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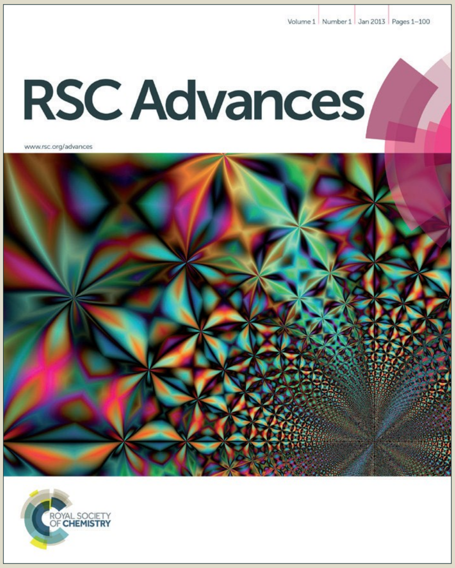

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Dual functionality of amphiphilic 1-alkyl-3-methylimidazolium hydrogen sulfate ionic liquids: surfactants with catalytic function

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Abstract

A series of amphiphilic 1-alkyl-3-methylimidazolium hydrogen sulfate ionic liquids were synthesized. Acidic hydrogen sulfate ionic liquids with the alkyl chains C_6-C_{14} are characterized by good surface properties. Their surface properties (adsorption and micellization parameters, degree of ionization of micelles, Krafft temperatures and thermodynamic parameters) was instrumentally determined. Synthesized ionic liquids were applied as co-catalyst in oxirane ring opening reaction in epoxidized fatty acid methyl esters. Their co-catalytic activities have been analyzed and discussed in a function of the structure and surface properties. It was found, that co-catalytic properties, both conversion and selectivity, of alkylimidazolium hydrogen sulfate ILs noticeably depend on the alkyl chain lengths, and in consequence their properties.

1 Introduction

The term "ionic liquids" (ILs) describes a group of organic salts, characterized by melting points below 100 °C and a number of unusual and diverse properties, e.g. low vapor pressure, non-flammability, high conductivity, thermal stability, good solvation properties etc. The wide interest of synthesis, physicochemical properties as well as application of ILs is a consequence of their extreme versatility; their properties can be readily modified by variation of the cation and anion species [1]. Most described in the literature ionic liquids are characterized by relatively strong ionic asymmetry, determining their low melting points, and exhibits the characteristics of amphiphilic compounds with specific hydrophilic and lipophilic centers. Studies on the surfactant properties of the ionic liquids have been developed intensively for many years. These results appointed in particular for imidazolium ILs, has been described in many papers and also collected in several reviews [2-16]. Based on variety of methods such as surface tension measurements[17], conductivity [4], calorimetry [18, 19], spectroscopy[20] etc. as well as molecular dynamics[21], relation between alkyl chain length in the IL cation as well as anion structure and susceptibility to micellar aggregate formation was proposed. Up to date surface activity and aggregation behavior of amphiphilic ILs was used in many synthetic, catalytic and separation applications. For example, micellar solutions of polymeric ILs were applied for Au nanoparticles preparation with controlled size due to the combination of the unique chemical and physical properties of ILs and micellar template as it was presented by Li et al.[22]. Dodecyltrimethylammonium bromide micelles can serve as size- and structure-directing template as well as stabilizing agent for formation of α-FeOOH nanoparticles [23]. Surface active properties of ILs were used for modification of the zeolite surface to enhance adsorptive removal of anionic contaminants such as chromate from water [24]. Pino et al. proposed application of the 1-hexadecyl-3-methylimidazolium bromide micellar solution for extraction of the polycyclic aromatic hydrocarbons from sediments [25]. It was revealed that ionic liquids cannot be considered only as common cationic surfactants. The structure of the cation is far more complex than conventional quaternary ammonium salts that are most popular cationic surfactants. In the molecule of imidazolium ILs, with partially delocalized positive charge constituting the nucleus, it is possible to define a number of interactions (van der Waals, π–π interactions, hydrogen bonding), that have a significant impact on their surface properties, formation of micelles, and consequently, on the processes utilizing them.

Moreover, many chemical reactions, involving ionic liquids, is carried out in biphasic systems assisted by amphiphilic catalyst [23,24]. For this type of processes, progress of reaction is determined by diffusion taking place between the two immiscible phases. In reactions running with the use of the catalysts, besides isolation and purification of the product, an important element is to develop a method for catalyst separation from the post-synthesis mixture. However, most of this methods often do not work well when ionic liquids are used as catalysts due to poor solubility in the catalytic phase, particularly when it is water. On the other hand solubilizing properties of ionic liquids in combination with their surface properties can be a very promising alternative for the classical two-phase catalysis, being similar to common phase transfer catalysis (ptc) [26-31]. One of the features that distinguishes ionic liquids from most common solvents is their dual functionality in various aspects. The dual functionality of ILs in the "classic" form, where ionic liquid plays the role both of solvent and the catalyst, has been well described in literature [32-3736]. Interesting example of the dual functionality of ionic liquids was reported by Alizadeh [386]. In the condensation of aromatic carbonyl compounds with nitroalkanes 2-hydroxyethylammonium formate IL was used. It turned out that ammonium proton participated in the protonation of the aldehyde group in the first step of the synthesis.

In our studies we aim to investigate the dual functionality of the acidic ILs by means both of catalytic and amphiphilic properties. We reported for the first time synthesis and use of the amphiphilic Brønsted acidic ionic liquids as effective co-catalysts in biphase catalytic process of nucleophilic addition of water to oxirane ring. This reaction runs according to S_N1 mechanism and require acidic catalysts. Used in our study 1-alkyl-3-methylimidazolium hydrogen sulfate ionic liquids, due to their surface properties, will strongly affect the development of the interfacial surfaces. On the other hand, Brønsted acidic catalytic center will catalyze the process more efficiently (Scheme 1). In this regard, surface properties of the ILs were correlated with their catalytic activity in the reaction of epoxydized methyl oleate with water as nucleophile. Addition of water to oxirane ring in epoxidized fatty acid derivatives turns to corresponding glycols – valuable oleochemical by-products. Finally, based on the experimental studies the role of the IL structure as well as catalytic activity in that biphasic reaction was proposed.

2 Materials and methods

2.1 Materials

1-Bromohexane (99%), 1-bromooctane (99%), 1-bromodecane (99%), 1-bromododecane (99%) and 1-bromotetradecane were purchased from TCI Chemicals. 1- Methylimidazole was obtained from Merck Millipore (Poland). Potassium bisulfate puriss. (99%) was obtained from Sigma-Aldrich (Poland). Octyltrimethylammonium chloride (99%) was obtained from Sigma-Aldrich. Ethanol puriss. and diethyl ether puriss. were obtained from POCh (Poland). All chemicals were used without drying or any further purification. Epoxidized methyl oleate was synthesized according to procedure described in literature with the use distilled methyl oleate (min. 92 wt.%, GC), 30 wt.% aqueous solution of hydrogen peroxide and formic acid as active oxygen source [39].

2.2 Ionic liquids preparation

All ionic liquids used in this study were synthetized according to well know procedure described in literature [40]. Thus, a mixture of the 1-bromoalkane (0.2 mol) and 1-methylimidazole (0.2 mol) were placed in the 100 mL glass reactor. The mixture was then stirred under a nitrogen atmosphere for 18 h at 90 °C. The oily crude product was washed several times with diethyl ether in order to remove unreacted reagents. Residual volatile solvent was evaporated under vacuum (1-2 mbar, 2 h) to give corresponding imidazolium bromides as light yellow, viscous oils (C_6 - C_{10}) or white solid (C_{12} - C_{14}) . Obtained imidazolium bromides was then dissolved in 200 mL of isopropyl alcohol. Appropriate amount of $KHSO_4$ (20% molar excess) was added to the solution and stirred at room temperature for 18 h. White precipitate of KBr was filtered off and clear filtrate was evaporated under vacuum to give hydrogen sulfate ionic liquids as yellowish oils (C_6 - C_{10}) or hygroscopic solids (C_{12}, C_{14}).

