it is suspected because of the content of curriculum (experiments and teaching materials), learning, and assessment still focus on the dimensions of the content (knowledge of science) that are mostly done by memorizing whilst ignoring the other dimension of content (knowledge about science), process/competence (thinking skill) and the context of the application of science (e.g. technology).

The integration between contexts of the science application with modern technology is

the core idea of modern curriculum, as stated by Tausch & Bohrmann-Linde (2007) that the modern curriculum should be able to combine the established content and methods with something innovative. Modernization of curriculum content (especially chemistry) can be done based on the scheme in Figure 1.

Figure 1 shows that the chemistry learning content (Unterrichtsmaterialien) containing the model, media, concepts, and experiments are obtained from scientific sources (Wissenpool) in the form of chain reaction, techniques, definitions, phenomena and implementation. The sources of knowledge can be obtained from daily life in science, technology, environment and culture. Source of chemical science is the scientific explanation of the scientific community/chemist, while Unterrichtsmaterialien are teaching materials that can be taught (teachable), useful (fruitful) and makes it easy to learn (accessible). Sources

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of knowledge can be collected and filtered based on certain didactic and method into the learning contents.

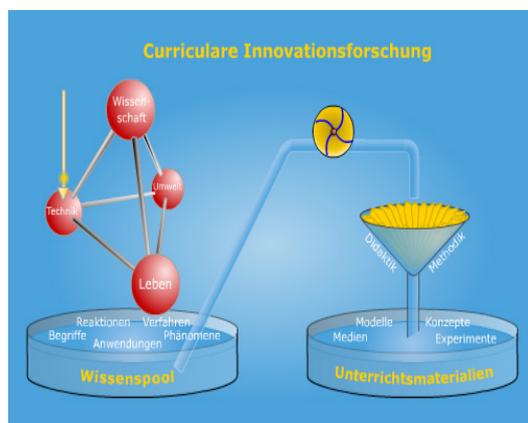


Figure 1. Schematic of Modernization Curriculum Content (Tausch and Bohrmann-Linde, 2007)

The idea of Tausch & Bohrmann-Linde (2007) is in accordance with the views of F. A. Kekule (German chemist) which states that research in Chemistry should relate to the process of metamorphosis of chemistry material in school. This shows that research in Chemical Education should relate to the process of metamorphosis in chemistry curriculum content. The basic knowledge of paradigm-based modern science; e.g. quantum physics, astronomy, molecular biology, and material chemistry; can be introduced to senior high school students in second and third years. Instruments of practicum for high school students should be replaced with ones which support the modern sciences, such as UV (ultraviolet) and VIS. It would also be much better when the high school students in Indonesia have been given the basic knowledge of IR (Infra Red) spectroscopy, NMR (Nuclear Magnetic Resonance) and MS (Mass Spectroscopy), as what happens to students in developed countries.

One of the chemical subjects which support the growth of modern technology is the ionic liquid. This modern material is an object that consists of only the ionic species (cation and anion) without neutral molecules. It maintains a relatively low melting point at the temperatures of <math><100-150\text{ }^\circ\text{C}</math>, generally at room temperature (Hagiwara, et al., 2000). Molten salt which usually has a high melting point and viscosity is also very corrosive. This is in contrast to the ionic liquids which stay in liquid form at room temperature while having a relatively lower viscosity. Moreover, ionic liquids do not have corrosive properties (Toma, et al., 2000). Ionic liquids have

a very wide liquidity range, non-volatile, non-flammable, and high stabilities of heat, chemical and electrochemical (in some cases it even shows thermal stability up to $400\text{ }^\circ\text{C}</math>). In addition, we can overlook the vapor pressure while having the ability to dissolve many organic and inorganic compounds as well as the various miscibility natures when it is mixed with water solvent organic solvents (Davis, et al., 2003).$

