

Physicochemical Properties of Long Chain Alkylated Imidazolium Based Chloride and Bis(trifluoromethanesulfonyl)imide Ionic Liquids

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Supporting Information

ABSTRACT: In this research synthesis, purification and characterization of six long-chain imidazolium based ionic liquids (ILs) including C_{10} , C_{12} , and C_{14} alkyl chain with chloride and NTf₂ anions was investigated. All of these studied ILs were characterized using NMR, CHNSO, and DSC, and some impurities such as water, chloride, and metal contents were reported. The temperature dependence of some physicochemical properties such as density, dynamic and kinematic viscosity, refractive index, surface tension, and thermal stability of the synthesized ILs were also studied in the



range 283.15 to 363.15 K, and the results were compared with those from the literature. Moreover, using the measured data, the thermal expansion coefficient and molar polarizability of the ILs were calculated. On the other hand the effects of alkyl chain length and anion were explained. The results revealed that although the refractive indices and viscosities increased as alkyl chain length increased, the density and surface tension results were reciprocally decreased. Besides, the results suggest that the synthesized ILs were the best choice as fuel additives.

INTRODUCTION

Ionic liquids (ILs) are salts composed of large organic cations and anions (inorganic or organic) with melting point below 373.15 K.¹ They are highly promising materials that offer novel solutions to the chemical industry²⁻⁴ as well as to its customers.^{2,5}

As a consequence of the special characteristics (negligible vapor pressure, thermal stability, high ionic conductivity and mobility, and large electrochemical window),^{6–10} they are attractive for many promising applications and a wide variety fields of research and processes, such as extraction,¹¹ absorption,^{12,13} corrosion inhibitors,¹⁴ separations,^{15,16} and electrochemistry.^{17,18}...

A wide range of arrangements of cations and anions have been used to synthesize ionic liquids as more efficient materials for specific applications.^{19–21} Therefore, terms such as "designer" or "task-specific" solvents are often applied to ILs.²²

The physicochemical properties of ionic liquids depend on the nature and size of their cation and anion components.^{6,23,24} To gain insight into the nature of ionic liquids, a fundamental understanding must be established for their thermophysical and electrochemical properties.^{25,26}

Most of the experimental and modeling studies have been focused on the imidazolium based ILs.²⁷ Although synthesis of chloride and bis(trifluoromethanesulfonyl)imide based ionic liquids has been reported by many researchers, useful data on the physical and thermodynamic properties are limited. The lack of some properties reported in the literature for the studied ionic liquids and the disagreements in reports were the motives

for this work. Domańska and co-workers²⁸ reported 1-octanol/ water partition coefficients of 1-alkyl-3-methylimidazolium chloride where n = 4, 8, 10, and 12. The melting point, enthalpies of fusion, and phase transitions were stated in their paper, but density, viscosity, and other properties of 1-alkyl-3methylimidazolium chlorides such as n = 10, 12, and 14 are not reported.

One of the benefits of ionic liquids is that their properties can be tailored to a given application. Long alkyl chain imidazolium ILs have a high degree of self-organization, which increases with the increasing chain length. They display the behavior of both lyotropic and thermotropic crystals.^{29,30} Recently, the advantages of long hydrocarbon tails as amphiphilic head in the preparation of ordered self-organized structures have received further attention.³⁰⁻³³ In petroleum science long alkyl chain ionic liquids with surface active properties are used as surfactants in enhanced oil recovery.^{34–36} Besides, 1-decyl-3methylimidazolium tetrafluoroborate in oxidative desulfurization of diesel exhibited high catalytic activity for the removal of dibenzothiophene in diesel.³⁷ 1-Alkyl-3-methylimidazolium hydrogen sulfate (C6-C14) ILs are also applied as surfactants with catalytic activities, as the authors found that "the cocatalytic properties, both conversion and selectivity, of alkylimidazolium hydrogen sulfate ionic liquids noticeably depended on the alkyl chain lengths, and as a of consequence

