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Ionic liquids as heat transfer fluids: comparison with known systems, possible applications, advantages and disadvantages

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The practical aspects and prospects of application of ionic liquids as heat transfer fluids are discussed. The physicochemical properties of ionic liquids (heat capacity, thermal conductivity, thermal and radiation stability, viscosity, density, saturated vapour pressure and corrosion activity) are compared with the properties of some commercial heat transfer fluids. The issues of toxicity of ionic liquids are considered. Much attention is paid to known organosilicon heat transfer fluids, which are considered to have much in common with ionic liquids in the set of properties and are used in the review as reference materials.
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I. Introduction

The development of new heat transfer fluids to be used as working fluids in industry, transport and for tailored applications is a highly topical task. Heat transfer fluids for a medium temperature range combining high heat capacity and low viscosity are used most widely. Meanwhile, a number of fields of science and technology impose special requirements on the properties of these fluids: high thermal stability is needed in ferrous and non-ferrous metallurgy, thermal and radiation stability are demanded in nuclear power engineering, low density and volatility are required for the space-rocket industry and so on. A priority trend of heat technology is the search for compounds and creation of fluid compositions possessing a desired combination of key physicochemical properties for solving non-

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trivial tasks. Of special interest in this respect are heat transfer fluids having acceptable thermophysical parameters and characterized by very low saturated vapour pressure at high temperature (>200 °C).

Ionic liquids (ILs) are low-temperature melts of organic salts, most often, formed by organic cations and inorganic anions. It is a relatively new class of compounds which finds more and more extensive use in various fields of science and technology. The advent of ILs brings hope that they would contribute to the development of fundamentally new areas and processes suitable for modern green chemistry.

This new class of solvents and media attracted attention in the mid-1980s. Salts that melt at rather low temperature (below 100 °C) are classified as ionic liquids,[1] although there are some ILs that remain liquid down to -80 °C. The properties and the behaviour of ILs being used as solvents or heat transfer fluids differ considerably from the properties of molecular liquids. Green chemistry imposes additional, more stringent requirements on these materials, namely, low ignitability and low explosion hazard, lack of combustibility, low volatility (vapour pressure) with retention of an acceptable viscosity and environmental safety.

During the last 10–15 years, the number of reviews, publications and patents devoted to various aspects of the preparation, study and application of ILs has reached several ten thousands (some publications were cited more than 1000 times[1–10]) and several books have been published.[11–15] However, most of these literary sources do not consider the possibility and efficiency of application of ILs as heat transfer fluids.

This review presents an analysis of the practical aspects and prospects of using ionic liquids as heat transfer fluids. A very important feature of ILs caused by the ionic character of the liquid state is the exceptionally low saturated vapour pressure under ambient conditions (10^{-10}–10^{-11} mm Hg at 25 °C).[13] Moreover, currently, ILs are the only class of organic compounds representatives of which, while having low viscosity, have very low saturated vapour pressure at temperatures of >200 °C ($<10^{-3}$ mm Hg). This accounts for the non-volatility and explosion safety of ILs and makes them especially attractive as heat transfer fluids and lubricants for operation under dynamic vacuum and, perhaps, in the outer space.

II. Modern organic and organosilicon heat transfer fluids

Any organic, heteroorganic and inorganic compounds that possess properties needed for a particular application can serve as heat transfer fluids. They are classified, most often, in terms of the range of working temperatures. Cryogenic and low-, medium- and high-temperature heat transfer fluids are distinguished. The last-mentioned type comprises thermally stable liquids: the upper limit of the temperature range may be as high as 200–250 °C for open systems and 350–400 °C for closed-loop systems for organic and organosilicon compounds and ~500–550 °C for inorganic salts. Liquid-metal heat transfer fluids are employed up to 1000–1200 °C.[16] The operation temperatures of most ionic liquids suitable for this application are in the range from 10 to 200 °C; however, the properties of particular representatives of this class of compounds go beyond the average temperature range. For comparison with ILs, it is most expedient to consider the existing medium- and high-temperature organic and organosilicon heat transfer fluids, because they have found most extensive use in various fields of heat technology.

Currently, industrial heat exchangers often operate using high- and medium-temperature heat transfer fluids based on aliphatic (Shell Thermia, BP Transcal, Mobiltherm, Addinol) and aromatic [Marlotherm (SH, LH, N), Dowtherm (A, G, Q, T), Therminol (VP-1, 59, 66, 72)] hydrocarbons, polyhydric alcohols (Ucon HTF 500, DOWCAL 200), organosilicon compounds [PMS, Penta-410, Sofeksil TSZh and TSZh-v, PMPS (4, 2/5), PES, Dow Corning (704, 705)] and so on.

II.1. Hydrocarbons

II.1.a. Aliphatic hydrocarbons

Mineral oils produced by selective purification of oil fractions with appropriate cut points are the most accessible organic heat transfer fluids operating at elevated temperature. 'Pure' mineral oils are mixtures comprising ~90% saturated linear, branched and cyclic hydrocarbons used as base oils for subsequent modification. The component ratio in the mixtures depends on the methods and degree of purification of the feedstock and determines the key thermophysical parameters of the oils. Synthetic base oils are formed most often upon catalytic oligomerization of α-olefins.[17] The high-quality mineral and synthetic oils to be used as heat transfer fluids such as Shell Thermia, BP Transcal, Mobiltherm, Addinol and so on are additionally treated by introducing blends of additives (antioxidants, viscosity modifiers, corrosion inhibitors, demulsifiers, antifoaming agents, detergents, dispersants, *etc.*). This markedly improves the performance of the oils. For examples, the additives present in the Mobiltherm 605, Shell Thermia Oil B and BP Transcal N oils boost the upper limit of the working temperature up to 315–320 °C for closed-loop systems and to 180 °C for open systems (Mobiltherm 605).[18]

II.1.b. Aromatic hydrocarbons

Heat transfer fluids based on aromatic hydrocarbons were obtained for the first time in the processing of mineral oils. The modern heat transfer fluids are mainly synthetic due to a higher level of requirements to some of their parameters and to the whole set of properties.

A popular heat transfer fluid is Dowtherm A — an eutectic mixture of biphenyl (26.5%) and diphenyl ether (73.5%), which melts at 12 °C (a similar product is manufactured under the trade name Therminol VP-1). This heat transfer fluid operates in the temperature range from 15 to 400 °C. At high temperature, the use of pressurized equipment is supposed (for Dowtherm A, pressure reaches 2.35 and 10.5 atm at 300 and 400 °C, respectively).[19] Both components of this heat transfer fluid are large-scale products of organic synthesis.

Two other heat transfer fluids of the same manufacturer — Dowtherm Q (mixture of diphenylethane and alkylbenzene) and Dowtherm T (mixture of C_{14}–C_{30} alkylbenzenes) — are meant for operation at temperatures from -35 to 330 °C and from -10 to 288 °C, respectively. The vapour pressure of Dowtherm Q at the limiting operating temperature is 3 atm, while that of Dowtherm T is 0.2 atm.[20,21] It is noteworthy that the latter value is fairly low among all listed organic heat transfer fluids. This is due to high molecular mass of mixture components, which simultaneously decreases the operating temperature (long

hydrocarbon chain is prone to destruction) and increases the viscosity.

Well known are heat transfer fluids under the trade names Marlotherm SH and Marlotherm LH, representing mixtures of isomeric dibenzylbenzenes and benzyltoluenes, respectively.[22,23] They operate in the temperature range from −5 to 350 °C.

Heat transfer fluids based on mixtures of isomeric terphenyls (mainly *ortho*- and *meta*-isomers) also allow operating temperature of ~380 °C in a closed-loop system to be attained. The *ortho*-isomer having the lowest melting point (T_m) melts at 59 °C. The T_m value of terphenyls is decreased by adding other thermally stable compounds able to form eutectic mixtures. A mixture of terphenyls, diphenyl ether and biphenyl [24] manufactured as Therminol 72 has T_m −18 °C and operates in the temperature range from −10 to 380 °C.[25] The presence of relatively volatile compounds (biphenyl and diphenyl ether) implies operation of heat transfer equipment under elevated pressure. One more method for extending the operating temperature range is partial hydrogenation of the terphenyl mixture (Therminol 66).[26] This heat transfer fluid has a somewhat lower maximum operating temperature (345 °C) than Therminol 72 but has a higher boiling point (359 °C).[27] In industry, terphenyls are formed as by-products of biphenyl synthesis by catalytic oxidative dimerization of benzene.

II.2. Polyhydric alcohols

Heat transfer fluids based on polyhydric and polymeric alcohols (polyethylene and polypropylene glycols) find both industrial and domestic use. The key advantages of these systems are water solubility and relatively low freezing points. However, they have markedly lower maximum admissible operating temperatures. For example, the operating range of Ucon HTF 500 based on polymeric glycol monobutyl ether[28] is from −18 to 260 °C,[29] while at 280 °C, the fluid rapidly decomposes.

Heat transfer fluids based on propylene glycol — DOWCAL 200 and Glythermin P — are used mainly as aqueous solutions. When the glycol concentration is >60%, the lower limit of the operating temperature range falls below −50 °C.[30] The upper limit in a closed-loop system can reach 160–175 °C; however, the pressure built up in the system at these temperatures can be 2 to 8 atm depending on the solution concentration.

