Original Article

Composite nanomaterials based on 1-butyl-3-methylimidazolium dicyanamide and clays

E.P. Grishina a,b, L.M. Ramenskaya a,*, N.O. Kudryakova a, K.V. Vagin a,b, A.S. Kraev a, A.V. Agafonov a

a G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Ivanovo, 1 Akademicheskaya St., Russia
b Ivanovo State University of Chemistry and Technology, Ivanovo, 7 Sheremetevsky Prospekt, Russia

ARTICLE INFO

Article history:
Received 17 June 2019
Accepted 25 July 2019
Available online 10 August 2019

Keywords:
Composite nanomaterials
Ionic liquid
Clay
Interaction
Decomposition temperature
Glass transition
Conductivity

ABSTRACT

Nanocomposites of ionic liquids with layered aluminosilicates represent a new class of functional materials that are promising when creating electrochemical devices, in environmental protection, in biomedicine, etc. Such nanocomposites contain environmentally friendly (clay) and easily regenerable components (ionic liquids), which makes them promising objects of green chemistry. In this paper, the interaction of 1-butyl-3-methylimidazolium dicyanamide ionic liquid with clays such as montmorillonite K10 (MMT K10), bentonite (Bent) and halloysite (Hal), which have a different molecular and mesoporous structure, as well as particles of different size and shape, was studied for the first time. Physicochemical methods such as FT-IR, TG, DSC, electron microscopy, viscosimetry and conductometry were used. The effect of the confinement of ionic liquid in the pores and immobilization on the surface of clays on the physicochemical properties of nanocomposites has been revealed. It was found that the interaction of ionic liquid with clays depends on the type of nanoclay, and the interaction strength changes in the following order: MMT K10 ≈ Bent > Hal. The resulting materials have the properties of pseudoplasticity, high ionic conductivity, which is promising when creating electrochemical devices. At low temperature, the electrical conductivity of the halloysite-based composite is higher than that of a pure ionic liquid. The conductivity of the studied materials obeys to a general trend, which depends on the specific interactions and the properties of the clay-filled ionic liquid.

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1. Introduction

Currently, the use of new types of high-performance materials and technologies is necessary to meet the requirements of modern green development. For example, promising developments are nanostructured catalysts for the photodegradation of water pollutants and air purification, new classes of highly porous materials, including covalently bonded stable porous structures, as well as biosimilar materials that combine environmentally friendly components in their structure [1–4]. Natural clays and ionic liquids are promising compounds in the field of green chemistry.

* Corresponding author.
E-mail: lmr@isc-ras.ru (L. Ramenskaya).
https://doi.org/10.1016/j.jmrt.2019.07.050
2238-7856 © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Ionic liquids (ILs) or room temperature ionic liquids (RTILs) are studied as a possible substitute for conventional molecular solvents for catalytic and organic reactions; their application allows sufficiently reducing the amount of water used in different technological processes. These compounds represent a relatively new and constantly widening class of salts with N- or P-containing organic cations and large inorganic or organic anions. These salts are in the molten (liquid) state at room temperatures. The unique combination of properties of ionic liquids – high ionic conductivity values, a wide temperature range of liquid state, low vapour pressure, high electrochemical and thermal stability – makes these RTILs quite attractive materials for creating new electrolytes for electrochemical energy storage units – electrochemical capacitors, lithium-ion batteries, photogalvanic cells, etc. [5–8]. The growing interest in ionic liquids is also caused by the prospects for their use in devices that work at elevated temperatures for a long time. Ionic liquids based on an N,N′-dialkylimidazolium cation and a bis(trifluoromethylsulfonyl)imide, (Tf2)N– anion are the most claimed. That is why their properties have been studied well [9–20]. However, a promising alternative to the above-mentioned salts for the use in electrochemical devices is the ILs with a dicyanamide, (CN)2N– (DCA–) anion because they, as a rule, have lower viscosity and, consequently, better ionic conductivity than other ILs, and remain stable for a long time under heating [21–28].

At the same time, an urgent problem to be solved in electrochemical power engineering is developing, based on ionic liquids, highly-efficient solid state devices that have improved functional characteristics and are safe-to-use, especially at elevated temperatures [29–31]. Therefore, the creation of quasi-solid electrolytes (ionogels, nanocomposites) through IL immobilization or confinement into various inorganic porous matrices is relevant. In such materials, when ILs are introduced into the nanopores or adsorbed on the surface of a porous material, some of their confinement effects can change the properties of ILs, although the ions retain their liquid-like dynamics and mobility [32]. Ionic liquids have been quite successfully introduced into a 3D-network made up by silica [29-43], without reducing the composite conductivity or electrochemical stability window in comparison with the pure ionic liquid [36,44-46].

