

APPLICATIONS OF IONIC LIQUIDS IN ELECTROCHEMICAL AND CATALYTIC STUDIES

Robbe Vervecken

Abstract: In this work, several ionic liquids were investigated regarding their electrochemical and catalytic properties as well as their ability to extract and oxidize different pigments.

Seven room-temperature ionic liquids formed from a combination of cations 1-alkyl-3-methylimidazolium (alkyl = butyl, hexyl or octyl, $[C_n\text{mim}]^+$, $n = 4, 6$ or 8), trihexyl(tetradecyl)phosphonium ($[P_{6.6.6.14}]^+$) or *N*-methyl-*N,N,N*-trioclyoctan-1-ammonium, and anions bis(trifluoromethylsulfonyl)imide ($[(CF_3SO_2)_2N]^-$, $[NTf_2]^-$), dicyanamide ($[DCA]^-$) or chloride, were investigated by cyclic voltammetry. The usable potential range of the said ionic liquids as well as the effect of their water content and the behavior of ferrocene in those media were investigated.

The applicability of trihexyl(tetradecyl)phosphonium dicyanamide, $[P_{6.6.6.14}][DCA]$, to the selective oxidation of cyclohexane to the cyclohexanol and cyclohexanone mixture catalysed by ferrocene, under mild conditions, was explored for the first time.

Moreover, liquid-liquid extraction of eight pigments by $[P_{6.6.6.14}][DCA]$ and the effectiveness of the extraction was examined in several conditions, such as exposure to the sun and in the presence of 30% hydrogen peroxide.

Introduction

To meet the demands of a growing population, the chemical processing industry has used yield oriented procedures, without including in the process design a way of minimizing the waste production. One of the major sources of waste is solvent losses that end up in the atmosphere or in ground water [1-6]. The use of these materials has a detrimental effect on human health, safety and the environment. This combined with their volatility and flammability led to increasing pressure for minimizing their use. Therefore, solvent selection should be considered systematically to improve synthesis conditions within the framework of green chemistry principles, [7] and there are a number of solvent selection guides available in the literature [1-6,8,9]. Chemically, the solvent would have a high capacity to dissolve the solute, in a little amount of volume. It would need to be inexpensive to produce, recyclable and robust, to face various processing environments [7,10,11].

Recently, however, a new class of solvent has emerged that fit perfect in the idea of green chemistry, namely ionic liquids. These solvents are often fluid at room temperature, and consist entirely of ionic species. They're non-flammable, have high thermal stability and are relatively undemanding and inexpensive to manufacture. Another big advantage is the absence of a measurable vapor pressure, with no emission of toxic, volatile organic compounds (VOC). Their special properties make them a field of interest for chemists. Although

ILs display many advantages, they have a high viscosity compared with molecular solvents. This will have to be taken into account during experiments and further use. [7,12,13]

ILs are called "designer solvents" because they consist of a cation and anion, which can be altered in order to tune the properties of the IL. In this way, the solvents can be designed with a particular end use in mind. Viscosity, density, electrical conductivity, hydrophobicity and also miscibility of water in ionic liquids can be changed dependent on the structure. Preferentially ILs which are liquid at ambient temperature are used; they are referred to as room temperature ionic liquids RTILs. [7,12,13]

Experimental part

Materials

Different ionic liquids are used, including $[P_{6.6.6.14}][Cl]$, $[P_{6.6.6.14}][DCA]$, Alliquat336, $[C_6\text{mim}]Cl$, $[C_4\text{mim}][NTf_2]$, $[C_6\text{mim}][NTf_2]$ and $[C_8\text{mim}][NTf_2]$. The ionic were dried for 12 h, using the vacuum line, with Edwards RV3 pump. Ferrocene, TBHP ($t\text{BuOOH}$), hydrogen peroxide solution (30% H_2O_2), acetonitrile and the dyes (Amaranth, Rhodamine 6G, Chrysoidine, Indigo, Tartrazine, Malachite green, methyl violet and Methylene blue) were purchased at Sigma Aldrich.