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Table	1.	Reactants	and	Solvents'	Specifications	Used f	or S	ynthesis	of	Ionic	Liqu	ids
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Chemical Name	Source	Initial Mole Fraction Purity	Purification Method	Final Mole Fraction Purity	Analysis Method
Methylimidazole	Merck	≥0.990	Distillation	≥0.999	GC ^a
1-chlorodecane	Merck	≥0.980	Distillation	≥0.995	GC
1-chlorododecane	Merck	≥0.95	Distillation	≥0.992	GC
1-chlorotetradecane	Merck	≥0.950	Distillation	≥0.995	GC
Lithium bis(trifluoromethanesulfonyl)imide	Merck	≥0.980	none		alkalimetric after ionic exchange
Diethyl ether	Merck	≥0.999	none		GC
1-decyl-3-methylimidazolium chloride	Synthesized		Rotary/vacuum drying	>0.99	Karl Fischer titration, Potentiometry and ¹ H NMR
1-dodecyl-3-methylimidazolium chloride	Synthesized		Rotary/vacuum drying	>0.99	Karl Fischer titration, Potentiometry and ¹ H NMR
1-tetradecyl-3-methylimidazolium chloride	Synthesized		Rotary/vacuum drying	>0.99	Karl Fischer titration, Potentiometry and ¹ H NMR
1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	Synthesized		Rotary/vacuum drying	>0.99	Karl Fischer titration, Potentiometry and ¹ H NMR
1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	Synthesized		Rotary/vacuum drying	>0.99	Karl Fischer titration, Potentiometry and ¹ H NMR
1-tetradecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	Synthesized		Rotary/vacuum drying	>0.99	Karl Fischer titration, Potentiometry and ¹ H NMR
^a Gas–liquid chromatography.					

their properties".³⁸ Recently the application of 1-dodecyl-3methylimidazolium chloride in integral membrane proteome analysis was studied by Zhao et al.³⁹

Additionally, understanding of the structure and features of NTf₂ based ionic liquids is of great interest due to their exclusive physicochemical properties. The measurement of physicochemical properties such as density, viscosity, surface tension, and refractive index for 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides with n = 10, 12, and 14 in different temperature ranges was reported before.^{40–44} Herein the synthesis of these six ILs (1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and 1-alkyl-3-methylimidazolium chloride as n = 10, 12, and 14) is reported, and their properties were accurately measured at atmospheric pressure and temperature from 283.15 to 363.15 K.

This research work was conducted as a part of a Ph.D. project in which ionic liquids are synthesized, characterized, and used as fuel additives such as water in crude oil emulsion demulsifier, pour point depressant, and scavenger. Herein the physical and chemical properties of synthesized ionic liquids were investigated and the dependence of thermal properties on cation and anion structure was studied.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals and solvents used in this study were purchased from Merck. The chemicals' detailed specifications are given in Table 1.

Characterization of CHNSO of the samples was performed using a Vario max elemental analyzer from Elementar (Germany). ¹H, ¹³C, and ¹⁹F NMR spectroscopy was used to characterize the structure of ionic liquids with a Bruker Avance 500 spectrometer (Germany).

The density and viscosity of the ionic liquids were measured using an automated Anton Paar (Austria) SVM-3000 (Stabinger viscometer) digital double-tube viscodensimeter. The precision was better than $\pm 2 \times 10^{-4}$ g·cm⁻³ for the density and $\pm 1 \times 10^{-4}$ mPa·s for the viscosity with standard uncertainty of ± 0.01 K for temperature. The measurements were performed based on ASTM D7024 (Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)). Three milliliters of IL was poured into the measuring cell of the SVM-3000 viscodensimeter by syringe. The instrument displays density and dynamic and kinematic viscosity. Each measurement was repeated to establish a repeat precision.