In addition to silica, it is possible to use nanoparticles of other inorganic oxides – SnO2 [47,48], ZrO2 [49] or TiO2 [50,51] – as the inorganic matrix for creating ionogels. The last few years have seen a growing interest in the development of hybrid materials based on ionic liquids and natural aluminosilicates – bentonite [52], montmorillonite [53–58], kaolinite [59], and halloysite [60]. Immobilization of ionic liquids by the surface of nanoparticles of minerals and intercalation of cations into the inter-layer space of the minerals can ensure high (of the order of 10−3 S cm−1) ionic conductivity [60], excellent thermal stability [52,58], which makes them potentially suitable for the use in high-temperature electrochemical devices maintaining their high capacity and a large number of charge cycles [56].

There are so far only a limited number of works devoted to creating ion-conducting composites using clay minerals. In this work, new nanocomposites based on ionic liquid of 1-butyl-3-methylimidazolium dicyanamide (BMImDCA) immobilized in the inorganic matrix of bentonite, halloysite or montmorillonite K10 were obtained; their physicochemical characteristics were studied compared to those of pure components. The present data are useful in creating environmentally safe operating electrolytes for high-performance electrochemical devices.

2. Materials and methods

2.1. Materials

The following materials were used in the work:

- Ionic liquid 1-butyl-3-methylimidazolium dicyanamide (BMImDCA, Sigma-Aldrich, CAS Number: 448245-52-1), the structural formula is given in Fig. 1;
- Montmorillonite K10 (MMT K10, Acros organics, Catalog No. AC456071000);
- Nanoclay, hydrophilic Bentonite (Bent, Sigma-Aldrich, CAS Number 1302-78-9);
- Halloysite nanoclay (Hal, Sigma-Aldrich, CAS Number 1332-58-7).

2.2. Preparation of IL-clay nanocomposites

The BMImDCA–clay nanocomposites were obtained through direct mixing of the components with a vibration shaker IKA VORTEX 4 basic (IKA-Werke GmbH & Co. KG, Germany). The mixture was kept in a vacuum drying oven LT-VO/20 (Labtex, Russia) at a temperature of 80 °C for 8 h. The obtained mechanical dispersions of clay mineral particles in the ILs were additionally treated in hermetically sealed capsules in an ultrasonic cleaner CT-431D2 (CIBrand Wahluen Electronic TOOL Co. Ltd., China) for 8 h. The obtained mixtures had the following molar ratios of the IL components: clay 2:1 (with Hal and with MMT K10) and 1:1 (with Bent), which corresponded to 60.4 wt.%, 53.5 wt.% and 53.3 wt.% of 1-butyl-3-methylimidazolium dicyanamide in the composite material.
2.3. Methods of study

The visualization of the clay minerals and ionic liquid-clay composites was made by the scanning electron spectroscopy method using an NVision 40 microscope (Carl Zeiss, Inc., Germany).

The specific surface area of the clay samples was measured using the BET method, while the pore size distribution was obtained by the Dubinin–Astakhov method with low-temperature nitrogen adsorption-desorption Quantachrome Nova 1200 equipment. All the samples had been degassed in a vacuum drying oven at 105 °C for 7 h.

The particle size distribution of the clay minerals and Z-potential were determined in distilled water with a particle size and Z-potential analyzer Zetasizer Nano (Malvern Instruments Ltd., UK).

A TG 209 F1 Iris calorimeter (NETZSCH, Germany) was used for thermal studies. A sample of about 10 mg in a platinum crucible was heated in an argon flow at a rate of 10 °C min−1 to a temperature of 800 °C. The accuracy of measuring the mass and temperature was ±10−5 g and ±0.1 °C, respectively.

A DSC 204 F1 Phoenix calorimeter (NETZSCH, Germany) was used to study the phase behavior of the pure ionic liquid and composites. A sample of approximately 10 mg in a hermetically sealed platinum pan was cooled with liquid nitrogen to −120 °C at a rate of 10 °C min−1 and then heated to 200 °C at a rate of 10 °C min−1. The measurements were carried out in an argon atmosphere. The accuracy of the mass and temperature measurements was ±10−5 g and ±0.1 °C, respectively.