Equipment/procedure

Potentiostat/Galvanostat Model 273 A by EG&G Princeton Applied Research with PowerSuite software is used for all the electrochemical experiments. The studies were conducted at a platinum disc working electrode ($d = 0.5$ mm) and at room temperature, in a three-electrode-type cell with a Luggin capillary connected to a silver wire pseudo-reference electrode (to control the working electrode potential) and a Pt wire as the counter electrode for the CV cell.

The solutions were saturated by bubbling N_2 before each run. The redox potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard.

The water content of every ionic liquid was measured with the Karl Fischer 831 Coulometer.

The gas chromatograph MFC 8000 from Fisons instruments, was utilized for the analysis of the products of the oxidation reactions of cyclohexane. It is a GC with flame ionization detector and capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) and the Jasco-Borwin v.1.50 software. 0.045 μ L of the sample got injected and subsequently

analyzed. A temperature program with an initial temperature of 100 $^{\circ}$ C (1 min) and a ramp of 10 $^{\circ}$ C/min with a final temperature of 180 $^{\circ}$ C (1 min).

Different UV-VIS spectrometers were used: PerkinElmer's Lambda 35 UV-VIS spectrophotometer, Jasco 7800 and the UV-3101 PC, UV-VIS-NIR Scanning spectrophotometer Shimadzu. Hellman quartz cells, with 1 cm path length, were utilized for all the measurements.

Results and discussion

Electrochemical studies

The cathodic and anodic potential limits, that is, the electrochemical stability window, of seven room-temperature ionic liquids formed from a combination of cations 1-alkyl-3-methylimidazolium (alkyl = butyl, hexyl or octyl, $[C_n\text{mim}]^+$, $n = 4, 6$ or 8), trihexyl(tetradecyl)phosphonium ($[P_{6.6.6.14}]^+$) or *N*-methyl-*N,N*-trioctyl-octan-1-ammonium ($[N_{8.8.8.1}]^+$), and anions bis(trifluoromethylsulfonyl)imide ($[\text{NTf}_2]^-$), dicyanamide ($[\text{DCA}]^-$) or chloride, were investigated by cyclic voltammetry. Results are given in Table 1.

Table 1 The oxidation potential, the reduction potential and the electrochemical window available in $[P_{6.6.6.14}][\text{DCA}]$, $[P_{6.6.6.14}][\text{Cl}]$, Aliquat 336, $[C_4\text{mim}][\text{NTf}_2]$, $[C_6\text{mim}][\text{NTf}_2]$, $[C_8\text{mim}][\text{NTf}_2]$ and $[C_6\text{mim}][\text{Cl}]$ at a platinum disk working electrode; $v = 200$ mVs $^{-1}$. Potentials are vs. an Ag quasi-reference electrode (QRE).

IL	$E^{\text{ox}} / \text{V vs. Ag QRE}$	$E^{\text{red}} / \text{V vs. Ag QRE}$	$\Delta E / \text{V}$
$[P_{6.6.6.14}][\text{DCA}]$	1.7	-1.8	3.5
$[P_{6.6.6.14}]\text{Cl}$	1.0	-3.0	4.0
Aliquat 336	1.0	-2.1	3.1
$[C_4\text{mim}][\text{NTf}_2]$	1.0	-1.7	2.7
$[C_6\text{mim}][\text{NTf}_2]$	1.8	-1.5	3.3
$[C_8\text{mim}][\text{NTf}_2]$	1.5	-2.0	3.5
$[C_6\text{mim}]\text{Cl}$	0.9	-1.5	2.4

As expected, the ILs with halides, and in particular the ones with the chloride anion (Table 1), are limited for oxidation applications above ca. 1 V, since the chloride undergoes oxidation at that potential. [14]

The best overall stability is delivered by $[P_{6.6.6.14}][\text{DCA}]$ which exhibits similar, and wide, useful limits at both positive and negative potentials.