II.3. Organosilicon fluids

Silicone oils, unlike hydrocarbon analogues, are not highly flammable compounds and, hence, they are most popular for applications in which the fire safety requirements are high. The most often used fluids include oligomeric and dimethylsiloxane polymers manufactured under the trade names PMS, Penta-410, Sofeksil TSZh, Sofeksil TSZh-v, Syltherm 800, diethylsiloxanes (PES), methylphenylsiloxane oligomers (PFMS-4, PFMS-2/5, FM-1 and the analogous foreign material called DC 705).

The liquids from PMS-5 to PMS-1000 are narrow fractions of oligo- or polydimethylsiloxane (PDMS), the numeral in the name corresponding to the kinematic viscosity. Neat polydimethylsiloxanes can be used at temperatures from −60 to 200 °C.[31] High-temperature PDMS (heat transfer fluids Penta-410, Sofeksil TSZh-v and Syltherm 800) are analogues differing only in the nature or the amount of low-molecular-mass thermal stabilization modifying additives. According to manufacturer recommendations, Penta-410 is suitable for operation at temperatures up to 400 °C in a closed-loop system and up to 250 °C in an open system,[32] while the operating temperatures of Sofeksil TSZh-v are in the range from −50 to 400 °C.[33] The manufacturer of the latter heat transfer fluid claims that the fluid is able to withstand short-term overheating up to 550 °C; however, no results of its chemical analysis and physicochemical parameters after the appropriate testing are presented.

The properties of polydiethylsiloxanes are similar to those of PDMS. Their distinctive features are the shift of the operating temperature range to low temperatures and better lubricating properties. The fluids from PES-1 to PES-4 retain acceptable viscosity values up to −50 °C (~1000 cSt for PES-4) [34] but, however, they are less stable at high temperatures than PDMS. The thermooxidative destruction of PES becomes noticeable even at 150 °C and the decomposition temperature is 240 °C. Polydiethylsiloxanes are fully compatible with hydrocarbon media; therefore, they are widely used as the bases for low-temperature oils and greases.[35]

The organosilicon fluid PFMS-2/5 is a narrow, rather low-boiling fraction of methylphenylsiloxane oligomer with a viscosity of 15–19 cSt and a vapour pressure of 4×10^{-6} mm Hg at 20 °C.[36] The fluid PFMS-4 has a viscosity of 600–1000 cSt and comprises a methylphenylsiloxane fraction with 8–10 units in the chain boiling above 360 °C at a residual pressure of not more than 0.2 mm Hg. It can be used as a heat transfer fluid suitable for long-term use at temperatures of up to 300 °C and for short-term use up to 350 °C.[37]

The high-temperature heat transfer fluid DC 705 is high-purity 1,3,5-trimethyl-1,1,3,5,5-pentaphenyltrisiloxane,[38] while FM-1, the Russian analogue of this fluid, is a narrow fraction containing ⩾70 mass % of the major component.[32] Both fluids operate in the temperature range from ~10 to 350 °C.

Formerly, aryl silicate-based liquids have been considered as promising heat transfer fluids.[39] In particular, tetra-*o*-cresol orthosilicate (TCS) was intended for the use to cool engines[40] and to heat extruders with operating temperature of up to 400 °C.[41] A benefit of this heat transfer fluid, apart from good thermophysical characteristics,[42] is a simple preparation method. Other aryl silicates were also tested as heat transfer fluids; however, as a rule, they had higher viscosity than TCS. Measurements of the viscosity change for (biphenyl-4-yl)triphenoxysilane in long-term experiments demonstrated that it is more stable during high-temperature operation than other aryl silicates.[43] However, all of the aryl silicates have one serious drawback: they are hydrolyzed in the presence of moisture to give polymeric products and fairly toxic volatile compounds, which precludes their use in household heat-exchange units and requires appropriate safety measures for industrial use.

The physicochemical parameters of the most popular organic and organosilicon heat transfer fluids are summarized in Table 1.

Each of the above-listed classes of compounds has both advantages and disadvantages when used as a heat transfer fluid. Aliphatic hydrocarbons are cheap but, like polyhydric alcohols, they lack high oxidative and thermal stability due to their chemical nature. The polymeric products and carboxylic acids formed upon mineral oil ageing can be

Table 1. Physicochemical parameters of heat transfer fluids.

Heat transfer fluid	Operation range /°C	p_{sat} (25 °C), /mm Hg	p_{sat} (200 °C), /mm Hg	T_{fr} /°C	υ (25 °C) /cSt	υ (100 °C) /cSt	ρ (25 °C) /g cm^{-3}	C_p (25 °C) /kJ kg^{-1} K^{-1}	C_p (100 °C) /kJ kg^{-1} K^{-1}	λ (25 °C) /W m^{-1} K^{-1}	λ (100 °C) /W m^{-1} K^{-1}	Ref.
Shell Thermia B	0 – 250	–	3.8	−12	45	4.7	0.86	1.90	2.18	0.132	0.127	44
Marlotherm SH	−5 – 350	$\ll 0.1$	3.7	< -34	47 [a]	3.1	1.04	1.57	1.85	0.130	0.120	45
Dowtherm A (Terminol VP-1)	15 – 400	< 0.1	180	12	3.52	0.97	1.06	1.59	1.80	0.138	0.126	19
Terminol 68	−26 – 360	< 0.07	61.8	−33	34.7 [a]	2.74	1.02	1.64	1.88	0.123	0.117	46
Ucon HTF 500	−18 – 260	< 0.01	< 0.1 [b]	−48	100	12	1.04 [a]	1.97	2.20	0.167	0.152	28, 29
Sofeksil TSZh-v	−50 – 400	$\ll 10^{-3}$	563	< -64	56.5	17.9	0.96	1.67	1.79	0.132	0.117	33
Syltherm 800	−40 – 400	< 1	710	−60	9.7	3.6	0.94	1.62	1.75	0.134	0.120	47
PMS-100	−50 – 200	10^{-4}	2	−62	100	28	0.97	1.44	1.66	0.161	0.147	34, 42
PES-4	−70 – 150	0.1	30	−110	40	7.9	0.97 [a]	1.68	1.85	0.142	0.131	34, 42
PFMS-4	0 – 250	$< 10^{-5}$	0.5	−20	659 [a]	31.4	1.09	1.55	1.75	0.148	0.138	34, 42
DC 705 (FM-1)	−10 – 300	3×10^{-10}	< 0.1	−25	175	–	1.09	1.52	1.74	0.128	0.120	34, 38
Tetra-*o*-cresol orthosilicate	0 – 400	–	–	−36	53 [a]	3.8	1.12	1.88	2.47	0.123	0.115	41, 42
$[C_4HC_1Im][Tf_2N]$	–	$10^{-10} – 10^{-11}$	3×10^{-4}	−4	35.5	6.88 [c]	1.44	1.35	1.44 [d]	0.128 [a]	0.124 [c]	13, 48 – 52
$[C_4HC_1Im][TfO]$	–	$10^{-10} – 10^{-11}$	–	16	68.9 [a]	9.45 [c]	1.30	1.48	1.61 [d]	0.147 [a]	0.142 [c]	13, 51 – 54

Note. p_{sat} is the saturated vapour pressure, T_{fr} is the freezing temperature, ρ is density, C_p is heat capacity, υ is kinematic viscosity, λ is thermal conductivity, Tf = CF_3SO_2.
[a] At 20 °C; [b] at 260 °C; [c] at 80 °C, [d] at 95 °C.

deposited on vessel walls and induce metal corrosion. Aromatic hydrocarbons are thermally stable and more resistant to oxidation. The common drawback of all of the organic heat transfer fluids is high fire hazard.

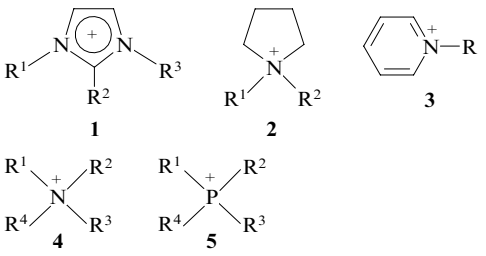
Virtually all organic heat transfer fluids used currently have been prepared from low-molecular-mass compounds and have low polarity and, hence, they are weakly associated media. Therefore, at high operating temperatures, the saturated vapour pressure of these fluids can be fairly high (for example, it is 10.5 atm for Dowtherm A at 400 °C), which requires the use of closed-loop equipment and enhanced fire protection measures.

Thermally stable organosilicon fluids possess a unique combination of properties and currently they are widely used as heat transfer fluids and high-temperature lubricants. Virtually all of them are chemically and corrosion inert, non-explosive and low-toxic. However, compounds having low viscosity (< 100 cSt at 25 °C) also have a relatively high saturated vapour pressure at temperatures above 200 °C (p_{sat} > 1 mm Hg, see Table 1). In addition, organosilicon fluids are much more expensive than organic ones.

III. Thermophysical and physicochemical properties of ionic liquids. A comparison with organosilicon heat transfer fluids

More than 90% of all ILs studied to date comprise one of the cations **1**–**5** in the molecule.