Ionic liquid-based modern technology are predicted to be able to be used as a context for learning chemistry in school for the following reasons: **First**, the attention of the scientific community and international technology in the use of ionic liquids as a new generation of green solvent, electrolyte material and fluidic technique in recent years keeps growing, in line with the strong demands of the industry for the provision of new materials that are reliable, safe, and friendly for various purposes (Earle, et al., 2000; Ohno, 2001 & Brennecke et al., 2001). Researches of ionic liquids in electrochemistry are directed as electrolyte materials in batteries, metal plating and sensor system (Bhatt, 2003 & Buzzeo, et al., 2004). Ionic liquids are also developed as green solvent in chemical synthesis, catalyst and biocatalyst (Olivier, et al., 2002; Vidis, et al., 2005 & Miao, et al., 2006). Field engineering uses ionic liquids as fluidic technique as the heat carrier, lubricants, surfactants and the liquid crystals (Ye, et al., 2001; Merrigan, et al., 2000; Awad, et al., 2004; Hollbrey, 1999 & Gordon, et al., 1998). **Second**, the scientific explanation related to the context of the ionic liquids contains a lot of facts, concepts, principles, laws, models and theories which can be used to reinforce the chemistry learning content as a media to develop thinking skill (process/competence) demanded by PISA. **Third**, modern technology based on ionic liquids can also be used as a discourse to empower students' science attitude.

DISCUSSION

Modernization of Curriculum Content via Context of Modern Technology of Ionic Liquids-Based

Chemistry education research in this framework is related to the effort to develop experimental design, concept-context and teaching materials that can interpret and communicate the modern science, which makes it easy to understand and attracts students. One of potential material to be used as the chemistry context in the school is ionic liquids in various segments of modern technology shown in Figure 2.

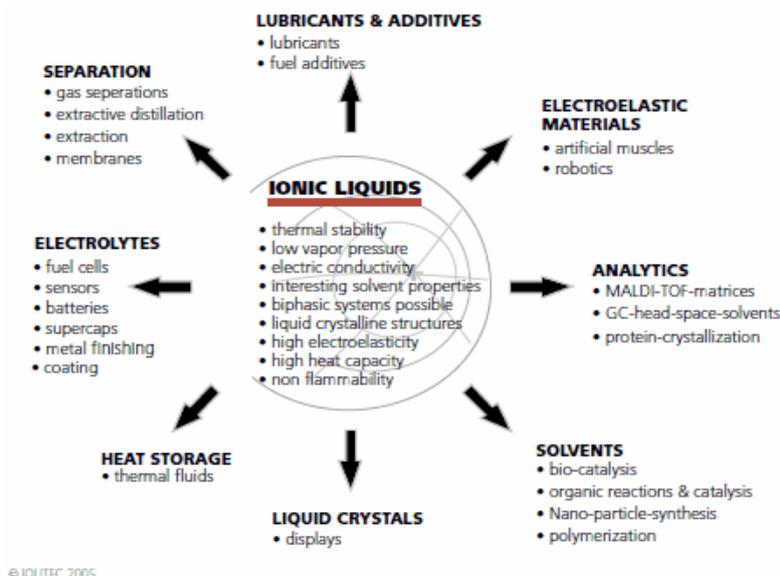


Figure 2. Context of Ionic Liquids Application in Modern Technologies (IOLITEC, 2005)

The ionic liquids are materials that solely consist of ionic species (cation and anion). Cation system in the ionic liquids (and ionic liquid crystal) is generally a bulky organic cation, such as N-alkilammonium, P-alkilposfonium, N-alkyl-pyridinium, S-alkylsulfonium, N-alkil-pirolidinium, N, N-dialkilpirazolium and N, N-dialkilimidazolium. The biggest fraction of the research focus has been geared to the cation N, N-dialkilimidazolium 1, because of the enormous differences in physicochemical properties that can be provided. The cation structure is shown in Figure 3.

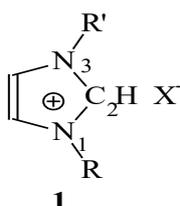


Figure 3. Structure of Cation N,N-dialkilimidazolium 1

The nature of ionic liquids such as thermal properties, electrochemical stability, ionic conductivity and viscosity can be set and adjusted by altering the structure of its cation and anion. These properties cause ionic liquids well-known as tailored-made solvents (Gordon, 1998). The melting point of salt ionic liquid 1-alkyl-3-methyl-imidazolium (with R = CH₃), for example will decline with the increasing length of the alkyl group r'. Having achieved the minimum price (usually in hexyl, heptyl, or octyl groups), the

melting point will increase in line with increasing length of the R group (Gordon, 1998).

