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WETTING OF SURFACES WITH IONIC LIQUIDS

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Abstract: The paper focuses on assessing wettability of surfaces modified with ionic liquid solutions. Dialkylimidazolium chlorides have been selected as the test group, because of their immediate availability and limited previous research. Contact angle of selected ionic liquid solutions have been measured with two methods: capillary rise test and simplified sitting droplet analysis, performed by means of digital camera. During tests the extremely high viscosity of dialkylimidazolium chlorides has been observed to drop rapidly with prolonged exposition to atmospheric moisture and measured experimentally with Karl-Fischer titration and viscosity measurements. Contact angles of selected ionic liquids have been presented.

Keywords: *ionic liquid, wettability, contact angle, capillary rise, surface interactions*

Introduction

Ionic liquids are a branch of novel, organic chemicals, distinguished by their unique properties. From a chemical point of view, ionic liquids are salts, composed most commonly of a large, organic cation and smaller, inorganic anion. However, unlike most of the salts, ionic liquids are, as the name suggests, liquid at low temperatures. They are most often defined as liquid salts with a melting point lower than 100°C, but remain liquid over a broad range of temperatures (Yang and Pan, 2005).

Ionic liquids (ILs) have been already utilized in many unit operations and processes and it was found out that may serve as substitutes for traditional solvents. However, the reason why ionic liquids find application in so many fields of research and industry is their extraordinary customization potential. Dialkylimidazolium cation-based ILs possess two alkyl chains that can be shortened, extended and branched with ease, and substitution of one anion with another can completely change physicochemical properties of the substance. Thousands of possible and useful configurations just wait to be discovered and implemented in new ways and they all differ in physicochemical

characteristics, like melting point, viscosity, surface tension, conductivity, reactivity or wettability.

The potential applications of ILs are numerous including usage as reaction media, extraction and separation technologies, electrochemistry and many others. For the applications involving heterogeneous systems and transport of ILs in capillary, fibrous, or porous environments, interfacial properties such as wettability has to be known.

Wettability is a tendency of a liquid to spread on a solid surface (Kumar and Prabhu, 2007). Measurement of the contact angle is the way to estimate wettability when the tested fluids are pure and the contact surface (solid or liquid) is perfectly flat, mainly because the surface tension of the interfaces is constant when no surfactants or other compounds are present to alter the wetting (Anderson, 1986). When using Young's equation it was assumed that the surface is rigid, homogeneous and perfectly flat – in such a case a single, specified contact angle for each three-phase system could be obtained. Estimation of contact angles for ionic liquids are, so far, very poorly investigated (Batchelor et al., 2009; Restolho et al., 2009), even though knowledge on their wettability is needed to select IL for many applications.

The surface tension is dependant on slight changes of temperature, surface characteristics or viscosity of the liquid, the equilibrium maintained by the interfacial tensions can be disrupted. The estimation of contact angles for given systems becomes useful only when the interaction potentials of two of those phases can be treated as constant or described numerically. Many simplistic models of wetting of solid materials, for example, have been developed for this purpose and when different surface types are used they are commonly described with their respective critical surface tensions (CST) (Zisman 1964).

The critical surface tension (CST) can be defined as a relative descriptor of wettability of solid surface (Zisman 1964). The test consists of plotting the cosine of the contact angles between several different liquids with defined, decreasing surface tensions on their interface with solid phase. CST is then defined by extrapolation of the line to $\cos \theta = 1$ (Ulosoy and Yekeler, 2004). However, this test can be applied only to low-energy solid surfaces (Sömnez and Cebeci, 2004), with CST values of the same magnitude as of the surface tensions measured in the tests.

Three common imidazolium-based species has been selected for this study, varying in alkyl chain length. This test group of chemicals has been chosen in a way that will permit correlation of obtained results with their molecular structure. All selected ionic liquids are dialkylimidazolium chlorides, which are also very hygroscopic and obtaining purified samples without detectable amounts of water is nearly impossible (Wassercheid and Welton, 2003). Therefore the influence of moisture has also been determined during this study.