2.3 Analytical methods

The composition of post-synthesis mixtures were determined by gas chromatography with MS detector. Analyses were performed on HP chromatograph Model 7890A (Agilent) equipped with MSD type 7000 GC/MS Triple Quad MS detector. For analysis HP-5MS column (l = 30 m, ø

= 0.25 mm, working temperature 70 – 280 °C, detector temperature 300 °C, He as carrier gas) was used. Analytical data were developed with the use of Mass Hunter software (Agilent).

The epoxide numbers both raw material and products were analyzed using FTIR method. For the determination of epoxide number 916 and 835 cm^{-1} bands assigned to the epoxy ring stretching region was applied. FTIR analyses were performed on THERMO Scientific FTIR Nicolet 6700 spectrophotometer. The reflection technique with (ATR), SMART ARK, using ZnSe crystals, the number of reflections = 7, and sample penetration depth by the IR beam = 1.11 m was applied. The hydroxyl numbers were determined according to DIN 53 240.

Surface tension (σ) of the IL solutions were measured at 25±0.1 ^{o}C using a video based optical contact angle meter (OCA 15, Dataphysics) along with the supportive software, SCA22 (pendant drop method), and a resolution of ±0.01mN/m. The temperature of the samples were controlled by a thermostatic water bath (PolyScience, AD07R-20). The error calculation was performed by the Dataphysics software.

The CMC values of ILs solutions were confirmed also by conductivity (κ) and isothermal titration calorimetry (ITC) methods. The conductivity measurements were done at the temperature of 25±0.1 ^{o}C using a conductivity meter equipped with an autotitrator (Cerko Lab System CLS/M/07/06, Poland) and a microconductivity electrode (Eurosensor, EPST-2ZA, Poland). A thermostatic water bath (PolyScience 9106, USA) was used to maintain a stable temperature of the measurement. The degree of ionization of the micelles (β) was calculated from the ratio of the $d\kappa/dc$ slopes of the two linear fragments of the conductivity curves [41, 42]. The conductivity method was also applied for the Krafft temperature (K_T) determination. For this purpose the aqueous solutions of ILs at concentrations ten times their CMC were placed in a refrigerator at a temperature of 253 K for at least 24 h to ensure complete precipitation of the salts in the form of hydrated crystals. The temperature (T) of the sample was then raised gradually using a thermostat bath and the conductivity of the sample was measured under stirring until a steady value was reached[43]. The measurements were carried out until the turbid solution became transparent. The Krafft temperature was taken as a discontinuity in the conductivity versus temperature curve. This temperature is analogous to that being the point of complete clarification of the solution judged visually.

The ITC experiments were performed with Nano-Isothermal Titration Calorimeter III (N-ITC III, CSC, USA). The IL solutions with concentrations of about ten times higher than the expected CMC values was applied to observe the demicellization process. The titration experiment consisted of 48 injections of 5.15 μL of IL aliquots into the sample cell loaded with 958 μL of water after a stable base line was achieved. The enthalpograms were created using Titration Bindworks software provided by CSC. From the enthalpograms the enthalpy of demicellization (ΔH_{dm}) and CMC were extracted [18, 43]. The surface excess concentration, Γ_{max}, and the minimum area per surfactant molecule, A_{min}, at the air/solvent interface were calculated using surface tension measurement values by means of given equations, (1) and (2):

$$\Gamma_{max} = -\frac{1}{RT}\left[\frac{d\gamma}{dlnc}\right]_{T,p} \tag{1}$$

$$A_{min} = \frac{10^{16}}{N_A \cdot \Gamma_{max}} \tag{2}$$

where R is the gas constant, T is the absolute temperature, N_A is Avogadro's number, γ is surface tension, and c is the concentration of the surfactant in the solutions. Surface pressure at the CMC, Π_{cmc}, was obtained by means of equation (3):

$$\Pi_{CMC} = \gamma_o - \gamma_{CMC} \tag{3}$$

The Gibbs free energy of micelle formation, ΔG_m, of a nonionic surfactant is related with the CMC by the following formula:

$$\Delta G_m = RTlnx_m \tag{4}$$

where x_m is the CMC expressed in mole fraction units. The standard entropy, ΔS_m, of the micellization was calculated from equation (5):

$$\Delta S_m = \frac{(\Delta H_m - \Delta G_m)}{T} \tag{5}$$

where T is the temperature.

2.4 Nucleophilic addition of water to epoxidized methyl oleate

Reaction were carried out in 100 mL laboratory glass reactor equipped with mechanical stirrer and water jacked connected with thermostat. Epoxidized methyl oleate (50 g), water solution of H_2SO_4 (63 mL) and additional co-catalyst were placed in the reactor, heated to desired temperature (thermostat) and stirred at 500 rpm for 7 h. After 1, 3 and 5 h of reaction time analytical samples were taken and analyzed. After completion of the reaction organic phase was washed to neutral pH and dried. An analogous procedure was applied in relation to the analytical samples.

3 Results and discussion

3.1 Surface properties of alkylmethylimidazolium hydrogen sulfate ILs

The solubility of ionic amphiphilic compounds in aqueous solutions is highly temperature-dependent. The characteristic feature is the Krafft temperature, being a minimum temperature at which the solubility of the salt monomer becomes high enough to start forming micellar aggregates, thus corresponding to the onset of the surface activity of the compound. In this regard, first of all we investigated the temperature range at which micellization of the ILs may occur. The selected relation of the conductivity measurements of the 1-tetradecyl-3-methylimidazolium hydrogen sulfate $[C_{14}mim]HSO_4$ solution versus temperature (in the range of 0-20 °C) used to determine the K_T is presented in Fig.**Error! Reference source not found.**1.

Below the Krafft temperature the surfactant is in the solid crystalline hydrated state, therefore the conductivity of the sample gradually increases with temperature due to progressive growth of the solubility in water. At K_T dramatic rise in the conductivity was observed reflecting an equilibrium among the ordered, solvated solid phase, dispersed monomers, and micellar aggregates. The lower slope in the conductivity profile after Krafft point is related with the limited mobility of the formed micelles as compared to the free ions. The Krafft temperature is strongly dependent on the surfactant structure, that is alkyl chain length, the type of polar head, the nature of the counterion as well as possible interactions (particularly hydrogen bonding). The results obtained for ILs presented in this study confirm chain length-dependency. Aqueous solutions of the ILs with alkyl chain length below or equal to 12 carbon atoms did not indicate a clear K_T above zero Celsius degrees. Therefore, K_T either fall below zero Celsius degrees or do not exist in these conditions since the solubility curve does not intersect the Krafft boundary, but rather the ice boundary [43, 44]. Only $[C_{14}mim]HSO_4$ IL have clearly detectable K_T at 10 °C. The K_T determined for C_{14} compound is higher than those characteristic for tetradecyltrimethylammonium chloride (< 0 °C) and bromide (~ 0 °C), as well as 1-tetradecyl-3-methylimidazolium chloride (< 0 °C) indicating lower hydrophilicity of the hydrogen sulfate ionic liquids. Nevertheless, these results are favorable from practical point of view due to wide range of use.

3.1.1 Effect of hydrocarbon chain length and the type of counterion

In order to investigate surface properties of 1-alkyl-3-methylimidazolum hydrogen sulfate ionic liquids the surface tension and conductivity methods were used. The surface tension measurements versus concentration of various ILs are shown in Fig. 2 whereas selected conductivity results are presented in Fig. 3. As a result of their amphiphilic structure and positive charge on the nitrogen atom, all ILs used in this study have ability to adsorb at the air/water interface, reduce surface tension of the aqueous solutions eventually forming micellar aggregates. It is well known that the hydrocarbon chain length as well as the counterion type are the most important factors determining the interface behavior and surface activity of the amphiphilic compounds. Therefore, typical for quaternary ammonium compounds behavior was observed, that is the longer the chain length in the cation, the lower concentration at which surface tension lowering begins. Micelles are not surface active agglomerates of amphiphilic compounds, therefore the surface tension of the dispersion after passing critical micelle concentration (CMC) is almost constant (plateau region in surface tension izotherms). Moreover, micellar aggregates have lower mobility in comparison with monomers in solution, therefore the lower slope after the discontinuity was observed in the conductivity curve. The adsorption and micellization parameters, characterizing behavior of the ILs in the aqueous systems, were collected and compared in Table 1.