An infrared Fourier spectrometer VERTEX 80v (Bruker, Germany) was used for spectrophotometric measurements. The FT-IR reflection spectra were recorded in the region from 500 to 4000 cm−1 at room temperature using a diamond crystal. The spectral resolution was 2 cm−1.

A Brookfield Programmable Viscometer Model DV2T (Brookfield, USA) was used to measure the dynamic viscosity (η). The measurement accuracy was ±1%. The temperature was varied from 10 to 80 °C.

A Solartron SI 1260A Impedance/Gain-Phase analyzer (Solartron analytical, UK) was used to determine the specific conductivity (σ). The measurement was carried out in a designed hermetic cell using platinum electrodes. The frequency range of the alternating current was from 1 to 100 kHz, the cell voltage was 10 mV. The value of the cell constant was determined using a 0.01 mol dm−3 KCl solution. The measurements were carried out in the range from −20 to 80 °C. The cell temperature was maintained using a liquid cryostat LIOP FT-316-40 (LOIP, Russia) with the accuracy of ±0.2 °C.

3. Results and discussion

3.1. Structural characteristics of clays

In this work, nanocomposites based on the ionic liquid BMImDCA were obtained using three types of clay minerals as structure-forming fillers with nano-size pores: hydrophilic bentonite, montmorillonite K10 and halloysite nanoclay. Several characteristics of these materials are presented in Table 1 and Table 2 in comparison with the available literature data [61–65].

The hydrophilic bentonite (Nanoclay) used in this work is an untreated hydrophilic clay (without organic modifications). It mainly consists of montmorillonite and different amounts of other minerals, such as quartz (SiO2), calcium and sodium feldspar [(CaAl2Si2O8), (NaAlSi2O8)] and represents aggregates of plates packed together via electrostatic forces and containing interlayer water in their structure [66]. The surface of bentonite aggregates has a negative charge which is compensated by the cations intercalated between the structural plates [67].

Montmorillonite K10 is an acid-activated and thermally treated montmorillonite. Untreated montmorillonite is a clay mineral, 2:1 silicate, a member of the smectite group (Fig. 2). Its original structure consists of two SiO4 tetrahedral layers, with their tops directed to each other and forming a sandwich with the central octahedral layer of aluminum hydroxide [68]. Montmorillonite contains a large number of mobile cations capable of ionic exchange, which is used for exchange of inorganic cations with organic cations and formation of an organically modified clay mineral [69,70]. During the acidic treatment, the crystal structure of the montmorillonite becomes partially destroyed, which leads to the formation of a highly porous substance with a larger surface area and nanopores [68]. As a result of the thermal treatment, montmorillonite K10 almost loses its ability to swell [71,72].

Halloysite is a hydrated tubular form of kaolinite [73,74]. The crystal structure of halloysite consists of aluminosilicate plates folded into nanoscrolls (Fig. 2). The crystallization water and OH groups of the kaolinite are in the gap between the layers [75]. On average, halloysite nanotubes have the external diameter of 50–100 nm, and the pore space diameters are about 12–15 nm at the length of about 1 μM. The internal surface of the kaolinite plates in the rolls has a positive charge, while the external one is charged negatively. The surface area can reach 50–500 m2 g−1 depending on the treatment method [76,77].

The structural characteristics of the clays used in this work to prepare nanocomposites are given in Table 1. The experimental data show that the specific surface area of MMT K10 is much larger than that of the other clay samples used, the Z-potential is negative in all the studied samples and is the least in the halloysite particles.

By comparing the average pore sizes of the clay minerals with the ionic liquids anion and cation volumes (Table 1), we can suppose that a large asymmetric cation and a rather large anion can easily penetrate into the pore or inter-layer space of the clay particles. In fact, it has been shown that cations of different ILs under certain conditions can be intercalated into inter-layer spaces of clay minerals and make them larger [57,58]. It is noteworthy that in all the prepared composites, the IL volume is more than 3 times bigger than the free volume of the pores of the mineral filler. That is why most of the IL is immobilized by the clay particle surface.