Experimental

Reagents

All 1-alkyl-3-methylimidazolium chlorides were obtained from Merck KGaA, Darmstadt, Germany, with a purity of $\geq 98\%$. All samples were degassed and dried at 70°C under vacuum prior to use. Glass beads (Interminglass; Poland) with diameter 150–250 μm were used. Prior to use, the beads were thoroughly cleaned and degassed, with methanol:acetone:chloroform (1:1:1 by volume) and dried at 130°C .

Direct contact angle measurement. Sessile drop method

Ionic liquid has been placed inside the Hamilton syringe, which was then placed inside the grip of the component with micrometric screw. The droplet was placed on the microscopic cover glass surface placed atop the glass pedestal and its image has been taken with digital camera. For the contact angle was calculated from equation, assuming a non gravitationally distorted spherical cap formed by a liquid drop (Woodward, 1999)

$$\theta = 2 \tan^{-1} \frac{2h}{d} \quad (1)$$

where: h – height of the droplet profile [pixel], d – diameter of the droplet base [pixel]

Precision of this method was significantly high, obtained angles differ no more than 1° . However, the authors are aware that a number of other numerical solutions exist, which also take the gravitational effects into account (Allen 2003).

Capillary rise method

Wettability of glass beds was determined by capillary rise methods based on the Washburn equation described elsewhere (Washburn, 1921; Siebold, 2000; Wolfrom, 2002; Trong, 2006; Joskowska, 2012). The glass capillary filled with a bed of sorbent was attached to a movable grip, which could be lowered and raised smoothly. When the experiment was started, the capillary was slowly lowered to touch the surface of tested liquid. Readings of the scale were taken in regular intervals and the change of mass of liquid could be observed when the sorbent bed was penetrated. As reference liquids dichloromethane has been for hydrophilic glass beads and 1-hexanol for hydrophobic glass beads (Hołownia and Kwiatkowska et al., 2008). The references liquids were chosen (from 30 available), that are ideal wetting liquids (contact angle zero) by suspending the beads on the surface of each liquid. The various controversies regarding the reference liquids in capillary rise methods are discussed by Kowalczyk et al. (2012).



Viscosity

Viscosity of the samples has been measured by cone-plate method with Brookfield LV-III Rheometer with a CPE-40 type spindle. Tests were performed under the temperature of 25°C.

Karl-Fisher titration

Water content in ionic liquid samples was determined by coulometric titration method using 831 Karl-Fischer Coulometr, Metrohm.

Results and discussion

Ionic liquid hygroscopicity and its influence on the contact angle sessile drop method

The values of contact angle of three ionic liquids with different chain length on glass plate was presented in Table 1. The contact angle of microscopic glass cover was determined by the sessile drop method.

Table 1. Results and statistical analysis of contact angle measurements performed by means of photographic method on microscopic cover glass. Values of $\log K_{ow}$ taken from literature (Thöming, Cho et al., 2011)

| Abbreviation | Θ , degree | Standard deviation | $\log K_{ow}$ |
|--------------|---------------------|--------------------|---------------|
| [HMIM][Cl] | 14.592 ± 0.539 | 0.507 | -1.730 |
| [OMIM][Cl] | 10.815 ± 0.301 | 0.293 | -0.600 |
| [DMIM][Cl] | 105.951 ± 1.295 | 0.949 | 0.311 |

Contact angle values of [HMIM][Cl] and [OMIM][Cl] were similarly low and both of these substances were found to almost wet microscopic cover glass effectively. However, contact angles for [DMIM][Cl] were extremely high, due to the inability of the molecule to interact with the glass surface. This was most probably caused by the alkyl chain, which at chain length 10 blocks the columbic interaction of the headgroup with the surface.