The electrochemical potential window of room temperature ionic liquids is sensitive to impurities. A change in the water

content of an ionic liquid will affect conductivity: as the water content increases, so does conductivity; thus decreasing the electrochemical potential window.

Hydrophobicity of an ionic liquid increases with increasing alkyl chain length. Adding CH_2 groups to the alkyl chain on the imidazolium cation promotes a larger surface area with more hydrogen available, making the interaction with the water molecules less relevant. For the series $[C_n\text{mim}][\text{NTf}_2]$ ($n = 4, 6, \text{ or } 8$) this theory is confirmed. $[C_4\text{mim}][\text{NTf}_2]$ is being the most affected; the evolution of can be seen in Figure 1.

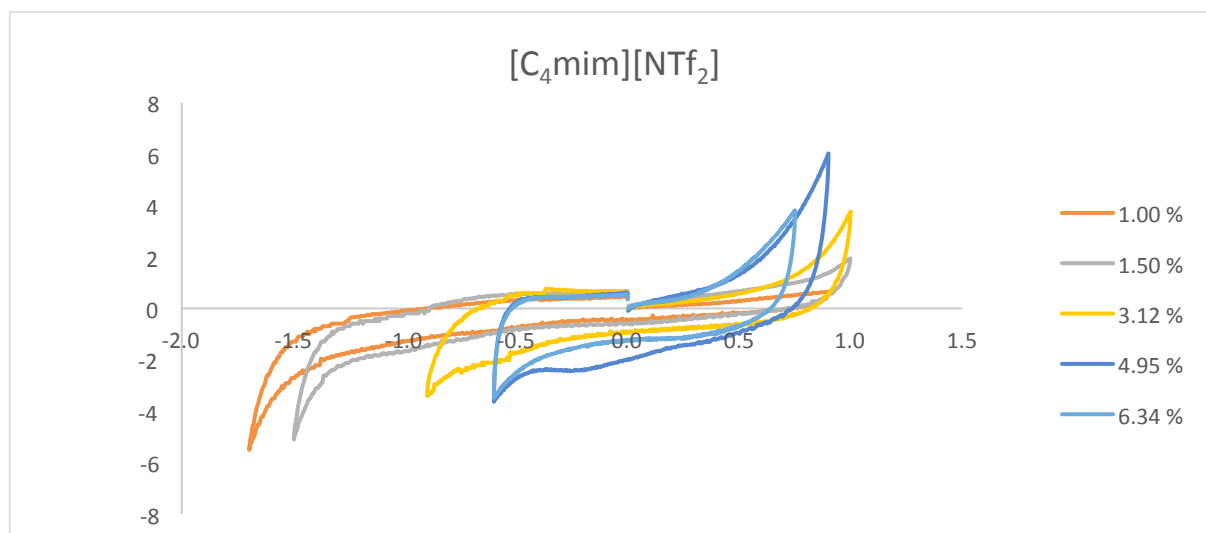


Figure 1 Cyclic voltammograms of $[C_4mim][NTf_2]$ for different water contents; 1.00 % (orange), 1.50 % (gray), 3.12 % (yellow), 4.95 % (dark-blue) and 6.34 % (light-blue) at a platinum disk working electrode; v , 200 mVs^{-1} . Potentials are vs. an Ag quasi-reference electrode (QRE).

The magnitude in which ILs containing $[Cl]^-$ as an anion and different cations got influenced by the water content is to be put in order as follows; $[P_{6.6.6.14}]^+$, $[N_{1.8.8.8}]^+$, $[C_6mim]^+$. An increase in the size of the cationic part, showed to promote hydrophobicity and therefore lowered the sensitivity of the presence of water molecules.

A bigger decrease in electrochemical window with an increase in water content is seen at $[P_{6.6.6.14}]Cl$ as

compared to $[P_{6.6.6.14}][DCA]$.