3.2. FT-IR spectra

Figs. 3–5 show the FT-IR reflection spectra for the BMImDCA–MMT K10, BMImDCA–Hal and BMImDCA–Bent
Fig. 2 – SEM-images of clay minerals used (on the left) and their mixtures with BMImDCA (on the right): a – MMT K10, mixture with IL, b – Bent, mixture with IL, c – Hal, mixture with IL.

composites, the pure ionic liquid BMImDCA and the original clay MMT K10, Hal and Bent in the region of 4000–400 cm\(^{-1}\). The spectra of all the composites are similar to those of pure IL and include bands of the inorganic matrix. One or two peaks at ca. 3700 and 3600 cm\(^{-1}\) belong to the stretching modes of the Si–OH group; the broad band of about 3600–3300 cm\(^{-1}\) and the slight peak at 1650 cm\(^{-1}\), are assigned to the \(\nu\)OH stretching mode and \(\delta\)OH bending mode from absorbed water, respectively [58,78,79]. Several peaks in the range of 3200–3000 cm\(^{-1}\) and 3000–2800 cm\(^{-1}\) are related to the \(\nu\)CH modes of the ring and aliphatic chains of the BMIm\(^+\) cation, respectively [19,80]. The strong peaks between 2400 and 2000 cm\(^{-1}\) are associated with the vibration of the N≡C bond of the DCA\(^-\) anion [81]. The peaks observed below 1600 cm\(^{-1}\) are due to the stretching and bending vibrations of various groups from the cation, such as \(\nu\)CH\(_2\)(N) and \(\nu\)CH\(_3\)(N) at ca. 1570 cm\(^{-1}\), ring CH\(_2\) and \(\nu\)CN at ca. 1460 cm\(^{-1}\), \(\nu\)CCC at ca. 1427 and 1380 cm\(^{-1}\), \(\delta\)as\(_{sp^3}\) ring and \(\delta\)CCC at ca. 1060 cm\(^{-1}\).
Table 1 – Physicochemical characteristics of the materials used.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ionic liquid</th>
<th>Montmorillonite K10</th>
<th>Hydrophilic bentonite</th>
<th>Halloysite nanoclay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{10}H_{15}N_5</td>
<td>Al_{2}H_{2}O_{2}Si_4</td>
<td>H_{2}Al_{2}O_{3}Si</td>
<td>Al_{2}Si_{2}O_{5}(OH)<em>{4} \times 2H</em>{2}O</td>
</tr>
<tr>
<td>Chemical composition (for clays), wt.%</td>
<td>IL ≥ 97 Water(^a), 0.11</td>
<td>O – 62.85</td>
<td>O – 58.12</td>
<td>O – 63.65</td>
</tr>
<tr>
<td>Na – 0.15</td>
<td>Na – 1.43</td>
<td>Na – 0.15</td>
<td>Si – 17.51</td>
<td>Al – 18.20</td>
</tr>
<tr>
<td>Mg – 0.80</td>
<td>Mg – 3.05</td>
<td>Mg – 0.15</td>
<td>Cl – 0.12</td>
<td>Ca – 0.11</td>
</tr>
<tr>
<td>Si – 27.66</td>
<td>Si – 24.12</td>
<td>Si – 27.66</td>
<td>Cl – 0.19</td>
<td>Fe – 0.13</td>
</tr>
<tr>
<td>Cl – 0.19</td>
<td>Cl – 0.32</td>
<td>Cl – 0.19</td>
<td>Ca – 1.50</td>
<td>Mg – 0.28</td>
</tr>
<tr>
<td>K – 0.63</td>
<td>K – 0.15</td>
<td>K – 0.63</td>
<td>Ti – 0.24</td>
<td></td>
</tr>
<tr>
<td>Na – 0.14</td>
<td>Na – 1.43</td>
<td>Na – 0.14</td>
<td>Ti – 0.16</td>
<td></td>
</tr>
<tr>
<td>Mg – 0.80</td>
<td>Mg – 3.05</td>
<td>Mg – 0.15</td>
<td>Fe – 2.55</td>
<td></td>
</tr>
<tr>
<td>Si – 27.66</td>
<td>Si – 24.12</td>
<td>Si – 27.66</td>
<td>Al – 18.20</td>
<td></td>
</tr>
<tr>
<td>Cl – 0.19</td>
<td>Cl – 0.32</td>
<td>Cl – 0.19</td>
<td>Fe – 0.13</td>
<td></td>
</tr>
<tr>
<td>K – 0.63</td>
<td>K – 0.15</td>
<td>K – 0.63</td>
<td>Mg – 0.28</td>
<td></td>
</tr>
<tr>
<td>Molecular weight, g mol(^{-1})</td>
<td>205.26</td>
<td>360.307</td>
<td>180.1</td>
<td>294.19</td>
</tr>
<tr>
<td>Density, g cm(^{-3})</td>
<td>1.06</td>
<td>0.370</td>
<td>0.6–1.1</td>
<td>2.53</td>
</tr>
<tr>
<td>Pore volume, ml g(^{-1})</td>
<td>–</td>
<td>0–80 nm: 0.36</td>
<td>0.004(^a)</td>
<td>1.26–1.34</td>
</tr>
<tr>
<td>Average pore size, nm</td>
<td>–</td>
<td>0–24 nm: 0.026</td>
<td>0.13(^a)</td>
<td></td>
</tr>
<tr>
<td>Particle size, nm</td>
<td>–</td>
<td>4.1(^a)</td>
<td>4.0(^a)</td>
<td>7.8(^a)</td>
</tr>
<tr>
<td>Cation volume, nm(^3)</td>
<td>&gt;63,000 (&gt;25%)</td>
<td>≤25,000</td>
<td>150–560(^a)</td>
<td>Diameter: 30–70</td>
</tr>
<tr>
<td>Anion volume, nm(^3)</td>
<td>0.150 [61]</td>
<td>220–430(^a)</td>
<td>90–280(^a)</td>
<td>Length: 1000–3000</td>
</tr>
<tr>
<td>0.198 [62]</td>
<td>0.089 [64]</td>
<td>0.069 [65]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.056 [63]</td>
<td>195(^a)</td>
<td>1.9(^a)</td>
<td>57(^a)</td>
<td></td>
</tr>
<tr>
<td>Surface area, m(^2) g(^{-1})</td>
<td>–</td>
<td>240</td>
<td>1.9(^a)</td>
<td></td>
</tr>
<tr>
<td>Z-potential(^a), mV</td>
<td>–</td>
<td>–28</td>
<td>–28</td>
<td>–13</td>
</tr>
</tbody>
</table>