Synthesis and the Characterization of Imidazolinium-Based Ionic Liquids

In summary, the workflow of the research is shown in Figure 4.

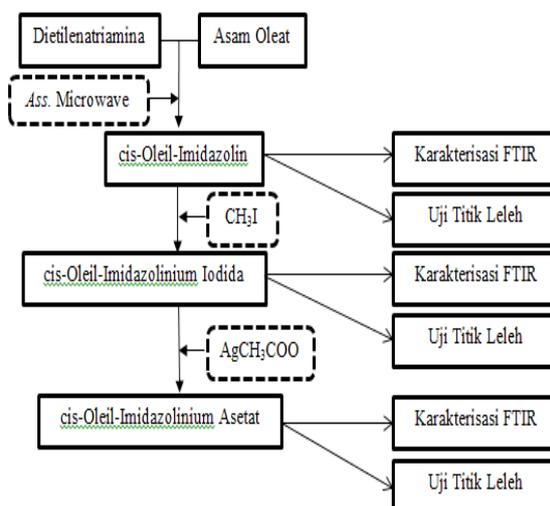


Figure 4. The process of synthesis and characterization of ionic liquids Cis-Oleil-midazolium-Acetate

a. Synthesis of Cis-Oleil-Imidazolium-Asetat

Synthesis of ionic liquids-cis-oleylimidazolium-acetate is conducted by synthesizing cis-imidazoline, methylation-kuartenerisasi, followed by the replacement of anion. Synthesis of cis-oleyl-imidazoline is performed by a method with microwave assistance. To synthesize cis-

oleyl-imidazolium iodide, the reflux method is used as suggested by Mudzakir et al. (2008). Substitution of anion is conducted by utilizing the principle of anion metathesis and Lewis basic acids to synthesize cis-oleyl-imidazolium-acetate.

Compound synthesis process Cis-Oleil-imidazolium-Acetate can be divided into three main stages, they are:

1) Synthesis of Cis-Oleil-Imidazolin

A total of 20 mmol (2.06 grams) of diethylenetriamine (DETA) and 11.29 grams of cis-oleic fatty acid was added to a 100 ml pyrex beaker then stirred until it was evenly distributed. Reactant mixture was irradiated using microwave at 800 watts for 30 seconds, and then cooled to room temperature. After reaching room temperature (25°C), the mixture was transferred into a three-neck round bottom flask which was then added 80 mL ethyl acetate and heated up to 40 ° C (boiling point of ethyl acetate), for 30 minutes. The hot mixture was filtered using a Buchner funnel connected to a vacuum pump then concentrated by evaporator to separate the ethyl acetate solvent. The results were characterized using FTIR instrumentation and its melting point was tested.

2) Synthesis of Cis-Oleil-Imidazolium-Iodida

A total of 1 mole (13.65 grams) of cis-oleyl-imidazoline was added with methylene chloride until dissolved and incorporated into the three-neck round bottom flask that had been coated with aluminium foil, added with 2 mol (6.17 grams) of methyl iodide. Subsequently, the mixture was refluxed at a constant temperature of 40°C while stirring it using a magnetic stirrer for 4 hours. The result is cooled down to room temperature, and then dried using a rotary evaporator at 80°C for 2 hours. Finally, we dried it in a fume hood. The results are characterized using FTIR instrumentation and its melting point was tested.

3) Synthesis of Cis-Oleil-Imidazolium-Asetat

A total of 10 mmol (7.4390 grams) cis-oleylimidazolium iodide was put in a beaker which had been wrapped in aluminum foil and then dissolved in 100 mL of methanol and added 10 mmol (1.67 grams) of AgCH₃COO. The mixture is stirred using a magnetic stirrer for 4 hours. The result was decanted and filtered using a cellulose-nitrate membrane (PTFE). The solvent of the filtrate was then evaporated by stored it in a fume hood until saturated. The results obtained were characterized using FTIR instrumentation and its melting point was tested.