The process $[Fe(C_5H_5)_2]^{+/0}$ of the traditionally used reference compound ferrocene has been studied at a platinum disk electrode in the ionic liquids $[C_6mim][NTf_2]$ and $[P_{6.6.6.14}][DCA]$.

A reversible, one-electron reduction process was observed (a typical cyclic voltammogram is shown in Figure 2), and the measured half wave potential versus a silver quasi-reference electrode are presented in Table 2.

Table 2 Half-wave potential values for the $[Fe(C_5H_5)_2]^{+/0}$ redox process in different ionic liquids.

Ionic Liquid	$E_{1/2}^{ox} / V^a$	ip_a / ip_c	Water content %
$[C_6mim][NTf_2]$	0.25	1.1	0.08
$[P_{6.6.6.14}][DCA]$	0.52	1.0	0.24
	0.57	1.5	0.19

^a Potentials are vs. an Ag quasi-reference electrode (QRE).

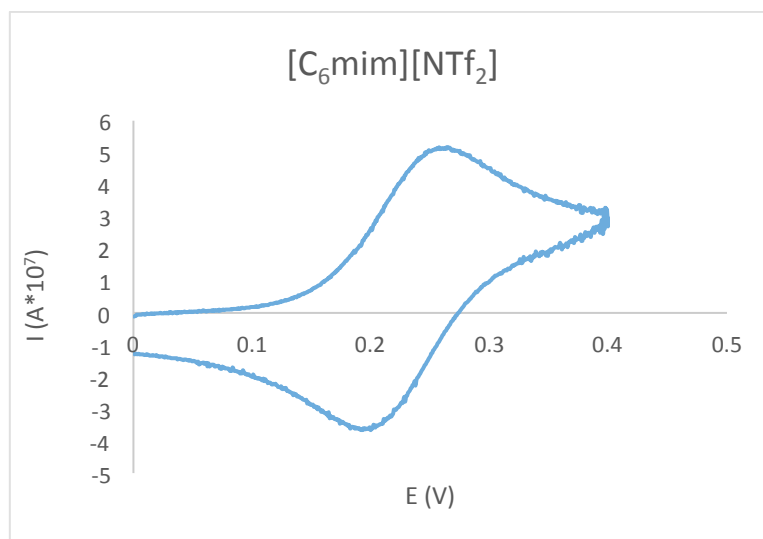


Figure 2 Cyclic voltammograms of ferrocene in $[C_6mim][NTf_2]$ at a platinum disk working electrode; $v = 200 \text{ mVs}^{-1}$. Potentials are vs. an Ag quasi-reference electrode (QRE).

Peroxidative oxidation of cyclohexane

The catalytic activity of ferrocene in trihexyl(tetradecyl)phosphonium dicyanamide, $[P_{6.6.6.14}][DCA]$, was tested as catalyst for the oxidation of cyclohexane with aqueous tert-butylhydroperoxide (ButOOH, TBHP) as oxidizing agent, at $50 \text{ }^\circ\text{C}$. Results are given in Table 3.

Only cyclohexanone was produced by oxidation of cyclohexane in the above-mentioned conditions (cyclohexanol was not

detected, not even traces). A maximum cyclohexanone yield of 15.7% was obtained in the presence of acidic medium. This selectivity is rare, being the cyclohexanol and cyclohexanone mixture the common products obtained.

Interestingly, both acidic and basic additives led to an enhancement of the amount of cyclohexanone produced.

Table 3 Selected data for the catalytic oxidation of cyclohexane catalyzed by ferrocene in $[P_{6.6.6.14}][DCA]$.^a

Entry	Catalyst amount (mol L^{-1})	Additive (mol L^{-1})	Time (min)	Yield % ^b			Total TON ^c	Total TOF ^d (h^{-1})
				Cyclo- hexanone	Cyclo- hexanol	Total		
1			30	1.5	0	1.5	91.1	45.0
2			60	0.7	0	0.7	44.6	22.3
3	2.47×10^{-4}	-	120	7.2	0	7.2	448.6	224.3
4			180	10.1	0	10.1	629.9	315.0
5			360	10.2	0	10.2	639.2	319.6
6		Na_2CO_3 (7.30×10^{-2})	120	14.3	0	14.3	892.9	446.5
7	2.47×10^{-4}	HNO_3 (1.60×10^{-1})	120	15.7	0	15.7	980.0	490.0