The ring method was used to measure the surface tension of the ILs, with a KRUSS-K9 tensiometer (Germany). The equipment was calibrated using ultrapure water and acetone. The measurement cell was thermostated in a temperature controller with a temperature stability of ± 0.02 K, regulated in a RC6 LAUDA thermostat. Measurements were performed between temperatures of 283.15 to 363.15 K. The maximum experimental uncertainty was ± 0.1 mN·m⁻¹.

Refractive indices were determined using a Rudolph refractometer model J357 (USA). The apparatus was calibrated at different temperatures from 283.15 to 363.15 K.

An 851 Titrando, Karl Fischer apparatus supplied by Metrohm (Switzerland) was used to determine the water content in the synthesized samples.

The melting point was measured using a differential scanning calorimeter from PerkinElmer DSC 8000 (USA). Samples were enclosed in a sample pan and heated from room temperature to 423.15 K and then cooled to 173.15 K and heated again to 423.15 K with a scan rate of 10 K min⁻¹.

All the instruments were under manufacturer recommendations and calibrated periodically by the related certified reference material.

SYNTHESIS OF IONIC LIQUIDS

In this work six ionic liquids containing imidazolium cations were coupled with two anions chloride (Cl) and bis-(trifluoromethanesulfonyl)imide (NTf₂). Ionic liquids with chloride anion are hydrophilic, while NTf₂-based ionic liquids are immiscible with water.

Synthesis of halide salts: 1-alkyl-3-methylimidazolium chloride ILs were synthesized according to a similar procedure described in the literature.^{44,45} In a typical synthesis, a balloon containing 0.1 mol of methylimidazole was cooled in a silicone oil bath. 0.11 mol of 1-chloroalkane (chlorodecane, chlorodecane, chlorotetradecane) was added dropwise by syringe to methylimidazole under vigorous stirring. The mixture was

Scheme 1	1. Molecular	Structure,	Abbreviation,	Formula,	and	Molecular	: Weight	of S	Synthesized	Ionic	Liquids	
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Ionic Liquid	Cation structure	Anion structure	Abbreviation	Formula	Molecular weight
1-decyl-3- methylimidazolium chloride	C10H21	CI⁻	[C ₁₀ mim][Cl]	$C_{14}H_{27}ClN_2$	258.83
1-dodecyl-3- methylimidazolium chloride	C12H25	CI	[C ₁₂ mim][Cl]	$C_{16}H_{31}CIN_2$	286.88
1-tetradecyl-3- methylimidazolium chloride	C ₁₄ H ₂₉	CI	[C ₁₄ mim][Cl]	$C_{18}H_{35}ClN_2$	314.94
1-decyl-3- methylimidazolium bis(trifluoromethan esulfonyl)imide	~ C ₁₀ H ₂₁		[C ₁₀ mim][NTf ₂]	$C_{16}H_{27}F_6N_3O_4S_2\\$	503.52
1-dodecyl-3- methylimidazolium bis(trifluoromethan esulfonyl)imide	C ₁₂ H ₂₅	F F F F F	[C ₁₂ mim][NTf ₂]	$C_{18}H_{31}F_6N_3O_4S_2$	531.577
1–tetradecyl–3– methylimidazolium bis(trifluoromethan esulfonyl)imide	C14H29		[C ₁₄ mim][NTf ₂]	$C_{20}H_{35}F_6N_3O_4S_2$	559.63

heated to 343.15 K and stirred at this temperature for 72 h under nitrogen atmosphere. Finally the product was washed 3 times with diethyl ether to remove unreacted materials and dried at 333.15 K under vacuum.

Synthesis of NTf₂ salts: NTf₂ ionic liquids were synthesized in a two-step metathesis procedure. At ease with the hydrophobicity of NTf₂ ILs, the anion exchange part was carried out in the aquatic phase. The analogous chloride IL was dissolved in deionized water; in the other beaker LiNTf₂ was dissolved in deionized water. The solution of LiNTf₂ was slowly added to the IL solution. At the time a white emulsion was formed. After 15 min of stirring it was separated into two phases. A nonaqueous phase containing NTf₂ ionic liquid was separated and washed with water until the chloride anion was removed completely. Then it was dried at 333.15 K under vacuum.