\(^a\) This work.

Fig. 3 – FTIR spectra of BMImDCA–MMT K10 (black trace), BMImDCA (red trace) and MMT K10 (blue trace) and in the region of 4000–400 cm\(^{-1}\); insert – Extended FTIR spectra in the regions (a) N\(~\)C (anion), (b) v\(~\)CH\(_2\)(N), v\(~\)CH\(_3\)(N), ring CH\(_3\), v\(~\)CN, v\(~\)CCl\(_2\) (cation), and (c) Mg–O (MMT K10).

1307 cm\(^{-1}\), \~\)CH\(_2\)(N)CN at ca. 1166 cm\(^{-1}\) [80]. The bands from Si–O, Al–O and Mg–O are observed around 1030 cm\(^{-1}\), 620 and 470–530 cm\(^{-1}\), respectively [58,79].

In contrast to the BMImBF\(_4\) ionic liquid confined in silica matrix [82], noticeable changes in the infrared spectrum can be observed in the studied systems. For example, the vSi–OH
modes of pure MMT K10 (3670 and 3622 cm\(^{-1}\)) and pure Bent (3625 cm\(^{-1}\)) disappear in the spectra of the composites, and the bands of absorbed water shift by 10 and 6 cm\(^{-1}\) to the higher frequency range (Figs. 3 and 5). However, there are no applicable changes in the spectrum of the Hal composite: two silanol peaks at 3697 and 3622 cm\(^{-1}\) of pure Hal are observed at the same frequencies at 3697 and 3625 cm\(^{-1}\) (Fig. 4). The \(v(Si-O)\) and \(v(Mg-O)\) modes show red shifts (\(\Delta v\)) increasing from Hal to MMT K10 and Bent (Fig. 3–5 and inserts (c) in Fig. 3–5). For example, the value of \(\Delta v(Si-O)\) is 6, 26 and about 40 cm\(^{-1}\) for the Hal, MMT K10 and Bent composites, respectively.