Based on the description of the three stages of the synthesis of cis-Oleil-imidazolium-Acetate, there were four basic ingredients used: diethylenetriamine, cis-oleic fatty acid, methylene chloride and silver acetate. These materials are related to the content of chemistry class XII on the subject of organic compounds reaction, thus this context can be used to enrich students' knowledge in recognizing chemical materials related with ionic liquids.

b. Structure characterization

To determine the success of the synthesis process stages and the overall synthesis process, we used chemical instrumentation including Fourier Transform Infra Red (FTIR) and melting point test.

1) FTIR analysis

Characterization using FTIR aimed to compare the condition of a sample before and after the process of synthesizing. This analysis used SHIMADZU FTIR-8400. The functional group of the FTIR spectra provided distinctiveness FTIR spectra pattern information of functional groups present in the sample before and after the process of synthesis. Based on the result, we obtained their suitability or peak difference of the functional groups observed in the spectra so that the changes in the structure before and after the process could be explained.

2) Analysis of melting point

Physics properties can be used for qualitative analyzing of a substance. The success of the process of synthesis of a pure solid sample can be characterized by means of determining the melting point.

Some application of basic ingredients of Cis-Oleil-imidazolium

1) Applied as Redox Electrolyte in *Dye Sensitized Solar Cells* (DSSC)

The materials used for the DSSC are: TiO₂ powder, Polyvinyl Alcohol (PVA), ethanol, potassium iodide, iodine, and three fatty imidazolium salt from synthesis result, isolation scotch, conductive glass (indium tin oxide, ITO) and chromophore source material.

In brief, the manufacture of DSSC was shown in Figure 5.

2) Applied as Electrolytes in Artificial Muscle System

The materials used are synthesized cis-imidazolium iodide, technical chitosan, technical acetic acid, chlorosulfonic acid p.a, and dimethyl formamide P.A. The procedure of making the raw material of artificial muscle system are briefly shown in Figure 6.