^aYield and TON determined by GC analysis (upon treatment with PPh_3). ^bMolar yield (%) based on substrate, *i.e.* moles of product (alcohol (OL) or ketone (ONE)) per 100 mol of cycloalkane. ^cTurnover number = number of moles of products per mol of catalyst. ^dTOF = TON per hour.

Martins *et al.* also found that the addition of HNO₃ promotes the activity of the [FeCl₂{η³-HC(pz)₃}]/CNT-Oxi-Na combination for the catalytic conversion of cyclohexane to both cyclohexanol as cyclohexanone. [15]

G.B. Shul'pin *et al.* showed that the addition of a base can have an accelerating-, retardation- or inhibiting effect on the decomposition of hydro peroxides. It is dependent on the composition of the base, oxidant and the catalyst used. [16]

Extraction and oxidation of pigments

Liquid-liquid extraction of eight pigments (see Table 4) by [P_{6,6,6,14}][DCA] was examined in several conditions, such as

exposure to the sun and in the presence of 30% hydrogen peroxide. For determining the influence of the concentration and pH for each pigment, a calibration curve was made for the working range of concentration and with the pH values used in the studies. Therefore, UV- spectra were taken, reading the absorbance at the highest point in the absorbance vs wavelength graph. A linear behavior was observed for all the pigments. Table 4 shows the absorbance values at the highest point determined for each pigment at the different pH values.

Table 4 Wavelength of maximum absorbance for the pigments at the studied pH values

Pigment	λ (pH=2) /nm	λ (pH=7) /nm	λ (pH=12) /nm
Amaranth	521	521	493
Rhodamine 6G	524	524	524
Chrysoidine	455	450	403
Indigo	610	610	610
Tartrazine	421	423	425
Malachite green	616	616	/
Methyl violet	582	582	/
Methylene blue	662	662	662

A qualitative experiment subjecting pigments, as a mixture of pigment and the ionic liquid [P_{6,6,6,14}][DCA], to the sun was done to investigate the evolution of the color intensity of the aqueous pigment solution. The ultimate goal is to see which pigment will migrate from the aqueous phase to the ionic liquid, comparing the color intensity of the aqueous phase as a function of time. Therein Amaranth, Chrysoidine and Indigo showed a considerable migration of the pigment from the aqueous phase to [P_{6,6,6,14}][DCA], with the aqueous phase still retaining its color partially.

To complement the study, examination of the change in color/color intensity of the ionic liquid, before and after the addition to the pigment solution by UV measurements was performed. Therein the acidity and basicity was altered to respectively pH is 2, 7 and 12. The big influence of the pH on the extraction ratio is to be seen in Table 5.

Table 5 Extraction ratios at a pH of 2, 7 and 12 of rAmaranth, Rhodamine 6G, Chrysoidine, Indigo Tartrazine, Malachite green, Methyl violet and Methylene blue.

Time pH value	Amaranth				Rhodamine 6G			
	0	5	10	30	0	5	10	30
2.0	8.4	11.5	12.3	12.3	0.0	0.1	0.0	0.5
7.0	0.8	1.3	1.8	1.8	5.2	7.1	7.7	7.9
12.0	4.7	10.0	12.4	15.1	16.0	16.3	18.6	31.6
Time pH value	Chrysoidine				Indigo			
	0	5	10	30	0	5	10	30
2.0	0.8	1.0	1.0	2.0	22.2	30.0	33.8	42.3
7.0	3.8	7.5	9.3	13.2	2.4	3.2	5.2	5.6
12.0	15.7	19.8	52.5	54.5	25.4	41.4	40.4	63.5
Time pH value	Tartrazine				Malachite green			
	0	5	10	30	0	5	10	30
2.0	10.4	14.2	15.9	18.8	5.4	11.7	15.8	20.5
7.0	12.0	20.0	24.8	31.7	0.1	1.5	2.2	2.2
12.0	2.0	10.5	16.2	22.4	3.4	2.5	2.5	3.2
Time pH value	Methyl violet				Methylene blue			
	0	5	10	30	0	5	10	30
2.0	3.4	2.5	2.5	3.2	0.5	1.5	1.0	1.0
7.0	1.9	1.1	0.3	0.1	1.5	1.1	0.9	0.9
12.0	/	/	/	/	1.5	3.7	4.8	8.2

