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ALKYLIMIDAZOLIUM IONIC LIQUIDS AS ECOLOGIC SOLVENTS FOR WOOD FINISHING MATERIALS

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Abstract: *In this paper the solubility of four frequently used wood finishing products, namely Paraloid B 72 thermoplastic resin, paraffin, rosin and bees wax in three types of alkylimidazolium-based ionic liquids (1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-hexyl-3-methylimidazolium hexafluorophosphate), at 23 ^{0}C and 90 ^{0}C, has been determined by using the turbidimetric method. It has been determined that the selected ionic liquids are able to dissolve the respective wood finishes, in amounts higher than those achieved by using traditional volatile organic solvents.*

Key words: *ecologic solvents, ionic liquids, turbidimetry, wood finishing.*

1. Introduction

Wood finishes are often used to improve the durability of wood by protecting it from scratching and wearing, minimising swelling when in contact with water or acting as UV stabilizers for lignin and cellulose [1-4], [7], [11], [12], [19].

Traditional wood finishes include tung oil or polymerized lineseed oil-based products, wax, shellac, rosin, parrafin, sinthetic polyurethane, acrylic resin and epoxy-based products [21], [3], [4].

One disadvantage of traditional wood finishes include the use of volatile organic solvents, such as toluene, acetone, or ethanol-acetone mixtures, which are expensive and posses an environmental risk, also by their capacity to transform theirselves in the atmosphere, under the influence of UV radiation and the catalytic action of the nitrogen oxides, in more aggressive species with carcinogenic potential. As consequence, the replacement of the traditional volatile solvents from wood industry with less toxic and volatile solvents became an important aim for the scientists working both in material science and in environmental protection [13-15].

Ionic liquids [IL] are a group of new organic salts that exist as liquids at a relatively low temperature (< 100 ^{0}C) [8], [13-18].

They have many attractive properties, such as chemical and thermal stability, nonflammability and low vapor pressure. In contrast to traditional volatile organic compounds, they are called "green" solvents and have been widely used in lignocellulosic materials dissolution studies [9], [10], [17], [18].

Also, they have shown to be effective as wood preservatives [20], in color restoration of old wooden artifacts [5], as plastifying

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agents [6], [22], or, more recently for anti-electrostatic control of wood [6], [20].

In this paper, the solubility of some common wood finishing products, such as bees wax, paraffin, Paraloid B72 and rosin in three alkylimidazolium ionic liquids, namely 1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-hexyl-3-methylimidazolium hexafluorophosphate (Figure 1) has been determined at different temperatures (23 ^{0}C and 90 ^{0}C) by turbidity measurements, in order to distinguish real dissolution from fine dispersion.

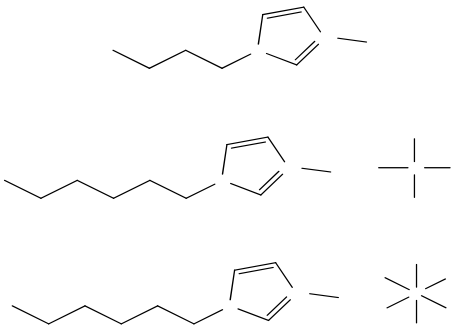

Fig. 1. *The ionic liquids used*

To our knowledge, the solubilization of these compounds in ionic liquids has not been reported previously in the reference literature.

2. Experimental

2.1. Materials

The three ionic liquids, 1-hexyl-3-methylimidazolium hexafluorophosphate ($HMIMPF_6$), 1-hexyl-3-methylimidazolium tetrafluoroborate ($HMIMBF_4$), 1-butyl-3-methylimidazolium chloride (BMIMCl) have been purchased from IoLiTec Ionic Liquids Technologies GmbH, Germany.

$HMIMPF_6$ and $HMIMBF_4$ are transparent viscous liquids; while BMIMCl is a white crystalline solid at room temperature. The purity of the purchased ionic liquids was 99.5%.