Structures 1 – 5



1 **2** **3** **4** **5**

R, R^1, R^2, R^3, R^4 = Alk(C_1–C_{16}), Ar

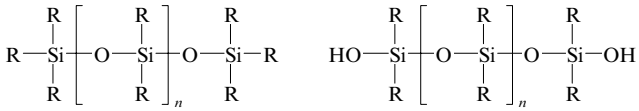
In this review, imidazolium ILs are designated using general formulae [$C_nC_1C_m$Im][X] and [C_nHC_mIm][X] for salts containing or not containing a methyl group in position 2 of the imidazole ring, respectively, [X] is anion. Pyrrolidinium ILs are designated by [C_nC_mPyrr][X] and the pyrididium compounds are depicted as [C_nPy][X]. The subscripts *n* and *m* in the formulae correspond to the number of carbon atoms in alkyl substituents.

III.1. Thermal stability

In up-to-date scientific literature, the thermal stability of chemical compounds and materials is most often characterized by the decomposition temperature (T_{dec}) determined from thermogravimetric analysis (TGA) data. In literary sources, T_{dec} is commonly defined as the value corresponding to the intersection point of the straight lines superimposed onto the horizontal and descending segments of the thermogram. However, it is obvious that the weight of the sample starts to decrease at a lower temperature. The difference between T_{dec} and the point that can be called the decomposition onset temperature ($T_{d.o}$) can be from 10 to 100 °C depending on the chemical nature of the substance, sample weight and experimental conditions. The same parameters affect the positions of T_{dec} and $T_{d.o}$ points. The higher the sample heating rate and weight, the higher these values. Therefore, to compare the thermal stabilities of different compounds, it is necessary to pay due attention to the experimental conditions indicated in the publication.

Currently, fluids of the organosilicon nature are most thermally stable and close to an ideal medium-temperature heat transfer fluid; therefore, they are good objects for comparison and evaluation of the benefits and drawbacks of ILs. Oligo- and polyorganosiloxanes (**6**, **7**) are used most widely as heat transfer fluids. The studies of their thermal stability as a function of the nature of substituent at the silicon atom and molecular mass and the type of terminal groups have been carried out for more than half a century.[55–62] The mechanisms of thermal decomposition of PDMS and polymethylphenylsiloxane (PMPS) polymers were studied. It was found that both types of compounds decompose *via* cleavage of the siloxane bond with predominant formation of cyclic tri- and tetrasiloxanes.[56–58] The PMPS polymers are somewhat more thermally stable than PDMS polymers and the thermal stability is less dependent on the type of terminal groups.[58]

Structures 6, 7

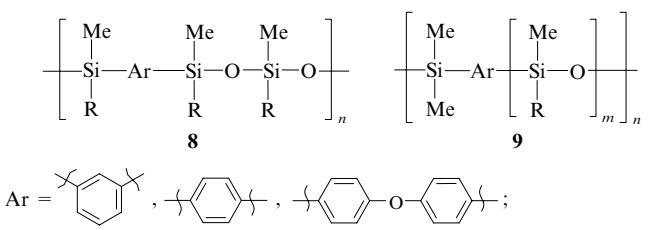


6 **7**

R = Me, Et, Ph; $n \approx 1-200$

A number of researchers[63–67] attempted to increase the thermal stability of organosilicon polymers by insertion of phenylene or diphenyl oxide bridges into the backbone (structures **8** and **9**); this modification prevents the formation of cyclic decomposition products on heating. Unfortunately, all of the obtained thermally stable silarylene–siloxane polymers have too high viscosity and are unsuitable as heat transfer fluids.

Structures 8, 9



8 **9**

Ar =

R = Me, Ph; $n \approx 10-100$; $m \approx 1-4$

The decomposition temperatures of PDMS and PMPS polymers for a sample heating rate of 20 °C min^{-1} are ~400 and ~420 °C, respectively.[68] For the silphenylene–siloxane polymer, $T_{dec} \approx 525$ °C under the same condi-

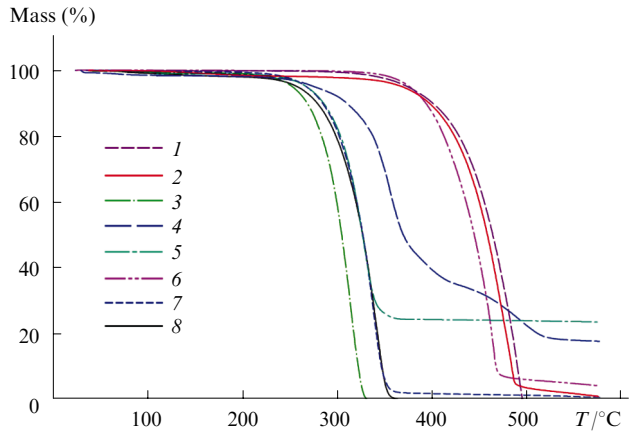


Figure 1. TGA curves of imidazolium salts recorded at a heating rate of 20 °C min^{-1} (see Ref. 72).
(*1*) $[C_1HC_1Im][Tf_2N]$, (*2*) $[C_4HC_1Im][Tf_2N]$, (*3*) $[C_1HC_1Im]Cl$, (*4*) $[C_1HC_1Im][BF_4]$, (*5*) $[C_1HC_1Im][MeSO_3]$, (*6*) $[C_1HC_1Im][PF_6]$, (*7*) $[C_1HC_1Im][DBS]$, (*8*) $[C_1HC_1Im]I$ (DBS is dodecylbenzenesulfonate).

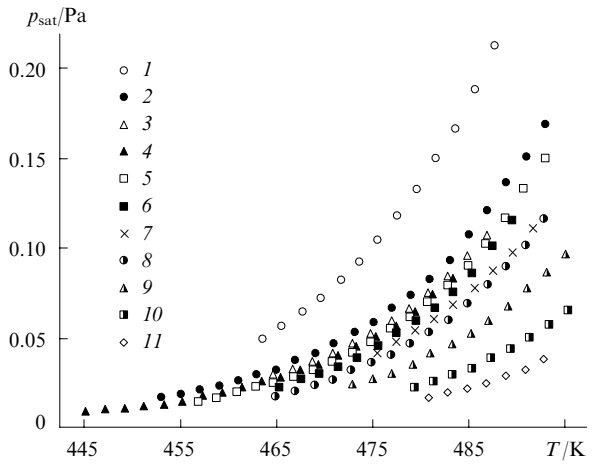


Figure 2. Temperature dependences of p_{sat} for 11 dialkylimidazolium bis(trifluoromethylsulfonyl)imides (the data from Refs 48 and 77).
(*1*) $[C_3HC_2Im][Tf_2N]$, (*2*) $[C_3HC_1Im][Tf_2N]$, (*3*) $[C_4HC_1Im][Tf_2N]$, (*4*) $[C_2HC_1Im][Tf_2N]$, (*5*) $[C_5HC_1Im][Tf_2N]$, (*6*) $[C_6HC_1Im][Tf_2N]$, (*7*) $[C_1HC_1Im][Tf_2N]$, (*8*) $[C_7HC_1Im][Tf_2N]$, (*9*) $[C_8HC_1Im][Tf_2N]$, (*10*) $[C_{10}HC_1Im][Tf_2N]$, (*11*) $[C_{12}HC_1Im][Tf_2N]$.

tions.[68] However, high T_{dec} values do not ensure equally high operating temperatures. Considering the decomposition rate of the samples at 400 °C,[68] one can conclude that the operating temperatures of organosilicon heat transfer fluids would be 150–200 °C lower than T_{dec}. Nevertheless, they are still fairly high and reach ~200 °C for PDMS, ~300 °C for polydiethylsiloxane and PMPS polymers under inert atmosphere. Under these conditions, the last-mentioned fluids can withstand short-term overheating to 350 °C.[37] The introduction of thermal stabization modifying modification additives into the polymers allows the operating temperature limit for PDMS fluids to be increased up to 400 °C for closed-loop systems.[32] However, in open systems, the efficiency of the additives is moderate.

Ionic liquids, being organic salts, do not possess in most cases so high thermal stability as organosilicon compounds. The thermal stability of ILs is determined by the type of the cation and the chemical nature of the anion. Most thermally stable are ILs with pyrrolidinium and imidazolium cations, while least thermally stable are pyridinium and acyclic tetraalkylammonium ILs. The thermal stability of anions decreases in the series $[(C_2F_5SO_2)_2N]^- > [Tf_2N]^- > [TfO]^- > [PF_6]^- > [BF_4]^- > [(NC)_2N]^- > Cl^-$ (Refs 14 and 69). According to TGA data obtained in a nitrogen atmosphere at a sample heating rate of 20° C min^{-1}, a number of alkylimidazolium hexafluorophosphates, tetrafluoroborates and bis(trifluoromethylsulfonyl)imides have T_{dec} ~ 450 °C.[70] However, it was shown that an increase in the heating rate of the IL from 10 to 20 °C min^{-1} increases the $T_{d.o}$ (and, hence, T_{dec}) by 10–20 °C.[71]

The effect of the nature of the anion on the thermal stability of a number of imidazolium ILs is vividly illustrated by TGA curves[72] presented in Fig. 1.

Despite fairly high T_{dec} values, the operating temperatures of ILs, like those of the above-considered organosilicon compounds, are substantially lower. By conducting TGA under isothermal conditions, the operating temperatures for three imidazolium ILs[73] were found to be in the ~200–250 °C range.