It was later assumed that the difference between observed contact angles for these samples may also related with different effects of moisture absorption into their structure. To compare the affinity of these ionic liquids towards water octanol water partition coefficient $\log K_{ow}$ (as shown in Table 1) may be used. For both [HMIM][Cl] and [OMIM][Cl], the $\log K_{ow}$ was found to be negative, proving their affinity towards water. Positive value found for [DMIM][Cl] is one of the reasons behind the extremely high contact angle observed in described procedure.



Ionic liquid hygroscopicity and its influence on the Washburn method

Contact angle values evaluated in the capillary rise test is dependant on the surface tension and viscosity of the tested liquid and the relation of these parameters with those exhibited by the reference wetting substance. The results are shown in Table 2. A number of researchers measured both viscosity and surface tension for a broad group of ionic liquids, determining them with different tools. Ghatee and Zolghadr (2008) measured surface tensions of several ionic liquids with modified capillary rise method utilizing digital cathetometer. Gomez et al., (2006) determined dynamic viscosities of few pure ionic liquids and their water solutions in various temperatures, by means of several commercially available viscosimeters. During the procedure it was observed that a small sample of tested ionic liquid becomes perceptibly less viscous after an hour of exposure to air, which proved that moisture is absorbed by these samples at a very high rate.

Table 2. Surface tension and viscosity values for pure ionic liquids used in this study

| Abbreviation | Surface tension, mJ/m ² , 25°C, | Viscosity, cP, 25°C |
|--------------|--|---------------------|
| [HMIM][Cl] | 41.8 ^a | 18089 ^b |
| [OMIM][Cl] | 31.9 ^a | 20883 ^b |

a – (Ghatee and Zolghadr 2008), b – (Gómez, González *et al.* 2006)

An effort has been put into further investigation of surface tension and viscosity changes related with increasing water content within the tested liquids. Literature concerning surface tension variation in ionic liquids and absorbed moisture has been reviewed. Freire et al. (2007) measured surface tensions of two species of saturated 1-alkyl-3-methylimidazolium ionic liquids at 30°C and for water content up to 15% molar ratio. For more hydrophilic [BMIM][PF₆] non-linear surface tension variation of 6% was noted. For [OMIM][PF₆] such a variation was insignificantly smaller, less than 1% (Freire et al., 2007). They concluded that the influence of water content on surface tension of ionic liquids is significant only for hydrophilic ionic liquids, with shorter alkyl chain. Klomfar et al. (2010) obtained similar results and found no apparent correlation between water content and surface tension of ionic liquid samples.

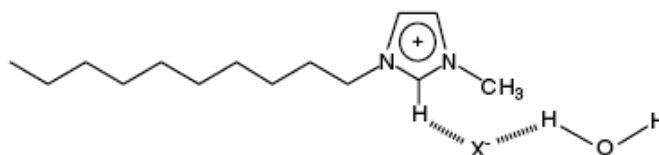


Fig. 1. Figure describing basis for networking of water molecules and ionic liquid. Both dialkylimidazolium cation and water form hydrogen bond with a given anion

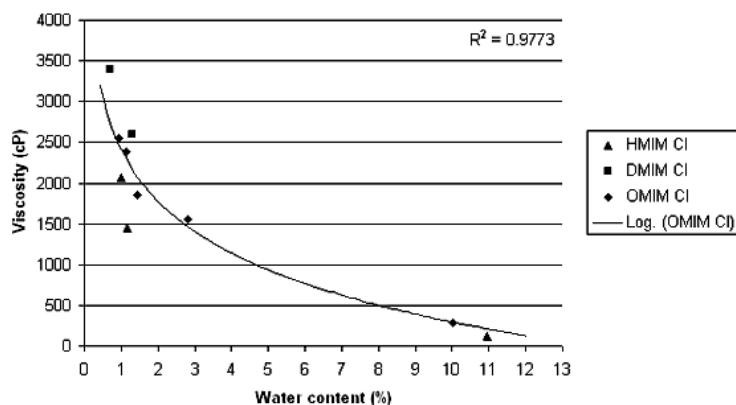


Fig. 2. Graph describing the relationship between increasing water content and viscosity of tested dialkylimidazolium chlorides