A decrease of the critical micelle concentration (CMC) from near 600 mM to about 2 mM was observed with increasing the number of the carbons atoms in the alkyl chain of the imidazolium cation from 6 to 16. It confirms that elongation of the hydrocarbon chain facilitate micelle formation due to increased energetically unfavorable contact of the chains with water, stronger hydrophobic interactions between alkyl chains and the more delocalized reducing the electrostatic repulsion. Analogous decrease in the CMC values were also observed for ILs with different anions, for example [C$_n$mim]Cl[17, 43], [C$_n$mim]Br[16, 47] and [C$_n$mim]BF$_4$[48]. Comparing the CMC values of the ILs with different anions the following order can be presented [C$_n$mim]BF$_4$ < [C$_n$mim]HSO$_4$ ≈ [C$_n$mim]Br < [C$_n$mim]Cl. This sequence reflects hydration, polarizability and size of the anions, thus, larger, less hydrated (more hydrophobic) anions easier interact with the micelle surface, thereby decreasing electrostatic repulsion and facilitating micelle formation. This can be confirmed by the values of the degree of micelle ionization (β) estimated based on the conductivity measurements that are lower than that for imidazolium ILs with BF$_4$ anion (presented as degree of counterion association to the aggregates) [48] and higher that determined for salts containing Cl anion [43]. In addition, ionization of the micelles increase with elongation of the alkyl chain length due to the larger size of micelles formed by the more highly ordered and compact micellar structures of the higher homologues.

The relationship between CMC and the number of carbon atoms in the alkyl chain (x) for a homologous series of linear single-chain amphiphiles can be described by the logarithmic rule:

$$log\ CMC = A - Bx \tag{6}$$

where A and B are empirical constants. The A value depends on the type and number of the polar headgroups in the amphiphile, whereas the value of B indicates the contribution of the methylene group in the hydrophobic chain to the micelle formation (Fig 5). Micellization is favored by smaller values of A or larger values of B [49]. The values of A and B calculated based on the equation (6) for [$C_n$mim]HSO_4 are 4.92 and 0.34 and are similar to proper A, B constants describing homologues series of the 1-alkyl-3-methyimidazolium salts with chloride and bromide anions [10].

The IL adsorption efficiency, being a concentration at which surfactant provide surface tension reduction of 20 mN/m (pC_{20}), was observed to increase from 1.07 as calculated for [C_6mim]HSO_4 to 3.2 determined for IL with the longest chain length in the imidazolium cation (e.g. C_{14}). The higher pC_{20} the more efficiently IL adsorbs at the interface and reduces surface tension. The values of surface tension at CMC, $\gamma_{CMC,}$ were found to be close to 34-35 mN/m for all of the ILs, whereas the surface pressure values, Π_{CMC}, were calculated to be in the range of 36-38mN/m. These both parameters describe effectiveness of the surfactant to adsorb at the interface and reduce surface tension, and for ionic compounds (such as ILs) are controlled by CMC, solubility or Krafft temperature [44, 50]. The efficiency and effectiveness of the 1-alkyl-3-methylimidazolium hydrogen sulfates was found to be consistent, in other words, the more efficient ILs more effective they are. When comparing these parameters with ILs possessing different anions, it can be observed that hydrogen sulfate derivatives are more surface active compounds when compared to halogen-based salts [48].

The estimated area per IL ion pair at the air/water interface, A_{min}, obtained from the Gibbs adsorption isotherm (equation 1 and 2), appeared to decrease from 0.87 to 0.67 nm^2 with increasing alkyl chain length in the imidazolium cation. The area occupied by the amphiphilic compound, reflecting the surface arrangement of surfactants at the air/liquid interface, is determined by the hydrophobic chain cross-sectional area, and the area required for closest packing of the head group. Therefore, it provides an information on the degree of packing and the orientation of the adsorbed surfactant molecules. The maximum surface excess concentration at the air/water interface, Γ_{max}, was observed to increase from 1.85 x 10^{-6} mol/m^2 as determined for [C_6mim]HSO_4 to 2.40 x 10^{-6} mol/m^2 for [C_{14}mim]HSO_4. Behavior of the [$C_n$mim]HSO_4 ionic liquids is characterized by larger

Γ_{max} and a correspondingly lower A_{min} values than [$C_n$mim]Br, indicating a denser arrangement of hydrogen sulfate-based compounds at the air-water interface compared to that of [$C_n$mim]Br [49].

3.1.2. Thermodynamic of micellization

The thermodynamic parameters of the micellization process provid valuable information about the driving force of self-assembly of ILs. By using the ITC technique a direct result of the CMC values as well as enthalpy of demicellization (ΔH_{dm}), and thereby the enthalpy of micellization (ΔH_m) [45, 46] can be determined. The ITC titration peaks obtained by addition of concentrated IL solution towards water, were integrated and normalized taking into account the number of moles of the solute. The selected enthalpograms obtained for ILs with C_{12} and C_{14} alkyl chain of the imidazolium cation are as shown in Fig. 4. At a concentration below CMC (titration of water with concentrated IL solution; first part of the entalpogram), an enthalpic effect is a consequence of the transition: micelles → monomers (heat of micelle dilution, demicellization and dilution of monomers in the solvent). Micellar aggregates formation is visible as a sharp increase of the heat effect (the second region in the enthalpogram). At concentrations above the CMC, being a third part of the entalpogram, the heat effect arises from dilution of the concentrated micelles into the micellar solution. Demicellization enthalpy was calculated from a difference between the enthalpy values of the terminal and initial regions of the enthalpogram (ΔH_{dm}), as it was previously shown in [18, 43]. The CMC was taken as the surfactant concentration at the midpoint of the titration curve inflection (the first derivative of the line from integrated peaks reaching maximum).

The enthalpy of micellization determined by ITC method as well as thermodynamic parameters ΔG_m, and ΔS_m, calculated using equations (4) and (5) are shown in Table 2. The values of free energy of micellization are negative indicating spontaneous micellization process. As it was expected elongation of the hydrocarbon chain length facilitate micelle formation. The experiments revealed that the micellization of the ILs with C_{10}-C_{14} alkyl chains at 25 °C is exothermic, whereas for C_8 endothermic and ΔH_m decrease with increasing chain length. Based on the observed trend it can be assumed that micellization of the ILs with alkyl chain shorter than C_8 is endothermic. Higher ΔH_m values are due to higher energy required to release the solvent molecules from the hydration layer and water cage surrounding hydrophilic and hydrophobic domains of the amphiphilic compound. Contribution to the overall ΔH_m value have also energy that is released when the hydrocarbons are transferred to the micelle and hydrogen bonding structure of the water around the micelle is recreated [43, 51]. Higher energy demands appear due to shorter chain length in the cation, and as a consequence higher affinity of the short-chained compounds to water.

An increase of the entropy change is a driving force of the micellization process, being initiated by a highly ordered structure of the solvents, mainly around the hydrophilic part of the surfactant. During micellization, water molecules become reduced in the hydration network providing an increase in ΔS_m and a decrease in ΔG_m. According to the Gibbs-Helmholz equation, ΔH_m and ΔS_m have an opposite effect on the free energy of micelles formation. For all of the ILs systems $-\Delta H_m$ is lower than $T\Delta S_m$ indicating entropy-driven processes.