The molecular structures of the cations and anions of the ILs are shown in Scheme 1. The confirmation of the formation of ionic liquids was carried out by elemental analysis (CHNOS) and NMR. The NMR spectra of synthesizes ILs are given in Figures S1-6 in the Supporting Information.

1-Decyl-3-methylimidazolium Chloride. ¹H NMR (D₂O, 300 MHz): δ 0.684 (t, 3H), 1.099 (d, 14H), 1.732 (d, 2H), 3.848 (s, 3H), 4.093 (q, 2H), 7.380 (d, 2H), 8.742 (s, 1H). ¹³C NMR (D₂O, 75 MHz): δ 13.69, 22.52, 26.02, 28.97, 29.27, 29.40, 29.52, 29.80, 35.81, 49.43, 122.5, 123.73, 136.20. C₁₄H₂₇ClN₂ (258.83): calculated C 65.0, H 10.5, N 10.8; found C 65.1, H 10.6, N 10.7.

1-Dodecyl-3-methylimidazolium Chloride. ¹H NMR (D₂O, 300 MHz): δ 0.690 (t, 3H) J= Hz, 1.133 (d, 18H), 1.740 (d, 2H), 3.83 (s, 3H), 4.117 (q, 2H), 3.372 (d, 2H), 8.726 (s, 1H). ¹³C NMR (D₂O, 75 MHz): δ 13.66, 22.51, 29.00, 29.33, 29.45, 29.64, 29.77, 31.80, 35.80, 49.40, 121.99,

123.68, 136.30. $C_{16}H_{31}ClN_2$ (286.88): calculated C 67.0, H 10.9, N 9.8; found C 67.2, H 11.2, N 9.6.

1-Tetradecyl-3-methylimidazolium Chloride. ¹H NMR (D₂O, 300 MHz): δ 0.697 (t, 3H) J= Hz, 1.124 (d, 22H), 1.739 (d, 2H), 3.894 (s, 3H), 4.123 (q, 2H), 7.326 (d, 2H), 8.647 (s, 1H). ¹³C NMR (D2O, 75 MHz): δ 14.095, 22.58, 29.16, 29.47, 29.64, 29.88, 35.87, 49.38, 121.99, 123.72, 136.197. C₁₈H₃₅ClN₂ (314.94): calculated C 68.6, H 11.2, N 8.9; found C 68.8, H 11.1, N 8.9.

1-Decyl-3-methylimidazolium Bis(trifluoromethane-sulfonyl)imide. ¹H NMR (CDCl₃, 300 MHz): δ 0.842 (t, 3H) J= Hz, 1.228 (d, 14H), 1.732 (d, 2H), 3.788 (s, 3H), 4.093 (q, 2H), 7.380 (d, 2H), 8.742 (s, 1H).¹³C NMR (CDCl₃, 75 MHz): δ 13.69, 22.57, 29.15, 29.215, 29.343, 29.581, 30.00, 36.09, 50.07, 117.62, 121.88, and 135.868, ¹⁹F NMR (D₂O, 300 MHz): δ – 79.218. C₁₆H₂₇F₆N₃O₄S₂ (503.52): calculated C 38.2, H 5.4, N 8.3, O 12.7, S 12.7; found C 38.5, H 5.6, N 8.2, O 12.9, S 12.6.

1-Dodecyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide. ¹H NMR (CDCl₃, 300 MHz): δ 0.873 (t, 3H) J= Hz, 1.250 (d, 18H), 1.826 (d, 2H), 3.929 (s, 3H), 4.149 (q, 2H), 7.321 (d, 2H), 8.707 (s, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 13.97, 22.96, 28.85, 29.28, 29.446, 29.561, 30.06, 36.27, 50.15, 117.64, 121.89, 123.79, and 135.745, ¹⁹F NMR (D₂O, 300 MHz): δ – 79.104. C₁₈H₃₁F₆N₃O₄S₂ (531.577): calculated C 40.7, H 5.9, N 7.9, O 12.0, S 12.1; found C 40.9, H 6.0, N 7.9, O 12.2, S 12.0.