Recently, advanced oxidation processes (AOPs) has been developed to oxidize organic pollutants into carbon dioxide, water and inorganic ions or transform into less complex structures. AOPs are based on the generation of highly reactive species such as hydroxyl radicals ($\cdot\text{OH}$), which have strong oxidation potential and oxidise a large number of organic pollutants using hydrogen peroxide. The influence of 30% H_2O_2 , as oxidant, was explored visually at different times. The color intensity of the aqueous phase of both the samples with as without $[\text{P}_{6,6,6,14}][\text{DCA}]$ were compared. The change in color of the IL before and after the addition to the pigment solution was examined as well.

The color was retained in the IL after 72 hours for Amaranth, Chrysoidine and Tartrazine. The ionic liquid ensures a protection against the oxidative effect of the hydrogen peroxide. Rhodamine 6G, Indigo and Methyl violet did not show any remainders of pigment after 72 hours, but after 30 minutes the ionic liquid phase did retain the color of the pigment significantly. Malachite green lost its color completely after 10 minutes, which

is opposed to Methylene blue that held its color partially in both phases. Both Malachite green and Methylene blue did not get influenced by the presence of $[\text{P}_{6,6,6,14}][\text{DCA}]$.

For the quantification, in the case of the oxidation with hydrogen peroxide (30%, v/v) the absorbance values were determined before and after the addition of the oxidant to the pigment solution. In order to examine the evolution of the absorbance with the time, measurements at different times were done. Then the reaction rate was calculated; the value is equal to the slope of the graph given in the right corner. For amaranth this is given in Figure 3.

The first order reaction rate is given in function of time for the oxidation of pigments, Figure 4. Methyl violet, Chrysoidine, Methylene blue and Rhodamine 6G show a linear behavior, thus being a first order reaction. The oxidation of Amaranth, Indigo and Malachite green on the other hand show a second order equation and will go through via a second order reaction. Tartrazine has more complex reaction rate, that will need to be further investigated.