3.2. Reaction of epoxydized methyl oleate with water

Oxirane ring opening by various nucleophiles runs according to two different mechanism depending on the character of the nucleophile. Strong nucleophiles like Grignard reagents, alkali hydroxides or alkali alcoxides reacts with oxirane ring according to S_N2 substitution mechanism. The key step of this mechanism is the nucleophile attack to the more substituted C atom of the oxirane ring. Weaker nucleophiles, like water or alcohols, reacts with oxirane ring according to S_N1 substitution mechanism. The key step of this mechanism is protonation of O atom in oxirane ring. This makes the acid catalysts have strong positive impact on this reaction. In this regard, reaction of epoxidized methyl oleate with nucleophiles like water runs according to S_N1 substitution mechanism and is catalyzed by various acidic catalysts. For preliminary assessment of this reaction in conventional reaction conditions and for comparison purposes a series of experiments with the use of various concentration of aqueous solution of H_2SO_4 as catalyst were conducted. The results are presented graphically in Fig 6. As can be seen concentration of H_2SO_4 has strong impact on the reaction efficiency. Changes of the epoxide number for concentration of 1 wt.% was observed to be negligible, however for concentration of 5 wt.% after 7 h the epoxide number decreased to 0 mg KOH/g, which corresponds to conversion of epoxide of 100%.

In the next step to the 1 wt.% H_2SO_4 aqueous solution Brønsted acidic ionic liquid [C_8mim]HSO_4 (chosen as a model IL) in amount of 2 wt.% (based on epoxidized methyl oleate) was added. The effect of the IL addition to the reaction system is presented in Fig. 6. Figure 6 clearly shows, that addition of acidic ionic liquid to a 1 wt.% of H_2SO_4 aqueous solution results in a strong increase of the reaction rate, which can be explained by the synergistic effect of the surface active IL on catalysis of nucleophilic addition of water to the oxirane ring in epoxidized methyl oleate. As it was presented above the surface properties of homologous amphiphilic ionic liquids, are highly dependent on the length of the hydrophobic alkyl chain. In this regard the analogous reactions of water addition to the oxirane ring using a series of amphiphilic ionic liquids [$C_n$mim]HSO_4, (n = 6 - 14) was carried out. The results were depicted in Fig. 7. As it was demonstrated by the results depicted in Figure 8, all the tested ionic liquids used as co-catalysts are characterized by a strong synergistic effect. After 7 h of reaction the epoxide number (L_{ep}) in each of the samples were close to 0 mg KOH/g, which corresponds to conversion close to 100%. Results presented in Figure 8 also revealed that for the shorter alkyl chain in the imidazolium cation of the ionic liquid catalytic effect is stronger. For the ionic liquid [C_6mim]HSO_4 the epoxide value L_{ep} = 0 mg KOH/g were obtained just after 5 h. Fig. 8 summarizes the results of syntheses, in which in the studied reaction different catalytic systems were used: 1 wt.% aqueous solution of H_2SO_4 containing the ionic liquid and either quaternary ammonium salt, and H_2SO_4 and the ionic liquid used separately.

Results of our studies clearly confirmed the dual functionality of the amphiphilic ionic liquids. This is clearly seen when comparing the two catalytic systems 1% H_2SO_4/IL and 1% H_2SO_4/common quaternary ammonium salt, octyltrimethylammonium chloride (OTMAC). In comparison to the classical ammonium salt surfactant ionic liquid has a significantly stronger co-catalytic effect. For the 1% H_2SO_4/IL system a faster growth in the conversion of epoxide was observed. After 7 h of reaction the conversion of epoxide was almost 100%, while for the 1% H_2SO_4/OTMAC after the same time was only 80%. For comparison, results obtained for H_2SO_4, and the ionic liquid [C_8mim]HSO_4 used independently as a main catalysts are also shown in Fig. 9. The strong mineral acid showed much weaker catalytic ability than H_2SO_4/IL mixture, however the ionic liquid as itself was characterized by only a little higher activity as compared to H_2SO_4. Examining the reaction of water addition to epoxide ring you should also take into account its selectivity. It is known that nucleophilic addition to the oxirane ring, running according to S_N1 mechanism, leads to two products formation. The main product of the addition is corresponding 1,2-diol (Scheme 2). Under the reaction conditions may, however, take place the isomerization of the epoxide ring leading to the ketone (Scheme 3) [51].

The isomerization reaction of oxirane ring is catalyzed by Lewis acids. The key step is the creation of a hydrogen bond with the oxirane oxygen atom. Imidazolium ionic liquids are also known, often under the reaction conditions, to behave as typical Lewis catalysts. In particular the imidazolium cation may act as a Lewis acid, which is reflected *inter alia* by the formation of hydrogen bonds with C2-H hydrogen atom [52-54]. In case of epoxy compounds in the presence of imidazolium ionic liquids the following complexes may be formed [55] (Scheme 4). Accordingly, as a results of water addition to the epoxidized fatty acid methyl esters two types of products can be created (Scheme **Scheme**5). Evaluation of the surface properties of the homologous series of the 1-alkyl-3-metyloimidazolium ionic liquids were presented in previous section. Based on that results the effect of the ionic liquids structure in the reaction of nucleophilic addition of water to epoxidized FAME was investigated. The obtained results are shown graphically in Fig. 7-9. Considering the theoretical assumptions shown in Scheme 4, assessment of the ionic liquid impact on the selectivity of addition reaction was performed. The results are summarized in Table 3.

Just as it did when assessing the effect of the alkyl chain length on the co-catalytic effect, alkyl chain length has also a noticeable impact on the selectivity of the studied reaction. The highest concentration of [C_6mim]HSO_4 IL causes the highest effect on the oxirane ring – imidazolium cation structure showed in Scheme 4. Formation of this structure favors formation of side product – ketone (Table 3, entry 5) compared to reaction conducted in absence of the IL (Table 3, entries 1, 2 and 3). In Fig. 10 a representative GC chromatogram of reaction product has been presented.

The results presented in Table 3 clearly show that the type of the catalytic system has a noticeable effect on reaction selectivity. The reaction carried out in the presence of sulfuric acid alone, strongly directed to 1,2-diol. The selectivity to diol was 83.3-84.5 % and did not depend on the acid concentration. The selectivity to the ketone was 16.7-15.5 % respectively. Application of the amphiphilic ionic liquid as a co-catalyst shifts the reaction a little more toward the ketone. For the catalytic system 1 wt.% H_2SO_4/IL selectivity to 1,2-diol was 66.6-79.2 % and the selectivity to the ketone 33.4-20.8 % respectively. Moreover, the results presented in Table 1 clearly show that the selectivity to 1,2-diol and ketone depends on the length of the alkyl chain in the ionic liquid. When the alkyl substituent is shorter, the content of the ketone in the post-reaction mixture is greater. These results are consistent with described in the literature effects of the chain alkyl length of imidazolium ionic liquids on their physicochemical properties.

3.3 Discussion of the catalytic activity

The systems that exhibits the highest efficiency of the catalytic opening of the epoxide ring is the epoxidized methyl oleate in the biphasic system containing 1 wt.% of H_2SO_4 and 2 wt.% of [C_6mim]HSO_4 or [C_8mim]HSO_4. For that ionic liquids, the epoxide number equal to 0 mg KOH/g, reflecting epoxide conversion almost 100 %, was obtained just after 5 h of the reaction time. In this regard, addition of the acidic 1-hexyl- or 1-octyl-3-methylimidazolium ionic liquid revealed the highest synergistic effect providing strong increase of the reaction rate in the comparison to the system without the IL. Moreover, these systems revealed also higher catalytic activity than analogous catalytic system containing 1% H_2SO_4/octyltrimethylammonium chloride, that was only 80% of conversion after 7h. The crucial difference between imidazolium and ammonium compounds is the presence of the acidic C2-H hydrogen atom in the imidazolium ring that may interact with the oxygen atom in the oxirane ring. Dong et al. studying the physicochemical properties of the alkylimidazolium ionic liquids has shown experimentally, that the number of the carbon atoms in the alkyl chain have noticeable effect on the C2-H bond length [55]. For longer alkyl chains, C2-H bond is shorter, thus affecting the acidity of this proton. Therefore, elongation of the alkyl substituent in the imidazolium ionic liquids decreases the pKa of the imidazolium cation, which is characterized by lower acidity. This affects the low stability C2 - H - O (epoxy) hydrogen bonds and consequently the stability of the hydrogen complexes oxirane-IL. This observations was also confirmed by studies conducted for model systems using NMR spectroscopy [56-59]. The ionic liquids containing long alkyl chains, for example R = C_{10}, shifts reaction of water addition to epoxidized FAME towards the more preferred dihydroxy compound (1,2-diol). In turn, in the presence of the ionic liquids with shorter alkyl chains, for example R = C_6, a side reaction towards ketone becomes a bit more important.