1-Tetradecyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide. ¹H NMR (CDCl₃, 300 MHz): δ 0.852 (t, 3H) J= Hz, 1.231 (d, 22H), 1.744 (d, 2H), 3.902 (s, 3H), 4.103 (q, 2H), 7.325 (d, 2H), 8.698 (s, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 13.99, 22.96, 30.03, 30.61, 31.50, 31.87, 36.19, 50.09, 117.63, 121.88, and 135.97, ¹⁹F NMR (D₂O, 300 Table 2. Density (ρ), Dynamic Viscosity (η), Kinematic Viscosity (ν), Refractive Index (n_D), Surface Tension (σ), and Thermal Expansion (α_p) of [C_{10} mim][Cl], [C_{10} mim][NTf₂], [C_{12} mim][NTf₂], and [C_{14} mim][NTf₂] from 283.15 to 363.15 K at 101 kPa^a

T/K	$ ho/(extrm{g}\cdot extrm{cm}^{-3})$	$10^4 \ \alpha_p/{ m K}$	$\eta/(\mathrm{mPa}\cdot\mathrm{s})$	$ u/(\mathrm{mm}^2 \cdot \mathrm{s}^{-1}) $	n_D	$\sigma/({ m mN}{\cdot}{ m m}^{-1})$
[C ₁₀ mim][Cl]						
293.15					1.5002	
298.15	0.9840	6.13			1.4988	
303.15	0.9797	6.16			1.4972	34.0
313.15	0.9744	6.21	3716	3814	1.4937	30.2
323.15	0.9681	6.26	1613	1667	1.4897	28.4
333.15	0.9624	6.31	778.9	809.4	1.4864	27.8
343.15	0.9564	6.36	411.2	429.9	1.4834	27.0
353.15	0.9507	6.42	233.7	245.9	1.4806	26.2
363.15	0.9438	6.47	141.7	150.2	1.4788	25.5
[C ₁₀ mim][NTf ₂]						
273.15	1.2927	6.87				
289.15	1.2873	6.85				
293.15	1.2823	6.82	139.9	109.8	1.4366	_
298.15	1.2784	6.80	101.2	79.67	1.4351	29.8
303.15	1.2742	6.78	79.17	62.53	1.4336	29.2
313.15	1.2653	6.73	50.86	40.46	1.4306	28.3
323.15	1.2563	6.68	34.51	27.65	1.4278	27.5
333.15	1.2475	6.63	24.50	19.76	1.4250	26.9
343.15	1.2394	6.57	18.08	14.69	1.4222	26.3
353.15	1.2306	6.52	13.78	11.27	1.4194	25.7
363.15	1.2223	6.46	10.79	8.885	1.4166	25.2
[C ₁₂ mim][NTf ₂]						
293.15	1.2531	8.14			1.4385	
298.15	1.2480	8.01	130.5	105.2	1.4370	28.1
303.15	1.2420	7.88	101.1	81.77	1.4354	27.7
313.15	1.2322	7.62	63.54	51.90	1.4324	26.9
323.15	1.2241	7.35	42.41	34.87	1.4295	25.9
333.15	1.2160	7.07	29.67	24.55	1.4265	24.9
343.15	1.2081	6.79	21.63	18.02	1.4237	24.1
353.15	1.2000	6.50	16.31	13.68	1.4209	23.3
363.15	1.1918	6.21	12.65	10.69	1.4179	22.5
[C ₁₄ mim][NTf ₂]						
303.15	1.1971	7.32			1.4384	26.3
313.15	1.1876	7.31	83.54	70.80	1.4352	25.3
323.15	1.1800	7.29	54.36	46.37	1.4322	24.5
333.15	1.1713	7.28	37.21	31.97	1.4292	23.7
343.15	1.1631	7.26	26.58	23.00	1.4262	22.9
353.15	1.1546	7.25	19.68	17.16	1.4233	22.3
363.15	1.1465	7.23	15.04	13.20	1.4204	21.7
^{<i>a</i>} Standard uncertainties	u are u(T) = 0.1 K, u(T)	$P) = 5 \text{ kPa, } u(\rho) =$	$= 0.010 \text{ g} \cdot \text{cm}^{-3}, u(n)$	$\eta = 0.08 \ \eta, \ u(n_{\rm D}) = 0$.002, and $u(\sigma) =$	$= 0.4 \text{ mN} \cdot \text{m}^{-1}.$