The ionic liquid confined in MMT K10 and Hal shows a minor blue shift (\(\Delta v\)) of about 3–4 cm\(^{-1}\) in the frequency range of the DCA\(^{-}\) anion relative to the pure IL (insert (a) in Figs. 3, 4). At the same time, the shift of about 9–15 cm\(^{-1}\) and a new band at ca.2153 cm\(^{-1}\) are observed in the spectrum of the Bent composite (insert (a) in Fig. 5). As for the BMIm\(^{+}\) cation, more significant changes are observed in the range of 1700–1200 cm\(^{-1}\): new bands appear in the spectrum of the MMT K10 composite at 1410 and 1507 cm\(^{-1}\) (insert (b) in Fig. 3), and the peak at 1302 cm\(^{-1}\) is blue-shifted by 5 and 3 cm\(^{-1}\) in the spectra of the Hal and Bent composites, respectively (insert (b) in Figs. 4 and 5). In the range of 3200–2800 cm\(^{-1}\), the \(v(CH)\)
modes exhibit a slight blue shift of about 1–4 cm⁻¹, with the largest value for the Bent composite (Figs. 3–5).

Thus, it has been found that some of the characteristic frequencies of both the ionic liquid and the clay are shifted in the spectra of their nanocomposites by a distance exceeding the instrumental resolution (2 cm⁻¹). This phenomenon is associated with the interaction of these compounds, mainly due to Coulomb and van der Waals forces. Apparently, the anion DCA⁻ also partially interacts with the silanol groups of the inner layer through hydrogen boning Si–OH···N. In accordance with the values of the observed shifts, these interactions become weaker in the series MMT K10 ≈ Bent ≈ Hal. Apparently, the water absorbed by the clay is partially desorbed and replaced by an ionic liquid, mainly an anion, and this ability decreases in the order mentioned above.

3.3. TG and DCS studies

Fig. 6 shows the DTA traces of the three composites and pure components. In all cases, a peak at a temperature below 100 °C corresponds to the departure of physically adsorbed water. For pure clay, a peak at a temperature above 400 °C is associated with the dehydroxylation of the aluminosilicate layers [53,78]. Pure ionic liquid shows the peaks at 314 and 393 °C corresponding to the decomposition of the DCA⁻ anion (Tₓ̂) and more stable BMIm⁺ cation (Tᵧ), respectively [18,83], followed by a small peak from the destruction of the residual IL fragments.

All the modified clay minerals exhibit lower temperatures for both the dehydroxylation and destruction of the ionic liquid (Fig. 6). This phenomenon is attributed to the lower crystallinity of the grafted materials [84]. It should be noted that the ionic liquid confined in MMT K10 and Bent shows a more significant depression of the temperatures Tₓ̂ and/or Tᵧ in relation to the pure ionic liquid than when it is enclosed in Hal. This thermal response is the result of different arrangements of the cation and anion, for example, on the surface, in the pores or inside the aluminosilicate layers. It was found that the BMImBr ionic liquid entrapped within silica nonpores has a higher crystallinity than the same IL adsorbed on the surface [85]. This result is confirmed by our data in Fig. 7, which shows DSC curves for the pure and confined ionic liquid.

All of the samples exhibit a wide endothermic wave at temperatures above 60 °C caused by water removal, as well as a glass transition (T_g) at low temperatures. Our T_g value for pure BMImDCA appeared to be slightly below −90 °C [86] due to the presence of water, which is known to lead to the salt amorphization [87]. It may be clearly seen from Fig. 7 that the IL entrapped in MMT K10 and Bent has the higher T_g values, and IL entrapped in Hal has a lower T_g value in comparison with the pure ionic liquid.

Thus, the thermal behavior of the BMImDCA ionic liquid in MMT K10 and Bent composites is similar, but different from that in the Hal composite. It is known that the properties of a confined ionic liquid differ from the properties of both adsorbed and bulk salts [53,88,89]. Based on the presented data, it can be supposed that the confined BMImDCA is located mainly on the surface of the Hal and in the pores of MMT K10 and Bent. In addition, the DCA⁻ anion partially intercalates into the aluminosilicate layers depending on the properties of the clay in the following order MMT K10 ≈ Bent ≈ Hal. This result is consistent with the above IR data.