The higher catalytic activity of the system containing ionic liquid can be related with surface properties of the ionic liquids. Due to the amphiphilic structure, IL reveal ability to adsorb at the oil/water interface and form micellar aggregates in the aqueous phase. Therefore, epoxidized methyl oleate may diffuse to the aqueous–organic interface, where interact with IL ions, followed by the increase of the solubility in aqueous phase *via* their incorporation into the micelles (solubilization). Analysis of the dependence of the alkyl chain length on the surface properties of 1-alkyl-3-methylimidazolium ionic liquids, in particular on CMC values, revealed that the shorter alkyl chain length (C_6) the higher critical concertation representing micelle formation. Effect of the alkyl chain length on the CMC values of homologous series of alkylimidazolium hydrogen sulfate ILs is presented in Table 1 and Figure 5. It should be mentioned that 2 wt.% concentration of the ILs added to the reaction system exceeds CMC values only in the case of the systems containing ionic liquids with C_{10}-C_{14} alkyl chain length. That means that only for these compounds we can expected micelles formation. For C_8 ionic liquid, the concentration applied in the experiment exceed concentration needed to decrease surface tension by 20 mN/m that is identified with complete (or close to complete) saturation of the interface. In contrary, [C_6mim]HSO_4 was used in the concentration that is lower not only than CMC but also C_{20} concentration meaning that saturation of the interface is not attained. It should be also remember that ILs reveal some affinity not only to water but also towards organic fatty acids phase due to presence of the hydrophobic part of the cation. Some partial solubility of the IL in the organic phase results in decrease of the [C_6mim]HSO_4 at the interface. In addition, ILs with shorter alkyl chain length are also characterized by the higher specific surface area values per IL ion pair at the interface (0.87 nm^2 for [C_6mim]HSO_4 and 0.67 nm^2 for [C_{14}mim]HSO_4. In other words, the cross-sectional area occupied by the amphiphilic compounds with shorter alkyl chain is higher. The short-chained ILs are not in the closed-packed arrangement to the surface normal but are probably to more tilted with respect to the interface than long-chained ones. As a consequence, the maximum surface excess concentration, that describe effectiveness of the amphiphile adsorption, is lower for IL with shorter alkyl chain. Based on these results we can assume that rather adsorption of the ILs at the oil/water interface than micellization/solubilization processes play crucial role in the mechanism of the epoxide conversion. Adsorption of the ILs at the interface results in lowering of the interfacial tension facilitating contact of the substrates in both phases. In addition, length of the alkyl chain influences also strength of the interaction between cation and anion of the ionic liquid. That is, the longer the hydrocarbon chain, the more delocalized is the charge, the more acidic character of imidazolium H2 hydrogen atom, and as a consequence the weaker is the interaction between ions. In this light, ionic liquids with higher catalytic activity (C_6 - C_8) are characterized by the strongest cation-anion interactions and lower acidity of C2-H hydrogen atom. On the other hand, elongation of the alkyl chain in the imidazolium cation may also result in stronger van der Waals interactions between hydrocarbons (shown as higher surface excess) and additional steric hindrance limiting ability of the imidazolium cation to interact with organic substrate. Similar conclusion has been reported by Xu et al. [60] in his study on dissolution of cellulose in 1-alkyl-3-methylimidazolium ILs. The increasing alkyl chain length leads to an increase in the acidity of the hydrogen atoms H2 and H4 in imidazolium cation which contributes to the hydrogen bond formation between acidic hydrogen and hydroxyl oxygen of cellulose and thus cellulose dissolution. However, as alkyl chain length further increases, the steric hindrance of the hydrogen bond formation between acidic hydrogen and hydroxyl oxygen increases, and the hydrophilicity of imidazolium cation decreases, which goes against cellulose dissolution.

4 Conclusions

In summary, a series of amphiphilic 1-alkyl-3-methylimidazolium hydrogen sulfate ionic liquids were synthesized and analyzed in terms of surface and co-catalytic properties. Surface properties (surface tension, micellization, degree of ionization of micelles and Krafft temperatures) have been instrumentally determined. The length of the alkyl chain substituents was found to have vital effect on the adsorption and micellization behavior. All acidic ionic liquids were tested as co-catalyst in oxirane ring opening reaction in epoxidized fatty acid methyl esters. Their co-catalytic activities were studied as function of surface and physicochemical properties. It was found, that co-catalytic properties, both conversion and selectivity, of alkylimidazolium hydrogen sulfate ILs noticeably depend on the alkyl chain lengths attached to imidazolium nitrogen atom, acidity of C2-H imidazolium hydrogen atom and micellization properties. Surface properties of 1-alkyl-3-methylimidazolium hydrogen sulfate ionic liquids were found to have noticeably impact on co-catalytic effect, whereas acidity of C2-H hydrogen atom influence selectivity of this reaction. Obtained results confirm specific dual functionality of the amphiphilic Brønsted acidic ionic liquids.

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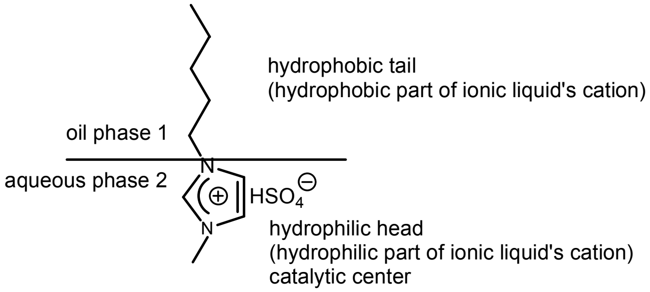
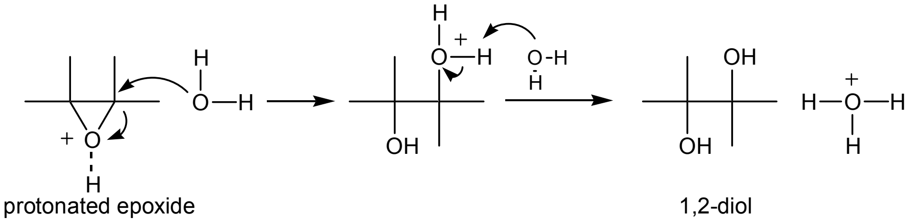
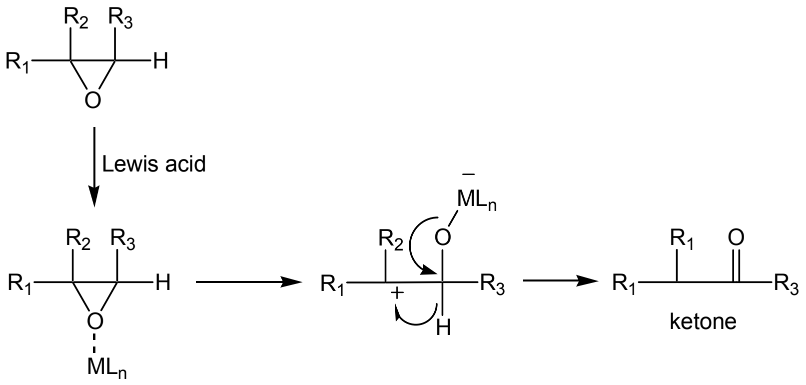