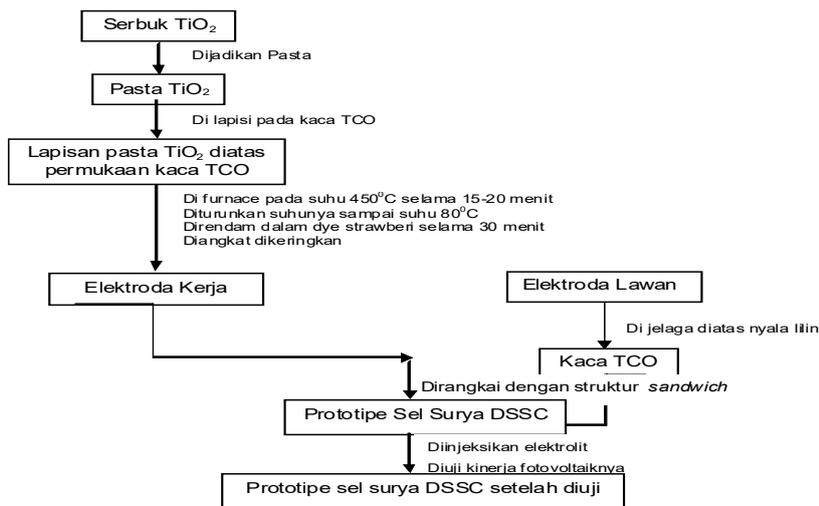


Figure 5. Creating Cis-imidazolium-asetat electrolyte-based DSSC solar cell

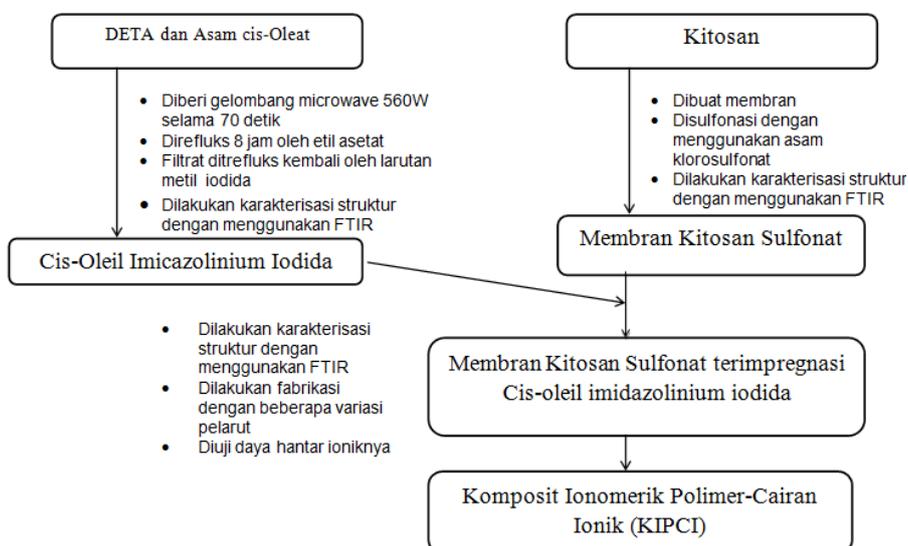


Figure 6. Alternative Procedure of Manufacturing ionic Liquids for Artificial Muscle

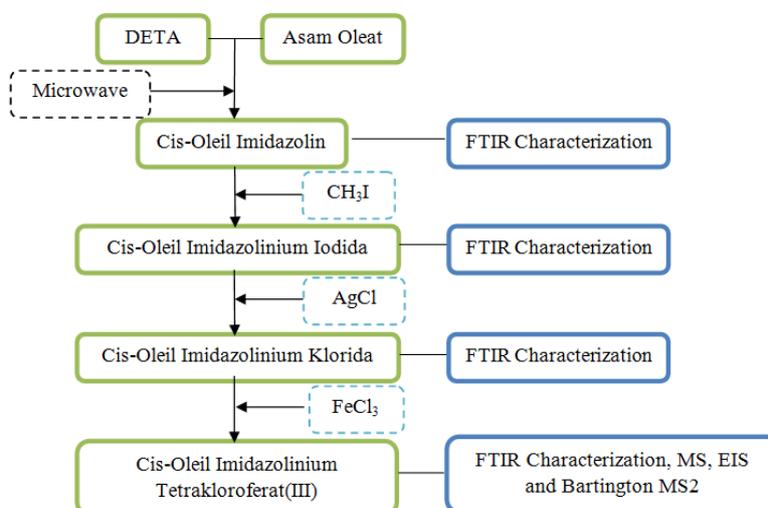


Figure 7. Alternative Synthesis Procedure of Ionic Liquids as Raw materials for Magnetic Lubricant

3) Applying Ionic Cis-Imidazolium as Magnetic Lubricant

The materials used are: acid cis-oleic extract pure, methyl iodide, dietilenatriamina p.a., methylene chloride technical, ethyl acetate technical, methanol, AgCl pa, iron (III) chloride pa, natural fibre waste, NaOH p.a., and Aquades.

Working procedure system was divided into three processes; the synthesis process of magnetic ionic liquid of cis-oleyl imidazolium tetrakloroferat (III), the manufacture of natural fibre materials, and the manufacture of magnetic paper with impregnation method. Ionic Liquids Synthesis process was shown in Figure 7.

CONCLUSION

Based on the data, we can conclude: Modernization of chemistry curriculum was required by utilizing the context of modern technology which is the source of knowledge in developing teaching materials. Ionic liquid material is the context that has the potential to be applied in the chemical content in the school. Some of the application of ionic liquids can be used in chemical content, e.g. the use as raw material for the manufacture of solar cells, artificial muscles and magnetic lubricant.