Bees wax (BW), paraffin (P), Paraloid B72 (B72) and rosin (R) have been obtained from the Faculty of Wood Industry, *Transilvania* University of Braşov. Paraloid B72 is a commercial thermoplastic ethylmetacrylate - metyl-acrylate copolymer, useful for impregnation and reinforcement of wood products [1].

Before solubility determinations, all of the wood finishing products have been ground into a fine powder (with average particle diameter of 0.5 mm), by using a Retsch ZM200 centrifugal mill.

2.2. Dissolution in ionic liquids

Closed glass cuvettes containing a precise quantity of ionic liquid (around 0.5 g) were placed onto the heating plate of a magnetic stirrer. The use of a hot water bath was avoided to limit the water uptake of ionic liquid by hygroscopy. Then, precise amounts of bees wax, paraffin, Paraloid B72 and rosin (around 10 mg) powder were added discretely into the cuvettes. In between each addition, at least 20 min were allowed for dissolution and then turbidity was measured.

The solubility tests were realized at 23 ^{0}C and 90 ^{0}C for $HMIMPF_6$ and $HMIMBF_4$, which are in liquid form at room temperature, while for BMIMCl the solubilization has been performed at 90 ^{0}C.

2.3. Turbidity measurements

Turbidity was measured with a Carl-Zeiss Spekol 20 spectrophotometer, with the scattered light detector at 45^0 from the incident light beam (Figure 2). The wavelength of the incident light was 650 nm.

The spectrophotometer was calibrated with the help of glass standards with different turbidity. Calibration was done

between 1 and 500 Nephelometric Turbidity Units (NTU). The latter corresponds to a milky opaque sample.

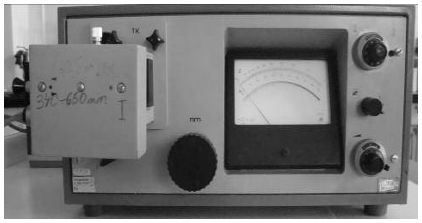

Fig. 2. *Carl-Zeiss spectrophotometer with turbidity accessory*

3. Results and Discussion

The results regarding the turbidity measurements of the ionic liquid - wood finishing product systems are shown in Figure 3 to Figure 7, for all the ionic liquids and temperatures used.