III.2. Saturated vapour pressure

It has been believed for rather long period that ILs are devoid of detectable vapour pressure.[1] It was only in 2003 that the first attempt to determine the volatility of $[C_4HC_1Im][PF_6]$ by the Knudsen effusion method was reported.[74] However, due to the thermal destruction of ILs in vacuum, the researchers failed to obtain reproducible results. The use of $[C_4HC_1Im][Tf_2N]$ samples[75] and later other alkyl-substituted imidazolium bis(trifluoromethylsulfonyl)imides[48,76,77] made it possible to measure p_{sat} values for 11 ILs (the generalized experimental data of Refs 48 and 77 are shown in Fig. 2).

Ionic liquids occupy an intermediate position between the molecular organic liquids and inorganic salt melts. At a liquid–vapour equilibrium, transition of species forming the liquid phase into the gas phase is hampered by association of the species. In inorganic salt melts, the cations and anions are inolved in strong Coulomb interactions. In the case of molecular liquids, association is due to van der Waals forces and, if possible, hydrogen bonding.

The association of ions forming the ILs is due to both Coulomb and van der Waals forces. The electrostatic interaction between the ions is weaker in this case than that in typical inorganic salt melts, which is caused by much larger size and molecular mass of the IL ions. The elementary positive or negative charge is delocalized over a group of several atoms, for example, the aromatic imidazolium ring or the CF_3SO_2 groups of the bis(trifluoromethylsulfonyl)imide anion. The van der Waals interactions occur mainly between non-polar moieties of the IL structure, for example, between alkyl substituents.

In Fig. 2, the IL are arranged in the order of decreasing volatility from $[C_3HC_2Im][Tf_2N]$ to $[C_{12}HC_1Im][Tf_2N]$, which can be used to evaluate the contributions of the two

above factors (Coulomb and van der Waals interactions) to the degree of association of ions. Indeed, the curve for the temperature dependence of volatility for the ILs formed by the $[C_1HC_1Im]^+$ cation having the smallest size and molecular mass occupies an intermediate position among the other curves. An increase in the length of substituents at nitrogen results in a decrease in the average charge density of the cation and, hence, in a weakening of the Coulomb interaction between the ions. This trend is followed in the series $[C_1HC_1Im]^+ - [C_2HC_1Im]^+ - [C_3HC_1Im]^+$. The highest volatility is characteristic of $[C_3HC_2Im][Tf_2N]$, which is caused by both the more symmetrical structure of the cation and more pronounced charge shielding by the alkyl substituents. Further increase in the carbon chain length from $[C_4HC_1Im]^+$ to $[C_{12}HC_1Im]^+$ enhances the van der Waals interactions and, hence, the vapour pressure decreases monotonically in the series of ILs.

It is commonly accepted [78] that the temperature dependence of the IL vapour pressure obeys the Clausius–Clapeyron equation and is mainly determined by the enthalpy of vaporization.

A comparison of the vaporization thermodynamics for the series of structurally similar ILs can serve to evaluate the degree of influence of a particular structure difference on the volatility of ionic liquids. The molar enthalpies of vaporization of a number of ILs were measured by mass spectrometry.[79] It was found that IL vapour consists exclusively of neutral ion pairs. Vaporization is described by zero-order kinetics at a constant vaporization area. From the thermodynamic data given in the paper cited, it follows that elongation of the alkyl substituents in the cation results in some increase in the molar enthalpy of vaporization. For example, a change in the alkyl chain length in the imidazolium cation by six carbon atoms ($[C_2HC_1Im][Tf_2N]$ *vs.* $[C_8HC_1Im][Tf_2N]$) induces an increase in the enthalpy of vaporization from 134 to 149 kJ mol^{-1}.

The nature of the cation plays a commensurable role. Thus ILs with dialkylpyrrolidinium cations have $\sim$17 kJ mol^{-1} higher enthalpies of vaporization than imidazolium ILs. The nature of the anion has a more substantial effect and can account for a difference between the molar enthalpies of IL vaporization at a level of 30 kJ mol^{-1}. For example, at 227 °C, $[C_2HC_1Im][Tf_2N]$ has a vapour pressure of $\sim$0.1 Pa, while in the case of $[C_2HC_1Im][TfO]$, the vapour pressure is 0.013 Pa,[69] which is caused by a higher charge density of the anion and, as a consequence, stronger Coulomb interaction between the ions. A more pronounced increase in the enthalpy of vaporization occurs only on going to doubly charged cations. It was also shown [79] that an increase in the molar volume of the IL leads to a decrease in the Coulomb contribution and increase in the van der Waals contribution to the association of ions.

As the temperature rises, the vapour pressure above the liquid starts to be determined to an increasing extent by the kinetics of IL decomposition giving more volatile products and not only by the thermodynamics of vaporization of the IL itself.[80]

In 2005, the possibility of high-vacuum distillation of IL was demonstrated for the first time in relation to $[C_{10}HC_1Im][Tf_2N]$ and $[C_{12}HC_1Im][Tf_2N]$,[81] and a year later, this process was studied in detail using 20 samples of various compositions and structures.[82] It was found that vacuum distillation of ILs containing an ammonium or phosphonium cation and an anion such as tris(pentafluoroethyl)trifluorophosphate ($[FAP]^-$), $[EtSO_4]^-$ or $[C_9H_{19}CO_2]^-$ at 300°C is accompanied by most pronounced decomposition. The imidazolium and pyrrolidinium ILs with the $[Tf_2N]^-$, $[TsO]^-$ (Ts is *p*-toluenesulfonyl) and $[PF_6]^-$ anions have a minor content of decomposition products in the distillate under the same conditions. It was shown in relation to $[C_6HC_1Im][Tf_2N]$ that the decrease in the process temperature to 150–200°C provides ILs with a purity of >99%.

For most organosilicon compounds that are of interest as heat transfer fluids, saturated vapour pressures are 10^{-6}–10^{-10} mm Hg at 25°C and 10^{-1}–10^{-2} mm Hg at 200 °C (see Table 1). The increase in the molecular mass upon chain elongation (for linear oligomeric siloxanes) or upon introduction of aromatic groups into the molecule may substantially reduce p_{sat}. However, this approach has certain limitations, as the increase in the molecular mass is always accompanied by an increase in the viscosity, which is, moreover, fairly high in the case of introduction of aromatic groups. The high-molecular-mass PDMS and PMPS polymers, like the oligomeric analogues, have $p_{sat} \sim 10^{-2}$ mm Hg at temperatures of >200–250 °C. This is attributable to both the presence of low-molecular-mass fractions, which are inevitably formed during polymerization, and to the appearance of volatile products of thermal destruction.

III.3. Viscosity

In the literature, dynamic viscosity (η) measured in Poises (P, g cm^{-1} s^{-1}) or kinematic viscosity (υ) measured in Stokes (St, cm^2 s^{-1}) are used in most cases in describing the rheological properties of liquids. The kinematic viscosity is equal to the ratio of dynamic viscosity to the density of a substance measured at the same temperature.

The viscosity of ionic liquids varies over a broad range: from $\sim$10 to >5500 cP.[12, 83] This value is affected by both van der Waals forces and hydrogen bonding, which are inherent in molecular liquids, and the amounts of charge and Coulomb interactions between the ions characteristic of salt systems. Thus the viscosity of ILs containing the $[C_4HC_1Im]^+$ cation decreases in the following order depending on the nature of the anion:[84, 85] $Cl^- > [PF_6]^- > [NO_3]^- > [BF_4]^- > [TfO]^- > [CF_3CO_2]^- > [Tf_2N]^- > [(NC)_2N]^- > [(NC)_3C]^-$ The structure of the cation is also significant. In most cases, the introduction of long alkyl, bulky phenyl or hydroxyl-containing substituents increases the viscosity.

One more feature of many ILs is that the viscosity is strongly temperature-dependent. For example, in the case of ILs with dialkylimidazolium cations and cyano groups in the anion ($[SCN]^-$, $[(NC)_2N]^-$, $[(NC)_3C]^-$ or $[(NC)_4B]^-$), a temperature rise from 25 to 30 °C entails a decrease in the viscosity by 14%–22%.[85] The temperature dependences of viscosity for other anions [86] are shown in Fig. 3.

Currently, the diversity of the available anions and variation of the number and sorts of substituents in the cation make it possible to obtain compounds with desired viscosity for a particular application.