3.4. Viscosity η and Ionic conductivity κ

When nanoporous fillers are introduced into an ionic liquid, an important problem to be solved is maintaining high ionic conductivity in the quasi-solid state of the composite, and this problem is solved quite successfully, for example, when nanoporous silica are used [38,41,90]. In this work, at the pre-
Table 2 – Physicochemical properties of the BMImDCA ionic liquid and nanocomposites.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BMImDCA</th>
<th>BMImDCA–MMT K10</th>
<th>BMImDCA–Bent</th>
<th>BMImDCA–Hal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$, °C</td>
<td>314</td>
<td>280</td>
<td>310</td>
<td>300</td>
</tr>
<tr>
<td>$T_g$, °C</td>
<td>−94.4</td>
<td>−90.6</td>
<td>−88.1</td>
<td>−98.5</td>
</tr>
<tr>
<td>$H$, Pa s</td>
<td>0.031</td>
<td>18.67</td>
<td>4.42</td>
<td>0.86</td>
</tr>
<tr>
<td>$K^a$, Pa s m$^{-1}$</td>
<td>0.964</td>
<td>0.398</td>
<td>0.554</td>
<td>0.840</td>
</tr>
<tr>
<td>Walden product$^b$, Pa s S m$^{-1}$</td>
<td>0.029</td>
<td>7.431</td>
<td>2.449</td>
<td>0.722</td>
</tr>
<tr>
<td>$E^b$, kJ mol$^{-1}$</td>
<td>22</td>
<td>21</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>$T_0$, °C</td>
<td>−115.9</td>
<td>−120.1</td>
<td>−128.8</td>
<td>−138.9</td>
</tr>
</tbody>
</table>

$^a$ Temperature 20 °C.
$^b$ The values are calculated for the temperature range of 20–80 °C, $R^2 \geq 0.998$.

determined ratio of components, the obtained composites represent pastes of different consistency that do not segregate for a long time (Fig. 2). For the studied systems, we have obtained dependences of shear stress ($\tau_r$) on shear rate ($D_r$) (Fig. 8). Pure BMImDCA, just like BMImBr that was investigated by us earlier [91], has properties of Bingham (or plastic) fluids: $\tau_r = \tau_0 + \eta D_r$, here $\tau_0$ is the yield stress, below which the liquid does not flow, $\eta$ is the Bingham viscosity. The composites based on IL behave in a similar way. Values $\eta$, obtained for the systems under study, are given in Table 2.

The temperature dependence of the BMImDCA ionic conductivity in the bulk state and in immobilized state in clay minerals is shown in Fig. 9a,b. As it shows, despite the fact that the viscosity grew by 1–2 orders of magnitude when nanoporous aluminosilicate thickeners were introduced into the IL and the bulk concentration of ions decreased, the conductivity in the composites remained high. For example, in the considered temperature range, value $\kappa$ of the solid-state composite with the lowest conductivity among the objects in question (BMImDCA–MMT K10) exceeds that of the pure N,N′-dialkylimidazolium ILs with a (Tf$_2$N$^-$) anion that we studied earlier [19,20]. The temperature behaviour of all the ion-conducting composites studied in this work in the range from 30 to 80 °C can be described by the Arrhenius equation ($R^2 \geq 0.998$) with similar values of effective energy of activation of specific electric conductivity (Table 2). Widening of the temperature range leads to a deviation from linear behaviour, and the dependence $\kappa(T)$ can be described by the Vogel–Fulcher–Tammann (VFT) equation related to the ordinary en masse diffusion (vehicle mechanism) [9,92]:

$$\kappa = \kappa_0 \exp \left[ -\frac{k_\kappa}{T - T_0} \right],$$

where $\kappa_0$ is the limiting electric conductivity, $k_\kappa$ is a constant related to the Arrhenius activation energy, and $T_0$ is the ideal glass transition temperature. The values of $T_0$ depend on the chosen temperature range but are always lower than the experimentally determined glass transition point $T_g$ [20,93] and, according to the literature data, in most cases $T_0/T_g \approx 0.75$ (T$_0$, K; T$_g$, K). For the studied IL and nanocomposites based on it, the ratio $T_0/T_g$ equals 0.87 (BMImDCA), 0.84 (BMImDCA–MMT K10), 0.78 (BMImDCA–Bent) and 0.76 (BMImDCA–Hal) in the temperature range (253–353 K).