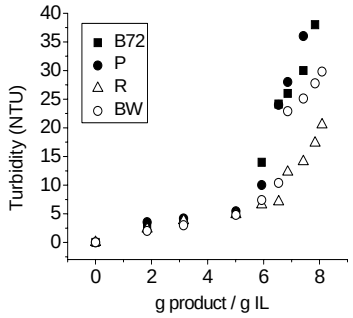

Fig. 3. *Turbidity of wood finishing products - BMIMCl systems at 90 ^{0}C*

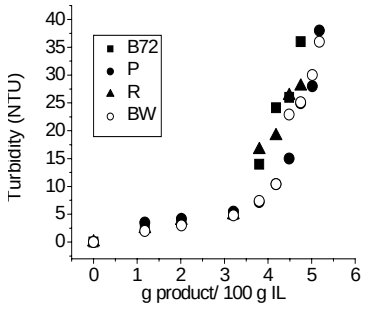

Fig. 4. *Turbidity of wood finishing products - HMIMBF$_4$ systems at 23 ^{0}C*

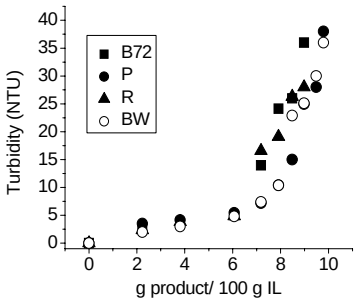

Fig. 5. *Turbidity of wood finishing products - HMIMBF$_4$ systems at 90 ^{0}C*

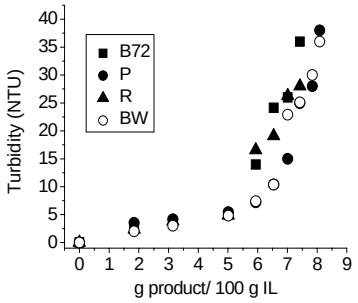

Fig. 6. *Turbidity of wood finishing products - HMIMPF$_6$ systems at 23 ^{0}C*

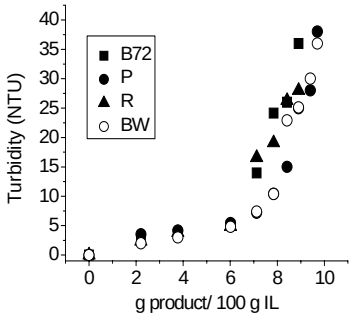

Fig. 7. *Turbidity of wood finishing products - HMIMPF$_6$ system at 90 ^{0}C*

As it can be seen from Figure 3 to Figure 7, the dissolution of Paraloid B72, paraffin, rosin and bees wax occurred in the studied ionic liquids, both at room temperature and 90 ^{0}C.

Generally, it can be observed that the addition of wood finishing compounds to ionic liquids does not lead to a significant

increase in the turbidity of the system (part 1 of the dependency) until the point corresponding to the solubility limit of the respective compounds in the selected ILs. After reaching of solubility limit, a pronounced increase in turbidity can be observed (part 2 of the dependency).

The solubility limit of the respective compounds in the ionic liquids can be calculated by linearly fitting the two parts of the dependencies of the systems turbidity with the amount of wood finishing product in the system, and using the equations of the two straight lines to calculate the point of their intersection.

The solubility limits of the wood finishing products in the selected ionic liquids are given in Table 1.

Solubility of the wood finishing products in ILs Table 1

Ionic liquid	**Temperature (^{0}C)**	Solubility limit (g product/100 g IL)			
		Paraloid B72	Paraffin	Rosin	Bees Wax
BMIMCl	90	5.90	6.55	4.99	5.14
$HMIMBF_4$	23	3.19	3.84	3.23	3.25
	90	5.08	7.27	6.11	7.87
$HMIMPF_6$	23	4.99	5.94	5.04	6.47
	90	5.03	7.20	6.03	6.67

As it can be seen from Table 1, the highest solubility for the Paraloid B72 resin has been achieved in the BMIMCl ionic liquid at 90 ^{0}C, while for paraffin, rosin and bees wax, the best solubility has been achieved in $HMIMBF_4$ and in $HMIMPF_6$ ionic liquids at 90 ^{0}C.

Higher temperatures are favourable in breaking the intermolecular bonds and facilitate the interaction of the molecule with the solvent.

As rosin, paraffin and bees wax are dominating hydrophobic, they tend to dissolve better in the ionic liquids with the same dominating hydrophobic character, namely $HMIMBF_4$ and $HMIMPF_6$.

It is to be noted that Paraloid B72 is hard to solubilise in traditional volatile organic solvents, using toluene at 50 ^{0}C a 5% wt. concentration can hardly be achieved [2-4]. By using ionic liquids, at 90 ^{0}C, according to Table 1, more concentrated solutions could be obtained. In the case of paraffin, rosin and bees wax, the obtained solubilities are similar to those obtained by using ethanol, toluene, isopropanol or acetone [2-4].

4. Conclusions

The solubility of four traditional wood finishing products, namely Paraloid B 72 thermoplastic resin, paraffin, rosin and bees wax in 1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquids, at 23 ^{0}C and 90 ^{0}C, has been determined by using the turbidimetric method.

It has been determined that in the case of Paraloid B72, the obtained solubilities are higher than those reported for the traditional organic solvents. For paraffin, rosin and bees wax the obtained solubilities are similar to those reported by using volatile organic solvents.

Taking into account that the studied ionic liquids are non-volatile, electrically conductive, that they possess anti-fungal character and they are able to plastify wood, their use as solvents for finishes could impart some useful properties to the treated wood, such as higher workability and durability.

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