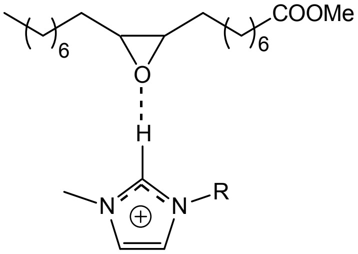
Scheme 1. Amphiphilic ionic liquid – surfactant with catalytic function



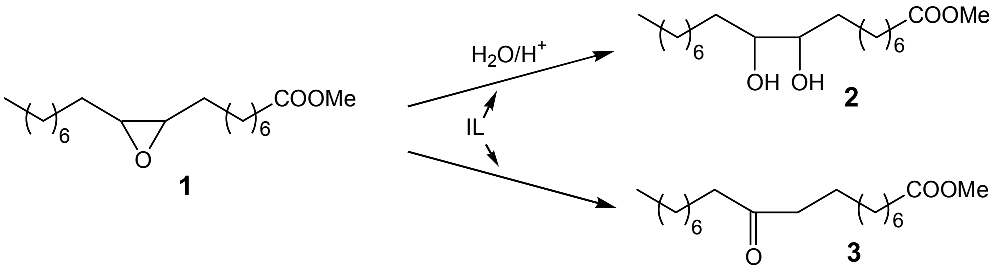
Scheme 2. Nucleophilic addition of water to epoxide, 1,2-diol route



Scheme 3. Lewis acid catalyzed isomerization of epoxide, ketone route



Scheme 4. Ionic liquid – epoxyFAME complex



Scheme 5. Nucleophilic addition of water to epoxidized FAME, alternative route

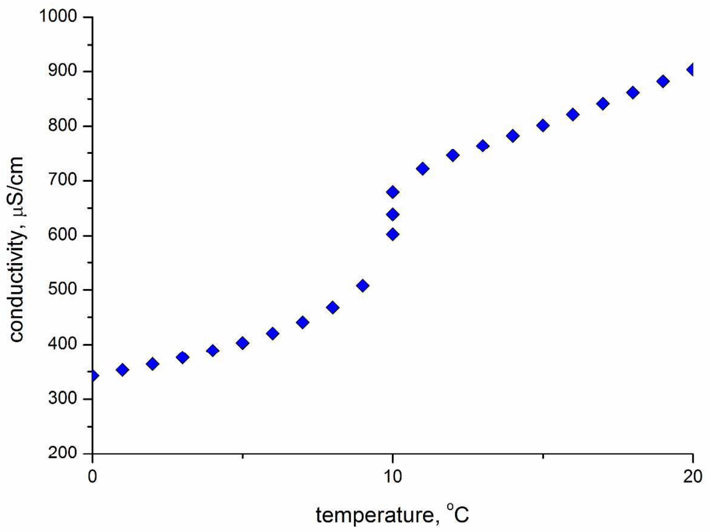


Fig. 1. Krafft temperature (K_T) determination for

1-tetradecyl-3-methylimidazolium hydrogen sulfate

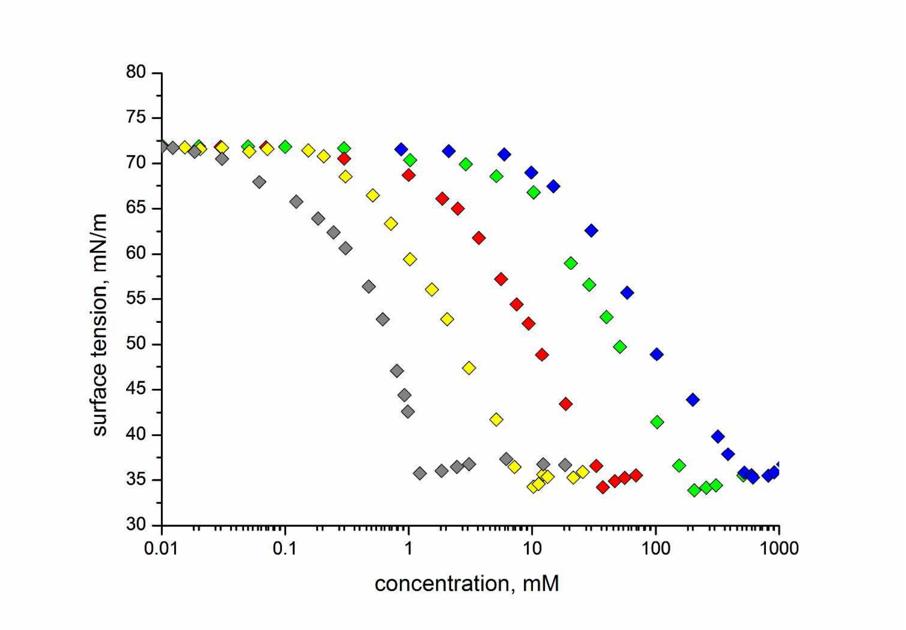


Fig. 2. Surface tension data vs. IL concentration isotherm measured at 25°C for aqueous solutions of (from the right side) [C$_6$mim]HSO$_4$ (◆), [C$_8$mim]HSO$_4$ (◆), [C$_{10}$mim]HSO$_4$ (◆), [C$_{12}$mim]HSO$_4$ (◆), and [C$_{14}$mim]HSO$_4$ (◆)

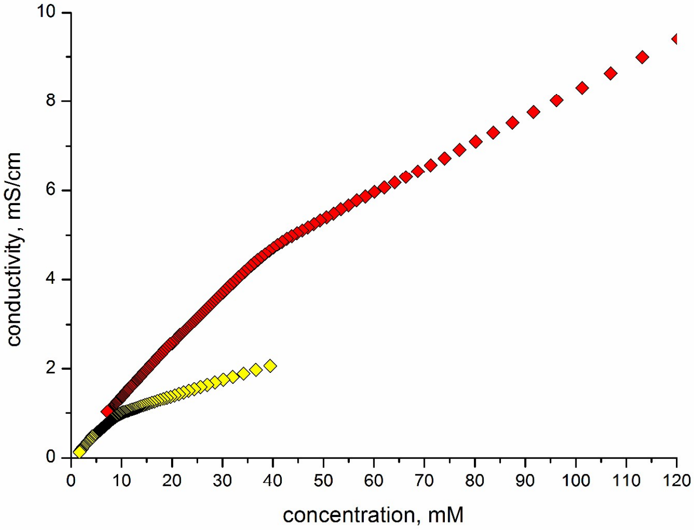


Fig. 3. Exemplary results of specific conductivity variation vs. concentration of [C$_{10}$mim]HSO$_4$ (◆), and [C$_{12}$mim]HSO$_4$ (◆) in aqueous solutions at 25^{o}C