The viscosity of most organosilicon liquids having a low saturated vapour pressure under normal conditions ($<10^{-8}$ mm Hg) is higher than 15 cP. Dimethylsiloxane oligomers and polymers have a substantially lower viscosity than methylphenylsiloxane derivatives with the same degree

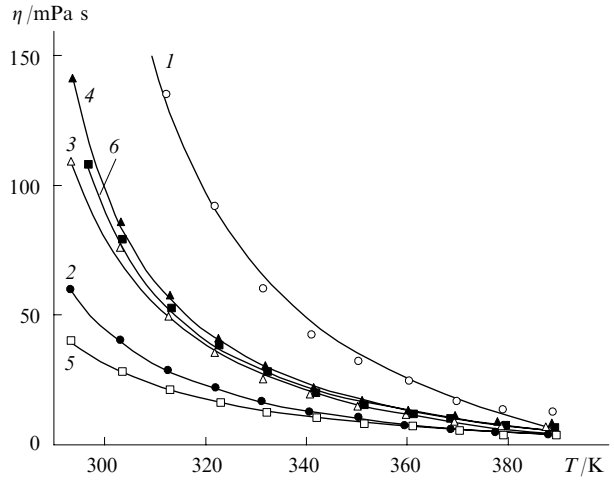


Figure 3. Viscosity *vs.* temperature for a number of ILs.[86] (*1*) $[C_4HC_1Im][PF_6]$, (*2*) $[C_4HC_1Im][Tf_2N]$, (*3*) $[C_4HC_1Im][BF_4]$, (*4*) $[Me_3Bu^nN][Tf_2N]$, (*5*) $[C_2HC_1Im][Tf_2N]$, (*6*) $[C_2HC_1Im][EtSO_4]$.

of polymerization: for instance, for oligomers with ~10 units in the chain, the viscosity at 20 °C is ~9 and ~700 cP, respectively. The temperature dependences of the viscosity for the mentioned organosiloxane oligomers are substantially different. As the temperature rises from 20 to 200 °C, the viscosity drops approximately 9-fold for dimethyl- and almost 100-fold for methylphenylsiloxane oligomers.[42]

III.4. Density

Most ionic liquids have a rather high density (1–2.3 g cm^{-3}). The highest values are observed for ILs with perfluorinated alkyl substituents in the cation and the bis(trifluoromethylsulfonyl)imide anion.[87] The density of ILs with the dialkylimidazolium cation decreases in the following series depending on the anion nature:[84] $[Tf_2N]^- > [PF_6]^- > [EtSO_4]^- > [BF_4]^- > Cl^- > [(NC)_2N]^-$. The density also decreases as the length and the number of alkyl substituents in the cation increase (Fig. 4).

Thus, the IL densities are determined to a larger extent by the nature of the anion than by the nature and structure of the cation. The influence of the temperature on the density of ILs is slight: a temperature rise from 20 to 70 °C leads to a decrease in the density by 2%–3%.[88]

As compared with ILs, the density of PDMS and PMPS fluids is lower, being in the range of 0.85–1.1 g cm^{-3} at 20 °C, and depends not only on the chemical composition and temperature but also on the molecular mass. The dimethylsiloxane oligomers and polymers have a lower density at 20 °C (0.85–0.97 g cm^{-3}) than methylphenylsiloxane derivatives (1.0–1.1 g cm^{-3}). A slight increase in the density following an increase in the molecular mass was found for both PDMS and PMPS. For organosilicon compounds, this value has a somewhat more clear-cut temperature dependence than for ILs. As the temperature rises from 20 to 80 °C, the density decreases by 5%–7% for PDMS and by 4%–5% for PMPS.[42]

III.5. Heat capacity

The heat capacity (C_p) of various compounds and materials is calculated from the differential scanning calorimetry data. In most publications, the value reported for ionic liquids is the molar heat capacity measured in J mol^{-1} K^{-1} or, more rarely, mass heat capacity (kJ kg^{-1} K^{-1}).

The heat capacity of most of ILs at 25°C is in the range from 1.2 to 1.9 kJ kg^{-1} K^{-1} or from 300 to 1300 J mol^{-1} K^{-1} for the mass or molar heat capacity, respectively. This parameter increases virtually linearly in the temperature range from 20 to 200 °C and is determined by the chemical structure and composition of the IL. The temperature dependences of the heat capacity for six ILs are shown in Fig. 5.[89]

For all ILs, an increase in the length and the number of alkyl substituents in the cation entails an increase in the heat capacity. The nature of the anion exerts a somewhat more pronounced effect. However, if the ILs with the $[C_4HC_1Im]^+$ cation and various anions are arranged in the

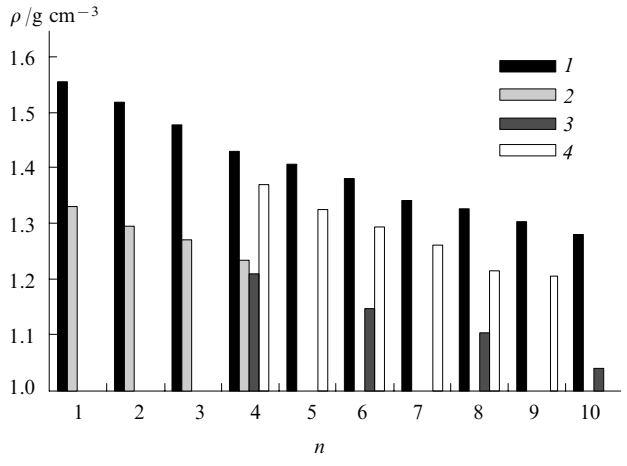


Figure 4. Effect of the anion and the cation on the density of imidazolium ILs $[C_nHC_1Im][X]$ at 25 °C (n = 1–10), [X] = $[Tf_2N]^-$ (*1*), $[AlCl_4]^-$ (*2*), $[BF_4]^-$ (*3*), $[PF_6]^-$ (*4*).[84]

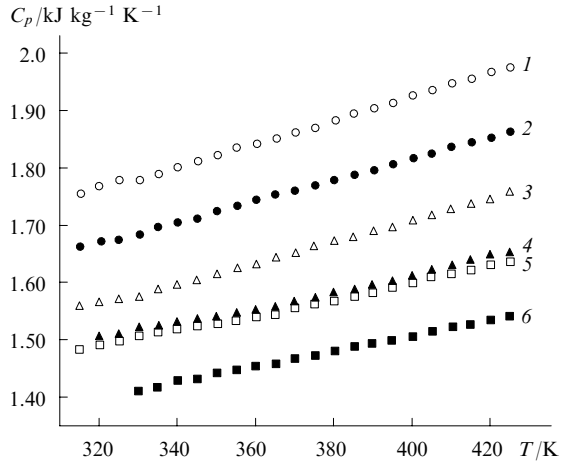


Figure 5. Heat capacity *vs.* temperature for a number of ILs.[89] (*1*) $[C_8HC_1Im][TfO]$, (*2*) $[C_6HC_1Im][TfO]$, (*3*) $[C_4HC_1Im][TfO]$, (*4*) $[C_6HC_1Im][Tf_2N]$, (*5*) $[C_2HC_1Im][TfO]$, (*6*) $[C_4Py][Tf_2N]$.

order of decreasing heat capacity, the series for the molar ($Br^- > Cl^- > [BF_4]^- > [(NC)_2N]^- > [PF_6]^- > [TfO]^- > [Tf_2N]^-$) and mass ($Cl^- > [(NC)_2N]^- > [BF_4]^- > [TfO]^- > Br^- > [PF_6]^- > [Tf_2N]^-$) heat capacity will not coincide.[88,90–92] The molar heat capacity is well correlated with the anion size and the molecular mass of IL.[93] The mass heat capacity values are more appropriate to characterize ILs as heat transfer fluids for the calculation and design of the facilities, as this enables comparing ILs with other compounds irrespective of the chemical nature, composition and structure.

The mass heat capacities of organosilicon heat transfer fluids (1.45 ± 0.05 and 1.55 ± 0.05 kJ kg^{-1} K^{-1} at 20 °C for dimethyl- and methylphenylsiloxane oligomers, respectively) are slightly greater than for ILs and they also increase with temperature rise.[37,42]

III.6. Thermal conductivity

At present, the number of publications devoted to the thermal conductivity of ionic liquids is relatively small, and only few papers present the results of experimental instrumental measurements rather than theoretical calculations.[51,94–97] However, the reported values cover about 20 most widely used ILs, which allows rather accurate evaluation of the effect of chemical composition, structure and physical properties on the thermal conductivity. The available data provide the conclusion that the thermal conductivity (λ) for virtually all of the studied ILs is in the range of 0.1–0.22 W m^{-1} K^{-1}. The most popular method for determining the thermal conductivity of ILs is the transient hot-wire method;[51,94–96] more rarely, the parallel plate method[97] and the transient grating method[98] are used. In the latter case, the thermal diffusion coefficient is determined; with known heat capacity, viscosity and density of the substance and the sound velocity in the substance, this allows one to calculate the thermal conductivity. The IL thermal conductivity values differ depending on the method used; in some cases, this difference may be significant. Indeed, the thermal conductivities of $[C_4HC_1Im][BF_4]$ and $[C_2HC_1Im][Tf_2N]$, calculated by the grating method are 0.162 and 0.120 W m^{-1} K^{-1}, respectively.[98] These values are lower by 13% for $[C_4HC_1Im][BF_4]$ and by 8% for $[C_2HC_1Im][Tf_2N]$ than the values determined by the hot-wire method.[51,94] This suggests that the grating method needs to be improved. The necessity to take into account a large number of significant parameters can also lead to accumulation of calculation errors. The discrepancy between the data obtained by the transient hot-wire and parallel plate methods is smaller and for many ILs it is within the error inherent in each of the methods. It was noted[97] that the discrepancy decreases with an increase in the dynamic viscosity of the IL, which can be attributed to the presence of unaccounted convective heat transfer in the hot-wire method. The presence of water or inorganic salt impurities in the IL sample also results in overestimation of the λ values.

The heat conductivity of ILs depends little on the temperature and on the cation type and structure; however, the nature of the anion has a considerable influence (Fig. 6).

The λ values given in Fig. 6 for eleven ILs were obtained by the hot-wire method in the temperature range from 20 to 80 °C. For all ILs, the thermal conductivity linearly decreases with temperature rise. The lowest thermal conductivity corresponds to the ILs with the FAP^- anion: in particular, for $[C_4C_1Pyrr][FAP]$, it is 0.107 W m^{-1} K^{-1} at 20°C. The heat conductivity of ILs with the $[Tf_2N]^-$ anion lies within a fairly narrow range of 0.124–0.134 W m^{-1} K^{-1} in the temperature range in question.