![Fig. 7 – DSC traces of BMImDCA (1), BMImDCA–Hal (2), BMImDCA–MMT K10 (3) and BMImDCA–Bent (4).](image)

![Fig. 8 – Dependences of shear stress $\tau_r$ on shear rate $D_r$ for BMImDCA (1) and its mixtures with MMT K10 (2), Bent (3) and Hal (4) at 20 °C.](image)
As Fig. 9 shows, the obtained values of specific electric conductivity essentially depend on the nature of the clay material. Despite a very big (about two orders of magnitude) difference in the specific surface areas and pore volume, as well as an almost four-time difference in the viscosity values (Table 2), the nanocomposites with MMT K10 and Bent at the same IL content (wt.%) have quite similar $\kappa$ values (0.40 and 0.55 S m$^{-1}$ at 20 °C, respectively), which are much lower than in the pure IL. In contrast to these systems, the conductivity of the BMImDCA–Hal composite is slightly lower in the region of positive temperatures, compared to the pure IL, and is even higher than that in the region of negative temperatures (0.84 and 0.92 S m$^{-1}$ at 20 °C; 0.15 and 0.11 S m$^{-1}$ at −20 °C, respectively). The nanocomposites with MMT K10 and Hal at the same molar ratio of the components are, however, very different from each other in their ionic conductivity. This may be caused by the electrostatic binding of a relatively larger number of cations with the highly developed surface of MMT K10 than in the composite with Hal. Besides, the lower negative charge of the surface and the larger pore size of Hal (Table 1) are not favorable for confinement ions, ion pairs and self-assembly complexes of the IL. That is why the higher conductivity of BMImDCA–Hal in comparison with BMImDCA–MMT K10 is associated with the effect of two structural factors – smaller specific surface and porosity and larger pore size.

It is worth mentioning that when plotted in the log$\kappa$ – logη$^{-1}$ coordinates (Walden plot), the points corresponding to different composites lie on the same straight line (Fig. 10, R$^2 = 0.9997$). And the slope corresponds to the power index in the fractional Walden rule $\nu_\infty$ = const, that can be applied to ionic liquids. Value $\alpha$ characterizes the degree of IL “ionicity”, and the value $\alpha < 1$ is the result of formation of ionic associates in them [94,95]. For the composites with different clay minerals, we have obtained the value $\alpha = 0.24$, which indicates that the degree of binding of conductivity ions with the surface is also high in the pores of the clay minerals.

4. Conclusions

The effect of the interaction of ionic liquid 1-butyl-3-methylimidazolium dicyanamide with layered aluminosilicates (montmorillonite K10, bentonite and halloysite), which have different particle shape and porous mesostructure, on the physicochemical properties of gel-like materials was studied. It has been established that the properties of the inorganic host matrix (porous structure, negative surface charge and the functional groups on the surface and inside the layer) affect the physicochemical properties of their composites with the ionic liquid used. The infrared spectra of composites revealed noticeable changes in the characteristic frequencies both clay (νSi–O, νSi–OH) and ionic liquid (νN=C, νCH$_2$(N), νCH$_3$(N), ring CH$_3$, etc.). Thermodynamic studies of a nanocomposites ionic liquid–clay showed lower temperatures for the processes of clay dehydroxylation and destruction of the ionic liquid, as well as a change in the glass transition temperature compared to the initial components. Based on the data obtained, a model of interaction and location of the ionic liquid in nanoclay was proposed. According to this model, the ionic liquid is located mainly on the surface of Hal and in the pores of MMT K10 and Bent. The immobilization of ionic liquid by the clay is apparently due mainly to the Coulomb interactions of the BMIm$^+$ cation and the Si–O groups, which provide a negative charge.
of the clay surface. The dicyanamide anion is introduced into the interlayer space of the clay due to the formation of the hydrogen bond Si–OH–N. According to IR spectroscopy, the interaction of ionic liquids with clay weakens in the order MMT K10 > Bent > Hal. Studies of viscometry have shown that both the composites under study and the pure BMImDCA have the property of pseudoplasticity (Bingham fluid). Compared to pure ionic liquid, the obtained nanocomposites have lower ionic conductivity due to a decrease in the number of free ions involved in the transfer process, owing to the interaction of the ionic liquid with the inorganic matrix. It was found that ionicity is equal to 0.24, and the fractional Walden rule is valid. At the same time, a quasi-solid electrolyte retains the properties of an ionic liquid with a high value of ionic conductivity.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgement

This work was funded by Russian Foundation for Basic Research grant № 18-29-12012 mk. The authors gratefully acknowledge to the center for joint use of scientific equipment “The upper Volga region centre of physico-chemical research”.

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