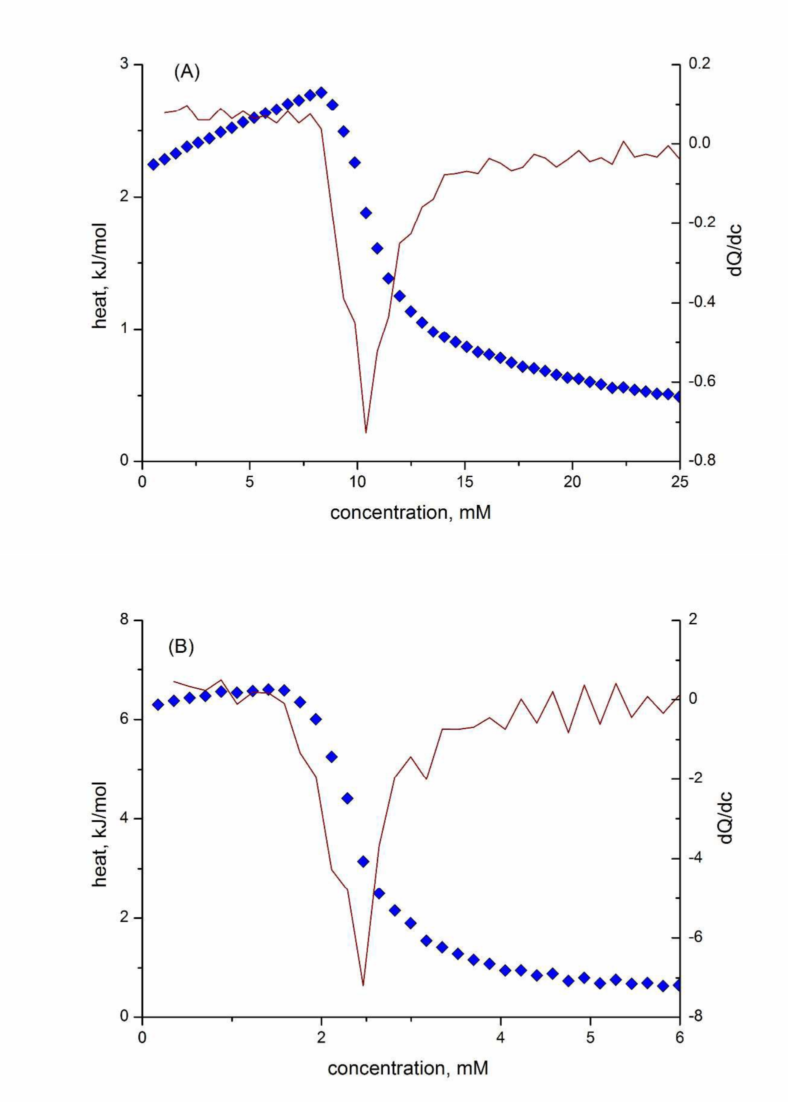


Fig. 4. Enthalpograms of ITC titration determined for [C_{12}mim]HSO_4 aqueous solution at concentration 102.5 mM into water (A), [C_{14}mim]HSO_4 aqueous solution at concentration 34.7mM into water (B). First derivative (dQ/dc) indicates the CMC of the solution

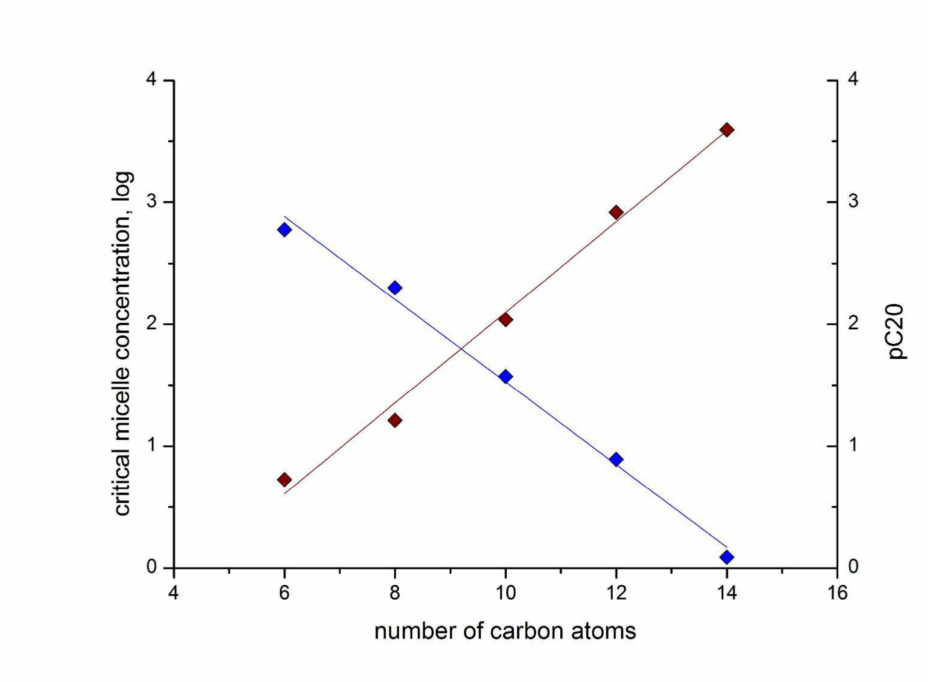


Fig. 5. Logarithmic dependence of CMC (◆) and pC20 (◆) on the alkyl chain length of 1-alkyl-3-methylimidazolium hydrogen sulfate ILs

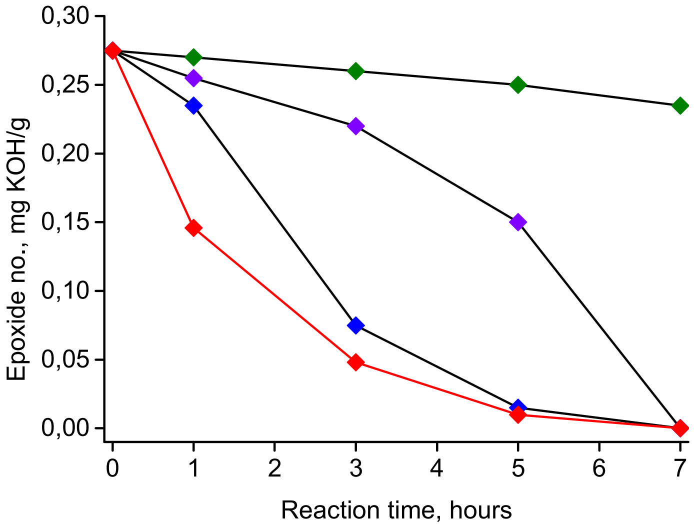


Fig. 6. Effect of used catalyst (H_2SO_4/IL) on epoxide number values in oxirane ring opening (T = 80 °C); 1% H_2SO_4 (◆); 2% H_2SO_4 (◆); 5% H_2SO_4 (◆); 1% H_2SO_4 + 2% [C_8mim]HSO_4 (◆)

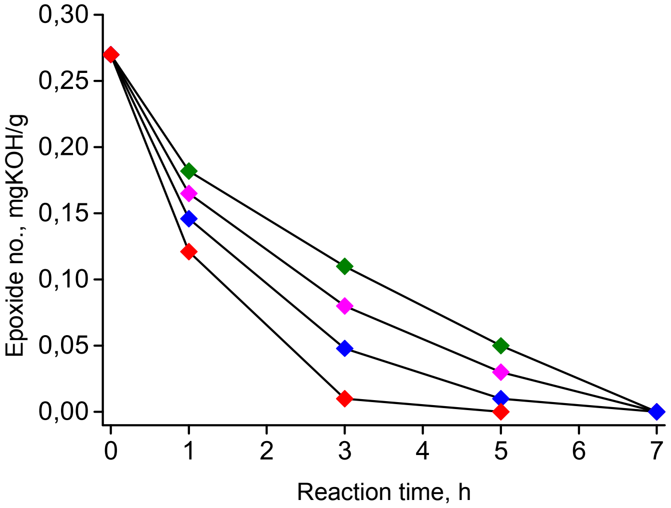


Fig. 7. Effect of type ionic liquid used as co-catalyst in reaction of hydrolysis of epoxidized methyl oleate. [C_{12}mim]HSO_4; (◆)[C_{10}mim]HSO_4; (◆); [C_8mim]HSO_4 (◆); [C_6mim]HSO_4 (◆)