The heat conductivities of the oligomeric organosiloxanes and ILs with the $[Tf_2N]^-$ anions are close to one another. Indeed, the λ values for PDMS and PMPS with a viscosity of 15 cSt are ~0.138 and ~0.131 W m^{-1} K^{-1}, respectively, at 20 °C.[42]

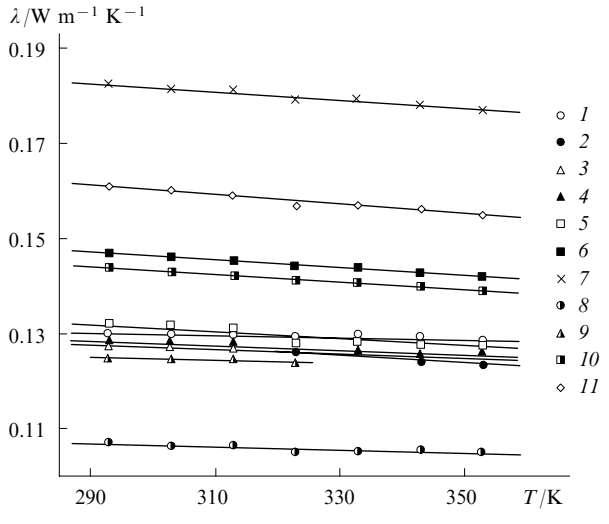


Figure 6. Thermal conductivity *vs.* temperature for a number of ILs.[51]
(*1*) $[C_2HC_1Im][Tf_2N]$, (*2*) $[C_4HC_1Im][Tf_2N]$, (*3*) $[C_6HC_1Im][Tf_2N]$, (*4*) $[C_8HC_1Im][Tf_2N]$, (*5*) $[C_1HC_1Im][Tf_2N]$, (*6*) $[C_4HC_1Im][TfO]$, (*7*) $[C_2HC_1Im][EtSO_4]$, (*8*) $[C_4C_1Pyrr][FAP]$, (*9*) $[C_4C_1Pyrr][Tf_2N]$, (*10*) $[(C_6H_{13})_3P(C_{14}H_{29})][Tf_2N]$, (*11*) $[(C_6H_{13})_3P(C_{14}H_{29})]Cl$.[51]

III.7. Corrosion activity

The corrosion activity of ionic liquids has been the subject of a large number of publications.[99–105] The studies were carried out both by electrochemical techniques and by the traditional gravimetric measurement of the rate of corrosion. The action of ILs on alloys that are often used in the chemical mechanical engineering (brass, bronze, various steels, Inconel) has been studied most comprehensively.

Apart from the IL chemical nature, the temperature and experiment duration, the metal corrosion is affected by some other factors such as the presence of water, oxygen and the presence of halide ions, which is especially often encountered. It is known that halide ions are activating agents which prevent passivation of the metal and promote the pitting corrosion.

Corrosion testing of copper, nickel, brass (60% Cu, 40% Zn), AISI 1018 steel (0.14%–0.20% C, 0.60%–0.90% Mn) and Inconel 600 alloy (Ni–Cr–Fe) in the medium of the $[C_4HC_1Im][Tf_2N]$ ionic liquid at room temperature was reported.[99] According to the data of quasi-stationary (0.1 mV s^{-1}) potentiodynamic measurements, the dependences for Inconel, nickel and brass are similar and have a clear-cut passivity region characterized by currents of ~3 μA cm^{-2}. In the case of copper, the current in the passivity region reaches several tens of μA cm^{-2}. The highest anodic currents were observed in

the case of steel. The corrosion tests carried out for 2 days at various temperatures in the range from 150 to 325 °C and in contact with air reveal a different relative stability of the samples. Coper proves to be the least stable, degradation of samples being visible even after relatively short experimental times. Steel, Inconel and nickel are stable at 250 °C, no weight loss is detected, the sample surface darkens but remains smooth. At higher temperature, pitting corrosion without a noticeable decrease in the sample weight takes place. Brass proved to be the most stable material (up to 300 °C). Pitting corrosion is detected only at 325 °C. X-Ray microanalysis of the brass sample surface showed that selective dissolution of the α-phase and surface enrichment with the more corrosion-resistant β-phase takes place in the corrosion pit. According to X-ray microanalysis data, a substantial amount of chlorides is present on the surface. The authors did not quantify traces of chlorides in the IL tested, although, as follows from the above data, the residual chloride ions can play a considerable role in the corrosion activity of the IL.

The interaction of the same ionic liquid, ($[C_4HC_1Im][Tf_2N]$), with brass, Inconel 600 and AISI 1018 steel for a longer period (20 days) was studied at 225 °C.[100] The corrosion rate was estimated by quantifying the products of dissolution of the tested alloys, which were immersed in the IL as discs with 30 mm diameter. In the case of Inconel, only traces of nickel (9 mg kg^{-1} of the IL) passed to the solution and chromium was not detected in the IL. The contents of brass and steel corrosion products (iron and copper) were two orders of magnitude higher (700 mg kg^{-1} for steel and 2700 mg kg^{-1} for brass). According to X-ray photoelectron spectroscopy (XPS), the alloy metals are present in the surface layer as oxides; in addition, fluorine bound to carbon (CF_3 groups of the $[Tf_2N]^-$ anion of the IL) and nitrogen, also bound to carbon, are detected. Thus, the retention of the CF_3 groups and the absence of detectable amounts of metal fluorides on the surface attests to fairly low corrosive action of the $[Tf_2N]^-$ anion as compared with other fluorine-containing anions.

The potentiodynamic measurements at room temperature were used to study the corrosion activity of the ILs with the dialkylimidazolium cation and various anions (Cl^-, $[PF_6]^-$, $[Tf_2N]^-$) towards steel.[101] For all IL, the corrosion rates were found to be rather low (6–13 μm per year). Voltammetric data [102] suggest high corrosion resistance of the AISI 304 stainless steel (the composition is similar to the Russian 08Kh18N10 steel) at room temperature in the medium of the $[C_4C_1Pyrr][Tf_2N]$ ionic liquid. The results obtained by cyclic voltammetry [103, 104] provide the conclusion that aluminium is passive in the ILs with the $[Tf_2N]^-$ anion over a broad range of potentials. The sufficient stability of aluminium in a variety of ILs with the mentioned anion is indicated by its extensive use as the cathode substrate in lithium ion cells with IL-based electrolytes.

An attempt was made to decrease the high-temperature corrosion rate in the IL medium by introducing inhibitors that are usually applied for this type of alloys.[105] The investigation objects included low-alloyed chromium steel (AISI 100Cr6) and bronze (CuSn8P). The experiments were carried out at temperatures of 150 and 175 °C for 2 weeks. Two ionic liquids were chosen, namely, 2-hydroxyethyltrimethyl and n-butyltrimethylammonium bis(trifluoromethylsulfonyl)imides, to which 1.5% water was added. The corrosion rate was estimated by determining the contents of iron (or copper) in the IL after the experiment. XPS analysis of the steel surface after exposure to IL demonstrated, apart from the presence of CF_3 groups, the presence of iron fluorides (which was not observed in the earlier study [100]). This may be related to hydrolysis of the $[Tf_2N]^-$ anion at high temperature. The nature of the IL cation also has a substantial effect on the corrosion rate: in the case of bronze, the IL with the $(HOCH_2CH_2)Me_3N^+$ cation shows a several times lower corrosion activity, while in the case of steel, the difference between the two ILs is insignificant.

The addition of stearic acid in a 0.5% amount to ILs results in a substantial decrease in the steel corrosion rate: by 80%–96% depending on the nature of the IL and temperature. Benzotriazole proved to be an efficient corrosion inhibitor for bronze, the corrosion rate being reduced by 45%–93%.[105]

The available published data provide the conclusion that the corrosive action of ILs with the $[Tf_2N]^-$ anion on stainless steels and aluminium is low.

The siloxane fluids (PDMS and PMPS) of high degree of purity have no corrosive action on the structural metals and alloys. However, the impurities present in these fluids can induce corrosion. For example, chlorides are corrosive for austenitic steels, sulfur compounds are detrimental to nickel and ammonia destroys copper alloys.