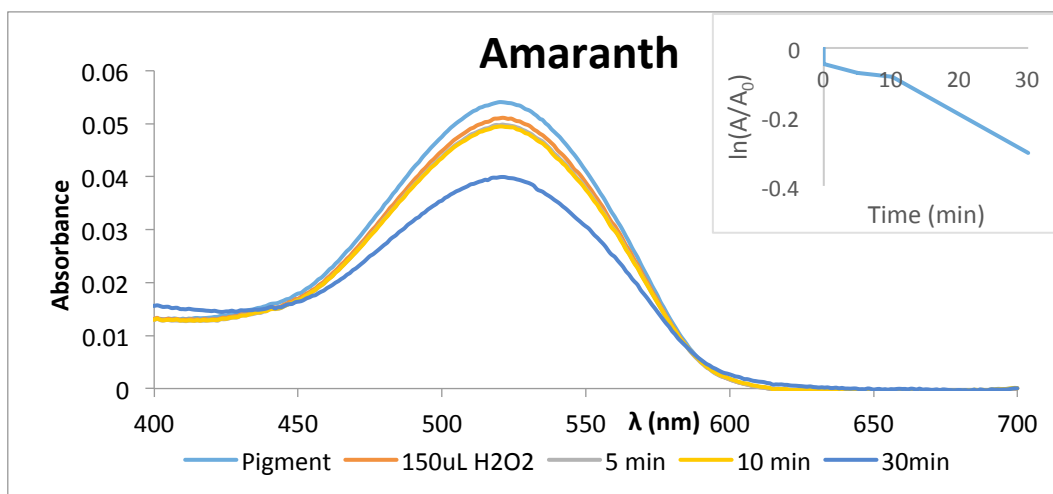


Figure 3 The evolution of the absorbance of Amaranth in time when influenced by 30 % H₂O₂ at pH=7, Right corner: The Napierian logarithm of the ratio of absorbance and the initial absorbance of Amaranth vs. time.

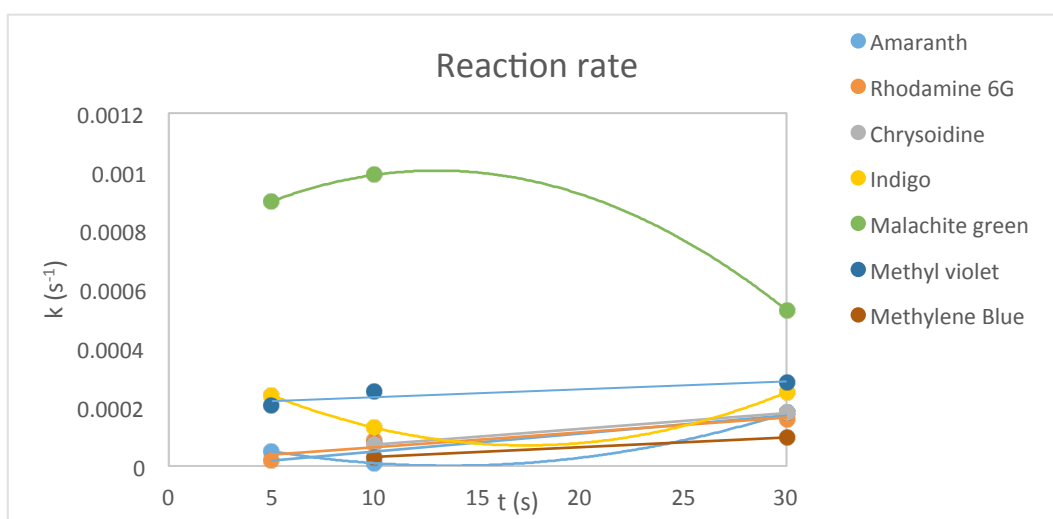


Figure 4 First order reaction rate vs. time for the oxidation of pigments with 30% hydrogen peroxide.

Comparisons of the liquid-liquid extraction of all the pigments by [P_{6,6,6,14}][DCA] shows that it does not occur by chemical sorption, which would form covalent and/or ionic bonds. Physical sorption on the other hand is more conceivable, since a big difference in ability of hydrogen bond formation is seen between the pigments. The hydrogen bonds are expected to be established between the dicyanamide and the reactive hydrogen's of the pigments.

Surprisingly Amaranth and Indigo do not show a big migration of pigment to the IL at a pH of 7, while the visual representation plus the higher extraction ratio at pH of 2 and 12 suggest otherwise. The extraction of Rhodamine 6G and Tartrazine by the IL on the other hand is considerable. Therein Rhodamine 6G gets significantly promoted by an increase in acidity, while the migration of Tartrazine to the IL is the best at a pH of 7. The pH factor is very important in the adsorption process especially for dye adsorption. The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye

molecules. As a result the rate of adsorption will vary with the pH of an aqueous medium [17].

Conclusion

The impact of the water content on the usable potential window is of major importance for the use of ILs as a medium in electrochemistry and is dependent on the structure of the ILs used.

A considerable yield, TON and TOF is obtained for the selective peroxidative oxidation of cyclohexane to cyclohexanone by ferrocene in trihexyl(tetradecyl)phosphonium dicyanamide. The addition of both a base or an acid increased promoted the oxidation reaction.