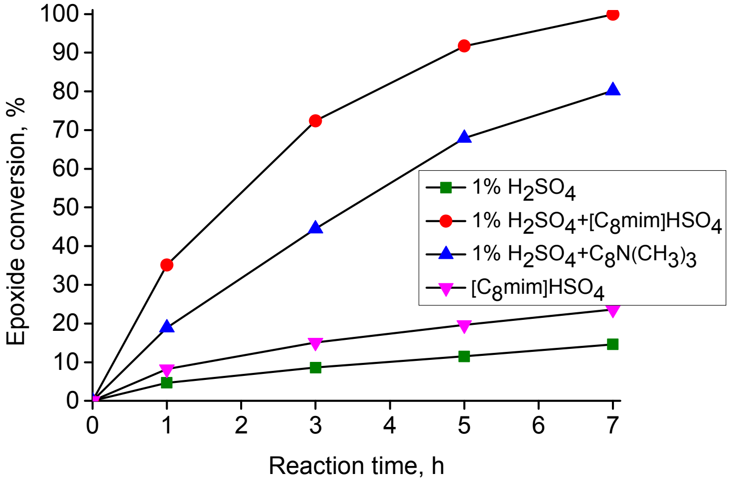


Fig. 8. Effect of catalyst system on conversion of epoxidized methyl oleate

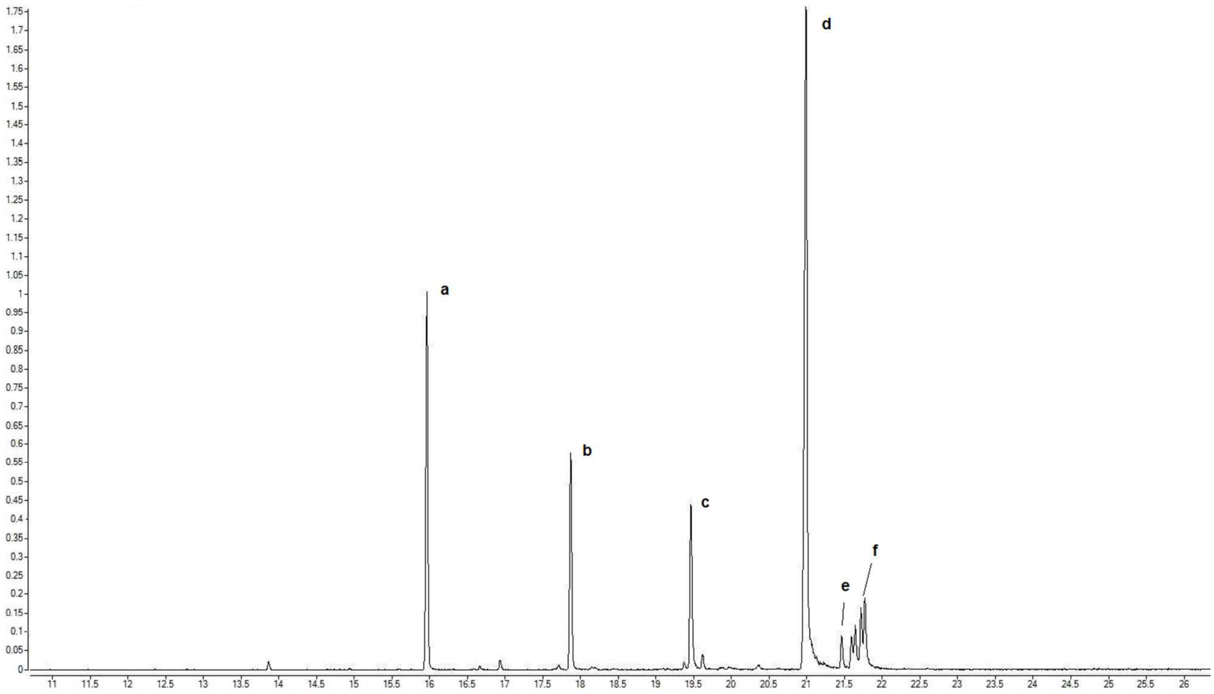


Fig.9. Representative GC chromatogram of product of reaction; (a) - fatty acid C_{16} Me ester; (b) - fatty acid C_{18} Me ester; (c) - ketone **3**; (d) - glycol **2**, (e) - epoxy oleic acid Me ester; (f) - diepoxides and diglycols

Table 1. The adsorption and micellization parameters determined for 1-alkyl-3-methylimidazolum hydrogen sulfates

Ionic liquid	CMC[a] (mol/L)	CMC[b] (mol/L)	CMC[c] (mol/L)	β	γ_{CMC} (mN/m)	pC_{20}	Γ_m x 10^6 (mol/m^2)	A_m (nm^2)	Π_{cmc} (mN/m)	ΔG_{ad} (kJ/mol)
[C_6mim]HSO_4	597±15	599±19	-	0.21±0.02	35.2	1.07	1.85	0.87	37.01	- 41.17
[C_8mim]HSO_4	205±10	206±10	-	0.33±0.02	33.9	1.32	2.18	0.74	38.16	- 38.52
[C_{10}mim]HSO_4	37.4±2.0	37.7±0.85	45.3±1.45	0.34±0.02	34.2	2.03	2.24	0.72	37.87	- 46.90
[C_{12}mim]HSO_4	10.25±0.9	9.86±0.36	10.05±0.70	0.36±0.03	34.3	2.69	2.33	0.69	37.53	- 50.95
[C_{14}mim]HSO4	1.23±01	2.18±0.08	2.34±0.26	0.38±0.02	35.7	3.20	2.40	0.67	36.10	- 56.2

[a] surface tension; [b] conductivity; [c] calorimetry

β - the degree of ionization, γ_{cmc}, the surface tension at the CMC; pC_{20} - the surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m; Γ_{max} - the maximum surface excess concentration; A_m - the minimum area per molecule at the interface; ΔG_{ads} - free energy of adsorption; ΔG_m, free energy of micellization; ΔH_m - enthalpy of micellization; ΔS_m - enthalpy of micellization;

Table 2. Thermodynamic parameters of selected [$C_n$mim]HSO_4 micellization in aqueous solution determined by calorimetry

Ionic liquid	ΔH_m [kJ/mol]	ΔG_m [kJ/mol]	$T\Delta S_m$ [kJ/mol]
[C_8mim]HSO_4	0.84±0.6	-21.23	22.1
[C_{10}mim]HSO_4	-0.49±0.8	-29.25	26.3
[C_{12}mim]HSO_4	-1.4±0.2	-34.93	33.6
[C_{14}mim]HSO_4	-5.1±0.14	-40.34	36.0

Table 3. Results of addition of water to epoxidized fatty acid methyl esters, effect of catalyst on selectivity of reaction (reaction time - 7 h; temp. - 80 °C)

Entry	$[C_n\text{mim}]HSO_4$ wt.%	H_2SO_4 aq. wt.%	Conversion %	Sel. to diol %	Sel. to ketone %
1	-	5	100	84.5	15.5
2	-	2	100	83.9	16.1
3		1	16.4	83.3	16.7
4	C_{10}, 5 wt.%	1	100	79.2	20.8
5	C_6, 2 wt.%	1	100	66.6	33.4
6	C_8, 2 wt.%	1	99.1	74.5	25.5
7	C_{10}, 2 wt.%	1	99.3	76.7	23.3
8	C_{12}, 2 wt.%	1	99.3	78.9	22.1
9	C_{14}, 2 wt.%	1	99.2	79.4	21.8

Dual functionality of amphiphilic 1-alkyl-3-methylimidazolium hydrogen sulfate ionic liquids: surfactants with catalytic function

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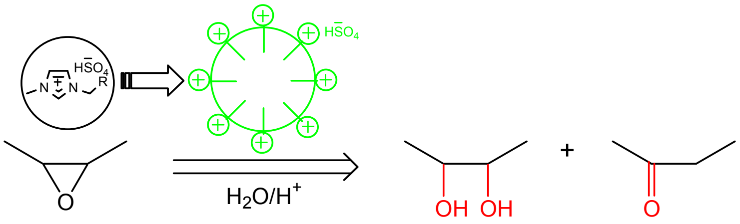

A series of amphiphilic 1-alkyl-3-methylimidazolium hydrogen sulfate ILs were synthesized. Their co-catalytic activities have been analyzed and discussed in a function of the structure and surface properties.