Viscosity of typical room-temperature ionic liquids rarely exceeds 200 cP. All dialkylimidazolium chlorides are exception to this rule and their extremely high viscosity is a result of hydrogen bonding between Cl^- anions and the hydrogen atoms (as shown in Fig. 1) on the imidazolium cation ring (Wassercheid and Welton, 2003). When water is introduced into such a structure, chloride anions bond with hydrogen in the water molecules, which, due to their smaller size when compared to dialkylimidazolium cation, are much more mobile. With the increase of water content, the process responsible for high viscosity in ionic liquids is disrupted and a rapid decrease of this parameter is observed. New bonding is strong enough to significantly hamper any procedures dedicated to removal of water content – even with prolonged vacuum drying used for samples tested in this paper, the water was still present in a quantity as high as 1% molar fraction.

As shown in Fig. 2 it was initially suspected, the viscosity was found to decrease rapidly with the increase of water content, giving us a strong, logarithmic correlation with the coefficient of determination as high as 98%. Data obtained for [HMIM][Cl] appears to further prove the validity of this correlation. Unfortunately, measurements for [DMIM][Cl] after more than 15 minutes were rendered impossible to performed due to gelation, whereby the liquid turned into a semi-solid matter.

This process has been observed and even induced earlier by many researchers, who investigated the nature of this and similar structures (Firestone et al., 2004; Kaper and Smarsly 2006; Inoue et al., 2007). This spontaneous self-organization is based upon formation of robust H-bonded network between dialkylimidazolium cation, chloride anion and water molecules (Fig. 1). Hydrophobic and hydrophilic segments of such a structure are segregated, which leads to formation of regions of confined water. Such a structure is one of the simplest forms of “ionogels”, physical gels based on ionic liquids (Firestone et al., 2004).

Uncertainty concerning the actual amount of water in samples during contact angle measurements is the source of greatest discrepancies in results presented in this paper. Viscosity data obtained for [HMIM][Cl] and [OMIM][Cl] after a three hour period was assumed to be the closest available estimation of viscosity observed during the capillary rise experiments. Although the capillary rise experiments took much less time than this, but the volume of liquids used in that procedure was approximately ten times smaller, while the area of exposure to moisture was the same in both cases.

The observed time of penetration indicate that the exact viscosity of [OMIM][Cl] during the test was significantly lower than the one estimated earlier. Moisture adsorbed on hydrophilic glass could have been the reason of such an occurrence. It should be noted, however, that the time of bead penetration for [OMIM][Cl] was slightly higher than the one for [HMIM][Cl] for the same beads, while this tendency is reversed in case of hydrophobic sorbent. This observation proves initial assumptions concerning hydrophobicity of both. Contact angle for [HMIM][Cl] on hydrophilic glass (Table 3) is close to the one observed during the photographic procedure. Very high contact angles exhibited by both ionic liquids on the hydrophobic glass prove that this type of sorbent is not wetted well by tested liquids, as shown in Table 4.

Table 3. Final results of contact angle measurements by means of capillary rise procedure for hydrophilic sorbent. Average times of penetration of bed by referential solvent (t_0) and tested liquid (t_1) have been used to calculate the final values, while highest and lowest values were used to estimate the margin of error

| Series | [HMIM] [Cl] | | [OMIM] [Cl] | |
|-------------------|----------------|-----------|-------------|-----------|
| | t_0 [s] | t_1 [s] | t_0 [s] | t_1 [s] |
| 1 | 2 | 360.5 | 2.5 | 388.5 |
| 2 | 2 | 365 | 3 | 392.5 |
| 3 | 1.5 | 327.5 | 2.5 | 379 |
| Mean value | 1.833 | 351 | 2.667 | 386.667 |
| t_0/t_1 | 0.00522 | | 0.00690 | |
| $K \cdot t_0/t_1$ | 0.955 | | 4.070 | |
| θ | 17.222 ± 8.862 | | – | |