The migration of some pigments to the IL, [P_{6,6,6,14}][DCA] is considerable, with Amaranth, Chrysoidine and Indigo having the greatest affinity for the IL-phase. Ionic liquids can interfere in the advanced oxidation process of the pigments by extraction

of those pigments and subsequently withstanding the effect of the oxidant.

[17] Muthuraman G., Teng T. T., Tan S. H. (2012), "Liquid-liquid extraction of Cibacron Red FN-R by TBAB as an extractant," *Desalination*, 284,135-141.

References

[1] Jiménez-González J., Constable D. J. C. (2011), "Green Chemistry and Engineering—A Practical Design Approach," John Wiley & Sons Inc., Hoboken, 3-39.

[2] Ahluwalia V. K. (2009), "Green Chemistry, Environmentally Benign Reaction," CRC Press & Francis Group, Boca Raton.

[3] Sheldon R. A. (2012), "Fundamentals of Green Chemistry: Efficiency in Reaction Design," *Che. Soc. Rev.*, 41 (4), 1437-1451.

[4] Dunn P. J. (2012), "The Importance of Green Chemistry in Process Research and Development," *Chem. Soc. Rev.*, 41 (4), 1452-1461.

[5] Ghernaout D., Ghernaout B., Naceur M. W. (2011), "Embodying the Chemical Water Treatment in the Green Chemistry: A Review," *Desalination*, 271 (1-3), 1-10.

[6] Capello C., Fischer U. and Hungerbuhler K. (2007), "What Is a Green Solvent? A Comprehensive Framework for the Environmental Assessment of Solvents," *Green Chem.*, 9 (9), 927-934.

[7] Huddleston J. G., Visser A. E., Reichert E. W., Willauer H. D., Broker G. A., Rogers R. D. (2001), "Characterisation and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation," *Green Chem.*, 3, 156-164.

[8] Slater C. S., Savelski M. (2007), "A Method to Characterize the Greenness of Solvents Used in Pharmaceutical Manufacture," *J. Environm. Sci. Health, Part A*, 42 (11), 1595-1605.

[9] Rundquist E. M., Pink C. J. and Livingston A. G. (2012), "Organic Solvent Nanofiltration: A Potential Alternative to Distillation for Solvent Recovery from Crystallisation Mother Liquors," *Green Chem.*, 14 (8), 2197-2205.

[10] Anastas P. and Warner J. (1998), "Green Chemistry: Theory and Practice," Oxford University Press: New York, 30.

[11] United States Environmental Protection Agency (2014, October 16), "Basics of green chemistry," Retrieved from <http://www.epa.gov>.

[12] Earle M.J. and Seddon K.R. (2009), "Ionic liquids: Green solvents for the future," *Pure Appl. Sci.*, 72 (7), 1391-1398.

[13] Yoshimoto S., Taguchi R., Tsuji R., Ueda H. and Nishiyama K. (2012), "Dependence on the crystallographic orientation of Au for the potential window of the electrical double-layer region in imidazolium-based ionic liquids," *Electrochem. Com.*, 20, 26-28.

[14] O'Mahony A. M., Silvester D. S., Aldous L., Hardacre C. and Compton R. G. (2008), "Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids," *J. Chem. Eng. Data*, 53, 2884-2891.

[15] Martins L. M. D. R. S., Peixoto de Almeida M., Carabineiro S. A. C., Figueiredo J. L., Pombeiro A.J.L. (2013), "Heterogenisation of a C-Scorpionate FeII Complex on Carbon Materials for Cyclohexane Oxidation with Hydrogen Peroxide," *ChemCatChem*, 5 (12), 3847-3856.

[16] Shul'pin G. B., Kirillova M. V., Shul'pina L. S., Pombeiro, A. J. L. Karslyan E. E., Kozlov Y. N. (2013), "Mild oxidative alkane functionalization with peroxides in the presence of ferrocene," *Catal. Com.*, 31, 32-36.