III.8. Radiation stability

Owing to the extremely low saturated vapour pressure, ILs can be considered as promising transfer fluids for the space industry. The radiation stability is a key parameter for this application. However, only few papers consider the radiation stability of the ILs.[106, 107] It was shown that the most extensively studied ILs are quite stable to γ-radiation. On exposure to ^{137}Cs radiation (1.175 MeV) in a dose of up to 1200 kGy, the amount of non-volatile radiolysis products accumulated in $[C_4HC_1Im][PF_6]$ and $[C_4HC_1Im][Tf_2N]$ is $\leqslant 1\%$. The ^1H and ^{19}F NMR spectra of samples after irradiation to the indicated dose exhibit unidentified signals of 0.5%–1.5% impurities. In addition, volatile and gaseous products are formed. The radiolysis of the cation is accompanied by dealkylation to give the corresponding alkyl radicals, the anion breaks to give the $F^{\bullet}$ (from the $[PF_6]^-$ anion) and $^{\bullet}CF_3$ (from $[(CF_3SO_2)_2N]^-$) radicals. The final decomposition products are water and some HF (in the case of $[PF_6]^-$). Also, coloured impurities are accumulated in the sample. The formation of coloured radiolysis products is especially characteristic of dialkylimidazolium ILs; in the case of dialkylpyrrolidinium ILs, this is observed to a lesser extent.[107] The viscosity of the $[C_4HC_1Im][Tf_2N]$ ionic liquid increases by 40% after irradiation to a 525 kGy dose.[106]

The change in the physicochemical properties of ILs during radiolysis can be regarded comparable with that for a solution of tri-n-butyl phosphate in dodecane, which is widely used in the nuclear fuel technology.[106]

The radiation stability of organosilicon compounds varies substantially depending on their composition and structure. Low-molecular-mass compounds with a high content of phenyl groups are most radiation-stable. For example, exposure of dimethylsiloxane oligomers and polymers to a dose of 100 kGy induces a substantial gelation, while methylphenylsiloxanes are still quite stable upon a dose of 1 MGy.[108]

The radiolysis of PDMS with an average molecular mass of ~80 000 induced by irradiation with electrons at a maximum energy of 800 keV in a nitrogen atmosphere was studied.[109,110] It was found that for absorbed doses of >25 kGy, traces of benzene-insoluble gel are formed. When the irradiation dose is 150 kGy, the yield of the gel is >80%. Apart from cross-linking processes, the formation of gaseous decomposition products takes place; among the products, hydrogen, methane and ethane were detected. An increase in the temperature of the irradiated sample results in higher yields of gaseous products (first of all, methane). The dependence of the degree of cross-linking on the temperature goes through a maximum at 100 °C. New functional groups formed in the polymer during cross-linking were identified by IR spectroscopy and from the results of chemical analysis of irradiated samples. It was shown that at low temperatures (−180 °C), cross-linking gives mainly $Si-CH_2-Si$ bridges and a lower content of $Si-CH_2-CH_2-Si$ bridges. As the temperature increases, the fraction of the $Si-CH_2-CH_2-Si$ moieties decreases and the formation of Si–Si bonds becomes possible.[109] The efficiency of various protective additives was studied for irradiation of PDMS under similar conditions.[110] During irradiation of the sample in an oxygen atmosphere under a pressure of up to 15 atm, the gelation decreased ~3-fold. No peroxides were detected. According to IR spectroscopy, the polymer methyl groups were oxidized to carboxyl groups, which prevented cross-linking. The addition of an antioxidant, ionol, exerts a commensurable effect only at very high concentrations (about 1 mol litre^{-1}). The formation of coloured products resulting from ionol addition to a gel-like polymer was detected; no such products were found in the non-cross-linked polymer after separation of the gel. Ionol is an efficient stabilizer for polymers even when present in very low concentrations but only if the reactions being inhibited follow a chain mechanism. Upon the addition of 10% of butanethiol, the minimum irradiation dose inducing gelation can be increased up to 300 kGy. In this case, the products of radiolysis are found to contain Si–H bonds.[110]

The effect of aromatic substituents on the radiation stability was studied in relation to the poly(dimethylsiloxane diphenylsiloxane) copolymers containing 5% and 25% of diphenylsiloxane units.[111] The samples were irradiated in air using a ^{60}Co source. The degree of compound modification on exposure to radiation was characterized by the viscosity ratio of non-irradiated and irradiated polymers. The dependence of this viscosity ratio on the absorbed dose proved to be almost linear. The radiation stability of the polymer depends also on the molecular mass. The dose corresponding to doubling of the viscosity is 220 kGy for PDMS with a molecular mass of 6400 and only 70 kGy for PDMS with a molecular mass of 30 000. Also, for comparison with polymers, radiolysis of the monomeric compound, hexamethyldisiloxane, was investigated. Only a slight viscosity change was found even after irradiation to a dose of 14 MGy.

The introduction of 5% diphenylsiloxane groups into the polymer backbone induces an increase in the doses that double the viscosity. For instance, this dose is 300 kGy for a 6800 molecular mass polymer and 100 kGy when the molecular mass is 30 000. If the fraction of diphenylsiloxane groups is increased to 25%, doubling of the viscosity of a 18 200 molecular mass sample occurs when the absorbed dose is 2.2 MGy. Relying on the obtained results and on calculation of the probability that sections comprising several dimethylsiloxane units are present in the polymer chain, the authors[111] deem that one diphenylsiloxane unit is able to protect the adjacent 5 or 6 dimethylsiloxane units from being cross-linked.

Among silicon compounds, aryl silicates possess fairly high radiation stability. For example, a study of tetrakis(2-biphenyloxy)silane on exposure to an electron beam with an energy of 1.5 MeV to a dose of 4 MGy showed only a little increase in the viscosity (from 66 to 75 cSt at 100 °C).[112]

III.9. Toxicity

The currently existing investigations concerning the toxicity of ILs are mainly aimed at evaluation of their environmental hazard, in particular, with respect to water. Therefore, a considerable part of the studies are devoted to the IL toxicity towards aquatic species, for example, daphnias. Also, a substantial part of works dealing with pharmacological and toxicological characteristics of the ILs are now carried out using cell cultures (as a rule, of malignant cells as they are capable of unlimited division). This data array is not considered in this review, as it is of little use for estimating the effect of ILs on a whole organism and for elucidating the hazard they present.

The research into the toxicity towards warm-blooded organisms aimed at predicting the industrial risks related to the use of ILs seems to attract less interest than the studies of environmental risks because ILs are traditionally ascribed to green chemistry. A favourable distinction of ILs from organic solvents is the lack of volatility, which by itself largely mitigates the industrial risks related to air pollution with vapours. The possibility of poisoning by inhalation may arise only in the case of formation of aerosols or volatile products of IL thermal decomposition. The protection of personnel being in contact with ILs to prevent the ILs from entering the body upon skin contact or upon swallowing is provided by routine safety measures usual for plants and laboratories.

The toxic action of ILs may be caused by the biological activities of the cations and anions forming the salts. The biological activity and toxicity of quaternary ammonium salts has been studied fairly comprehensively. First of all, the ganglion blocking effect should be noted. In particular, tetraethylammonium halides decrease the cardiac activity and the respiratory activity and cause a pupillary dilation and motor disturbances. The median lethal dose (LD_{50}), which kills half of the test animals, for tetraethylammonium chloride is 2630 mg kg^{-1} (rats, orally). The rate of compound administration into the body is significant. A slower administration decreases the toxicity. No noticeable chronic effects caused by sublethal doses were detected.[113]

Bis-quaternary ammonium salts also have a ganglion blocking effect and, hence, they are used as hypotensive and ganglion blocking drugs (pentamine, benzohexonium, pentolinium). For the latter compound, the LD_{50} value is 512 mg kg^{-1} (mice, orally)[114] and 890 mg kg^{-1} (rats, orally).[115]

The distribution and excretion kinetics of $[C_4HC_1Im]Cl$ were studied on mice and rats using radioactive labelling.[116] The administered substance in doses below 50 mg kg^{-1}

(LD_{50} = 550 mg kg^{-1}, mice, orally) was found to be rapidly and fully excreted by kidneys almost unmetabolized both upon oral and intravenous administrations. No marked effects upon repeated administration of the compound were detected either.

In the case of dermal administration (0.19 mg cm^{-2}), the amount of the absorbed compound substantially depends on the solvent. If IL is applied as a solution in DMF, the absorption is 12%, while in the case of aqueous solution, it is only 1.1%. The application in 1.9 mg cm^{-2} doses causes skin irritation. The use of even higher doses (2000 mg kg^{-1}; a mixture with water) also induces in rats only skin irritation rather than systemic poisoning. The dermal administration of the same amount of $[C_4HC_1Im]Cl$ mixed with DMF to mice resulted in a systemic toxic effect.[116]

Similar results were obtained in analogous experiments with *N*-n-butylpyridinium[117] and *N*-n-butyl-*N*-methylpyrrolidinium chlorides.[118] These compounds have somewhat higher bioavailability upon dermal administration than $[C_4HC_1$ Im]Cl. The effect of solvent nature on the penetration of ILs through skin is similar to that of $[C_4HC_1Im]Cl$. Upon repeated administration of $[C_4C_1Pyrr]Cl$ in a 50 mg kg^{-1} dose, the animals showed neither signs of poisoning no histologically detectable changes in the liver or kidneys.[118]

The effect of the alkyl radical length on the toxicity of imidazolium ionic liquids was studied in relation to diverse objects including malignant cell cultures, microorganisms, small aquatic species and snails. In all cases, the toxicity of ILs was found to increase with increase in the carbon chain length. Presumably, this is due to the increasing membranotoxic action on cells.[119] In mice experiments, it was shown that 1-methyl-3-n-octylimidazolium bromide has a clear-cut hepatotoxic action. Poisoning is accompanied by hepatomegaly and a change in the enzyme activity; the LD_{50} value is 35–52 mg kg^{-1} (mice).[120, 121] Thus, comparison of the toxicities of ILs with $[C_4HC_1Im]^+$ and $[C_8HC_1Im]^+$ cations shows that the carbon chain elongation leads to an increase in the metabolism : excretion ratio. This difference may be attributable, among other factors, to different activities of organic cation transporter proteins[117] towards cations with different lipophilicity.