Table 4. Final results of contact angle measurements by means of capillary rise procedure for hydrophobic sorbent. Data analyzed analogically to Table 5

| Series | [HMIM] [Cl] | | [OMIM] [Cl] | |
|-------------------|----------------|-----------|----------------|-----------|
| | t_0 [s] | t_1 [s] | t_0 [s] | t_1 [s] |
| 1 | 1.5 | 665.5 | 3 | 503 |
| 2 | 3.5 | 701.5 | 2.5 | 411 |
| 3 | 5 | 635 | 2.5 | 395 |
| Mean value | 3.333 | 667.333 | 2.667 | 436.333 |
| t_0/t_1 | 0.00500 | | 0.00611 | |
| $K \cdot t_0/t_1$ | 0.077 | | 0.305 | |
| θ | 85.573 ± 1.441 | | 72.254 ± 0.322 | |



Determination of contact angles

Results obtained with both photographic and capillary rise method have been summarized in the table below (Table 5). Values obtained for microscopic cover glass are difficult to compare to those relying on capillary rise measurements, as the two methods used are completely different, based on different principles. The quantity of water present in the samples played a significant role in determination of measured contact angles and no data have been obtained concerning its change during the actual experiments. Increasing length of the alkyl chain on the 1-alkyl-3-methylimidazolium cation increases the hydrophobic character of given ionic liquid. The extent of water-repelling properties of ionic liquids are less in the formation of stable contact angle then its type – [HMIM][Cl] and [OMIM][Cl] behave almost identically in all performed tests. Even only slightly hydrophilic ionic liquid, like [OMIM][Cl] will form a low contact angle on only slightly hydrophilic surface, like the microscopic cover glass. [DMIM][Cl] is barely hydrophobic and its contact angle observed on the identical surface is extremely high.

Table 5. Summary of contact angle results obtained for tested systems

| Solid phase | [HMIM] [Cl] (degrees) | [OMIM] [Cl] (degrees) | [DMIM] [Cl] (degrees) |
|-------------------------|-----------------------|-----------------------|-----------------------|
| Microscopic cover glass | 14.592 ± 0.539 | 10.815 ± 0.301 | 105.951 ± 1.295 |
| Hydrophilic beads | 17.222 ± 8.862 | – | – |
| Hydrophobic beads | 85.573 ± 1.441 | 72.254 ± 0.322 | – |

Conclusions

Wetting potential of ionic liquid group being the subject of this paper is related with many independent factors. Hydrophobicity of 1-alkyl-3-methylimidazolium ionic liquids is based on the length of an alkyl chain and has been described previously by $\log K_{ow}$. The water content is crucial factor concerning wetting process of all ionic liquids with chloride anion, especially when their extremely hygroscopic character is taken into account. Completely water-free samples of ionic liquid are extremely viscous and could not be used to wet any kind of surface efficiently. Water molecules disrupt the hydrogen bonding between chloride anion and hydrogen atoms of imidazolium ring, rapidly decreasing the viscosity of ionic liquids (Wassercheid and Welton, 2003). This process influence contact angle values differently for hydrophilic and hydrophobic specimen. Water molecules diffuse in hydrophilic samples and decrease of viscosity result in an exceptionally good wetting observed for hydrophilic surfaces and increase contact angle for hydrophobic solids. In case of hydrophobic dialkylimidazolium ionic liquids, water molecules are trapped in liquid crystalline structure of an ionogel, which is a semisolid matter, unable to wet any surface. If an ionogel structure cannot be formed for given species of ionic liquid, it can be assumed that its viscosity will decrease after addition of water or after moisture absorption.



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