REFERENCES

- Awad, W. A., Gilman, J. E., Nyden, M., Harris, R. H., Sutto, T. E., Callahan, J., Trulove, P. C., DeLong, H. C. & Fox, D. M. (2004). Thermal Degradation Studies of Alkylimidazolium Salts and Their Application in Nanocomposites. *Thermochemica Acta*, 3 (1), 409-414.
- Bhatt, A. I., May, I., Volkovich, V. A., Hetherington, M. E., Lewin, B., Thied, R. C., dan Ertok, N. (2002). Group 15 Quaternary Alkyl Bistriflimides: Ionic Liquids with Potential Application in Electropositive Metal Deposition and as Supporting Electrolytes. *J. Chem. Soc. Dalton Trans*, 1 (1), 4532-4542.
- Brennecke, J. F. & Maginn, E. J. (2001). Ionic Liquids: Innovative Fluids for Chemical Processing", *AIChE Journal*. 47 (1), 2384-2390.
- Buzzeo, M.C., Hardacre, C. & Compton, R.G. (2004). Use of Room Temperature Ionic Liquids in Gas Sensor Design. *Anal. Chem.*, 76 (1), 4583-4590
- Davis, J. H., & Fox, P. A. (2003). From Curiosities to Commodities: Ionic Liquids Begin the Transition. *Chem. Commun*, 1 (1), 1209-1214.
- Earle, M. J. & Seddon, K. R. (2000). Ionic Liquids: Green Solvents for the Future. *Pure Appl. Chem*, 72 (1), 1391-1400.
- Firman, H. (2007). Laporan Analisis Literasi Sains Berdasarkan Hasil PISA Nasional Tahun 2006. Jakarta: Pusat Penilaian Pendidikan Balitbang Depdiknas.
- Gordon, C. M., Holbrey, J. D., Kennedy, A. R. & Seddon, K. R. (1998). Ionic Liquid Crystals: Hexafluorophosphate Salts. *J. Mater. Chem.*, 8 (1), 2627-2635.
- IOLITEC. (2005). Ionic Liquids. *Chemfiles*, 5 (6).
- Hagiwara, R. & Ito, Y. (2000). Room Temperature Ionic Liquids of Alkylimidazolium Cations and Fluoroanions. *Journal of Fluorine Chemistry*, 105 (1), 221-230.
- Hayat, B & Yusuf, S.(2010). Mutu Pendidikan. Jakarta: Bumi Aksara.
- Holbrey, J. D. & Seddon, K. R., (1999). The Phase Behaviour Of 1-Alkyl-3-ethylimidazolium Tetrafluoroborates; Ionic Liquids and Ionic Liquid Crystal. *J. Chem. Soc., Dalton Trans*, 2 (1), 2133-2140.
- Merrigan, T. L., Bates, E. D., Dorman, S. C. & Davis, J. E. (2000). News Fluorous Ionic Liquids Function as Surfactants in Conventional Room Temperature Ionic Liquids. *Chem. Commun*, 2 (1), 2051-2060.
- Miao, W. & Chan, T-H. (2006). Ionic-Liquid-Supported Synthesis: a Novel Liquid-Phase Strategy for Organic Synthesis. *Acc Chem Res*, 39 (12), 897-902.
- Mudzakir, A., Permanasari, A. & Mahiyudin. (2008). The Influence of Social Issue-Based Chemistry Teaching in Acid Base Topic on High School Student's Scientific Literacy. *Proceeding of the First International Seminar of Science Education, Science Education Program Graduate School, Indonesia University of Education (UPI)*.
- OECD. (2013). PISA 2012 Results: What Students Know and Can Do, OECD Publishing.
- Ohno, H. (2001). Molten Salt Type Polymer Electrolytes. *Electrochim. Acta.*, 46(1), 1407-1415.
- Olivier, H. & Magna, L. (2002). Ionic Liquids: Perspectives for Organic and Catalytic Reactions. *J. Mol. Cat. A.*, 419 (1), 182-183.
- Taush, M.W. & Bohrmann-Linde, C. (2007). Curriculum Modernization in Chemical Education. *Proceeding of the 2nd European in Chemistry Education, Prague*.
- Toma, G., Gotov, B., & Solcaniova, E. (2000). Enantioselective Allylic Substitution Catalyzed by Pd0-Ferrocenylphosphine Complexes in [Bmim][PF6] IonicLiquid. *Green Chem.*, 2(1), 149-157.
- Vidis, A., Ohlin, A., Laurenczy, G., Küsters, E., Sedelmeier G., & Dyson, P.J. (2005). Rationalisation of Solvent Effects in The Diels-Alder Reaction Between Cyclopentadiene and Methyl Acrylate in Room Temperature Ionic Liquids. *Adv. Synth. Catal.*, 2 (1), 347,266.
- Ye, C., Liu, W., Chen, Y. & Yu, L. (2001). Room Temperature Ionic Liquids: a Novel Versatile Lubricants. *Chem. Commun*. 1 (1), 2244-2256.