III.9.a. Inorganic fluorine-containing anions

The toxicity of salts formed by inorganic fluorine-containing ions is moderate: the LD_{50} value is 1500 mg kg^{-1} for $NaPF_6$ (mice, orally)[122] and 550 mg kg^{-1} for $NaBF_4$ (rats, subcutaneously).[123] For the poorly soluble potassium tetrafluoroborate, the oral LD_{50} is much higher (5854 mg kg^{-1}, rats).[123]

Ionic liquids with these anions do not basically differ in toxicity from the halides. For $[C_4HC_1Im][PF_6]$, the LD_{50} value is 300–500 mg kg^{-1} (rats, orally) and >2000 mg kg^{-1} for dermal administration.[124] For 3-(n-hexyloxymethyl)-1-methylimidazolium tetrafluoroborate, the LD_{50} value is 1370–1400 mg kg^{-1} (rats, orally).[125]

III.9.b. Organic fluorine-containing anions

The salts of trifluoromethanesulfonic acid (triflates) have relatively low toxicity. The LD_{50} value reported for the sodium salt is ~2000 mg kg^{-1} (in relation to the triflate anion, mice, intravenously).[126]

The LD_{50} value of lithium bis(trifluoromethylsulfonyl)-imide (triflimide) is much lower (160 mg kg^{-1}, rats, orally);[127] however, in this case, lithium toxicity is also to be taken into account. Therefore, this value should not be treated as unambiguously characterizing triflimides as more toxic compounds. Meanwhile, in view of the ability of this anion to form hydrophobic salts, it cannot be ruled out, for example, that the anion interacts with charged sites of protein molecules, disrupting their conformations, and with cell membranes, which may be responsible for its enhanced toxicity in comparison with the smaller hydrophilic triflate ion.

Thus, ILs can be generally classified as moderately toxic compounds. Among the data integrated and considered in this review, there are no indications of cumulative effects, carcinogenic activity or mutagenicity of the IL.

The presented LD_{50} values are usual for many industrially important organic and inorganic compounds. Using reference data for comparing the toxicities of various classes of compounds and assessing the position of ILs among them, it is possible to compose a comparative table in which the compounds are arranged in the order of decreasing LD_{50} values, *i.e.*, increasing toxicity (Table 2).

In the case of dimethyl- and methylphenylsiloxane oligomers and polymers, no accurate LD_{50} values for warm-blooded organisms are reported in the literature, because in none of the experiments, was the lethal dose reached. Upon oral administration, PDMS is not metabolized and is rapidly excreted from the body unchanged. It does not cause skin irritation upon application onto the skin; however, in some cases, minor irritation of eye mucosa is detected.[131] It is noteworthy that the identified toxic action of organosiloxane polymers can be induced in some cases by impurities — unreacted monomers, solvents or polymerization initiators.

The toxicity of aryl silicates and other silicon compounds containing a Si–O–C group is caused almost in all cases by their hydrolysis and the toxicity of the resulting compounds.

Table 2. Comparative analysis of the toxicity for various compounds.

Compound	LD_{50} (orally) /mg kg^{-1}	Subject	Ref.
Ethanol	9000	rats	128
Sodium chloride	3700	"	129
Tetraethylammonium chloride	2630	"	113
Dowtherm A	2487	"	19
3-(n-Hexyloxymethyl)-1-methylimidazolium tetrafluoroborate	1370–1400	"	125
$[C_4HC_1Im]Cl$	550	mice	116
Pentolinium	512	"	114
	890	rats	115
Phenol	512	"	128
$[C_4HC_1Im][PF_6]$	300–500	"	124
Aspirin	200	"	128
Caffeine	192	"	128
As_2O_3	15	"	130

IV. Benefits and drawbacks of ionic liquids as heat transfer fluids

The physicochemical properties of ILs can vary over a very broad range, depending on the chemical nature of the cation and the anion. However, the nature of the anion has a much more pronounced effect than the nature of the cation. For example, combining some nitrogen-containing organic cations with anions such as $[Tf_2N]^-$, $[TfO]^-$ or $[PF_6]^-$ ensures rather high thermal stability and hydrophobicity of the compound. Ionic liquids with the $[(NC)_2N]^-$, NO_3^-, $[BF_4]^-$, Cl^- and SO_4^{2-} anions exhibit clear-cut hydrophilic properties. The introduction of $[(NC)_2N]^-$, $[Tf_2N]^-$ and $[BF_4]^-$ anions gives rise to organic salts with the lowest viscosity. Thus, by adjusting the anion–cation pair, one can optimize the IL properties for a particular application.

The thermal stability of ILs is the overall value determined by the type of the cation and the chemical nature of the anion. Most thermally stable are ILs with pyrrolidinium and imidazolium cations, while the pyridinium and acyclic tetraalkylammonium and -phosphonium derivatives are least stable. It follows from the available published data that the highest isothermal stability is inherent in the ILs with the $[PF_6]^-$ anion, although upon uniform heating (TGA), the highest thermal stability was found for ILs with the $[Tf_2N]^-$ anion.[72, 73]

While considering ILs as possible heat transfer fluids, one should bear in mind that their operating temperatures in a pure state are lower than those for methylphenylsiloxanes ($\sim$300 °C) and do not exceed 230–250 °C for the most thermally stable compounds.[73] However, for IL, as for most of the other modern heat transfer fluids, the operating temperature range can be substantially extended by introducing appropriate additives.

A principal specific feature of ILs, caused by the ionic nature of the liquid state, is exceptionally low saturated vapour pressure under normal conditions. This accounts for the non-volatility and explosion safety and for the lack of need to use personal protective equipment for respiratory protection when handling ionic liquids.

Currently, thermally stable polymers and ILs are the only classes of organic and heteroorganic compounds that have low saturated vapour pressures ($< 10^{-3}$ mm Hg) in the liquid state at temperatures above 200 °C. However, thermally and radiation stable polymers (silarylene – siloxanes and PMPS) have too high viscosity (> 1000 cSt at 25 °C), which is much higher than the maximum acceptable value for a heat transfer fluid. In the case of ILs, the viscosity depends appreciably on the nature of the anion. For example, the viscosity of imidazolium ILs with the $[PF_6]^-$ anion is almost an order of magnitude higher compared to the ILs with the $[Tf_2N]^-$ anion.

The type and degree of the corrosive action of ILs on metals and structural alloys is also dictated by the chemical nature of the anion. Among halogen-containing ILs, the lowest corrosion activity was found for compounds with the $[Tf_2N]^-$ anion. Metals and alloys that can be regarded as most stable in the IL medium include aluminium, steel and brass, while least stable are copper, iron and nickel. In the design of technological systems in which IL should contact with metal surfaces at high temperature for a long period of time, apart from the chemical nature of the IL itself and the type of structural alloy, other factors are to be taken into account. The presence of water and halide impurities in the IL and the presence of oxygen considerably enhance the corrosive action.

The development of new heat transfer fluids based on ILs comprises the search for ways of increasing the thermal stability and, in particular, operating temperature of ILs and minimizing the corrosive action on metals and structural alloys caused by their salt nature. A possible solution to these problems is the synthesis of hybrid organosilicon ILs by introducing various nitrogen-containing salt groups into low-molecular-mass organosiloxanes. On the one hand, this would reduce the saturated vapour pressure of the organosilicon compound down to values typical of ILs. On the other hand, one could expect a decrease in the viscosity and corrosive action of the hybrid IL on metals and possibly some increase in the thermal and radiation stability of ILs.

Currently, a considerable drawback of ILs as heat transfer fluids is their high cost due to both the absence of large-scale production and high cost of some reagents. The most expensive component of ILs that are suitable for this application is usually the anion. The source of the anion is most often a fluorine-containing organic or inorganic salt used in the exchange reactions. The minimum prices for alkali metal salts decrease in the series $[Tf_2N]^- > [TfO]^- > [PF_6]^- > [BF_4]^-$. The largest companies that currently manufacture ILs are IoLiTec, Merck, Cytec and BASF. The scope of applications of ionic liquids is extended from year to year, which results in higher demand and the necessity to optimize the methods of their synthesis. The industrial use of the microreactor technology and adjustment of processes for the ILs, which allows continuous synthesis, can be regarded as the achievement of the last five years. This may furnish up to 250 kg of high-quality ILs per week,[132] which actually corresponds to the capacity of a low-tonnage plant. The gradual decrease in the cost of ILs makes them more and more accessible for the use in industry, in particular, as heat transfer fluids. However, due to the high cost of the initial chemicals, this application would be economically feasible only provided that the waste ILs are regenerated and reused. Currently, the use of ILs is expedient only in those areas where physicochemical parameters rather than economic benefit play the crucial role.

* * *

The published data lead to the conclusion that substituted imidazolium and pyrrolidinium bis(trifluoromethylsulfonyl)imides are best suited as heat transfer fluids among the ILs studied. The thermophysical parameters of these ILs are quite similar to those of widely used organic and organosilicon heat transfer fluids. However, in view of the high cost of ILs and some specific characteristics (electrical conductivity and selective corrosion activity), it is inexpedient to consider ILs as general-purpose heat transfer fluids. An important feature that distinguishes ILs among other heat transfer fluids is the exceptionally low saturated vapour pressure at high temperature. This makes them non-volatile and non-explosive and especially attractive for operation under dynamic vacuum and perhaps in the outer space.

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