MHz): δ – 79.178. C₂₀H₃₅F₆N₃O₄S₂ (559.630): calculated C 42.9, H 6.3, N 7.5, O 11.4, S 11.5; found C 43.1, H 6.5, N 7.4, O 12.5, S 11.9.

RESULTS AND DISCUSSION

Physicochemical Properties of Ionic Liquids. In order for a full presentation of the physicochemical properties of liquid state synthesized ILs, experimental density (ρ), dynamic viscosity (η), kinematic viscosity (ν), refractive index (n_D), surface tension (σ), and thermal expansion (α_p) data over a range of 283.15 to 363.15 K were obtained as summarized in Table 2. It was noted that [C_{10} mim][Cl], [C_{10} mim][NTf₂], and [C_{12} mim][NTf₂] were room temperature ILs and [C_{14} mim][NTf₂] had a melting point about 307 K. On the other hand [C_{12} mim][Cl] and [C_{14} mim][Cl] were solid at temperatures lower than 369 and 332.15 K, respectively. Therefore, all studies were performed on $[C_{10}mim][Cl]$, $[C_{10}mim][NTf_2]$, $[C_{12}mim][NTf_2]$, and $[C_{14}mim][NTf_2]$.

From the results it is observed that ρ , σ , η , and n_D data fit in eqs 1 and 2 with different values of correlation parameters which were found by fitting to the experimental data as listed in Table 3. An exponential model for the temperature dependence of viscosity was first proposed by Reynolds in 1886. Fortunately, a good correlation between experimental data and the suggested equations (eqs 1 and 2) resulted from calculated R^2 as given in Table 3.

$$y(\rho, \sigma, or n_D) = a_0 + a_1 T (K) + a_2 T^2 (K^2)$$
 (1)

$$\ln \eta \, (\text{mPa} \cdot \text{s or mm}^2 \cdot \text{s}^{-1}) = a_0 / T \, (\text{K}) + a_1 \tag{2}$$

Table 3. Evaluated Correlation Parameters of the Density, Viscosity, Refractive Index, and Surface Tension of $[C_{10}mim][C1]$, $[C_{10}mim][NTf_2]$, $[C_{12}mim][NTf_2]$, and $[C_{14}mim][NTf_2]$ from eqs 1 and 2

Physical property	a_0	a_1	<i>a</i> ₂	R^2
[C ₁₀ mim][Cl]				
$ ho/(extrm{g}\cdot extrm{cm}^{-3})$	1.1571	0.0006	-6.00×10^{-8}	0.9991
$\eta/(\text{mPa}\cdot\text{s})$	7421.5	-15.555		0.9995
$ u/(\mathrm{mm}^2 \cdot \mathrm{s}^{-1}) $	7350.1	-15.302		0.9974
n _D	1.7027	-0.001	1.00×10^{-6}	0.9983
$\sigma/(\mathrm{mN}\cdot\mathrm{m}^{-1})$	334.59	-1.7190	0.0024	0.9632
$[C_{10}mim][NTf_2]$				
$ ho/(extrm{g}\cdot extrm{cm}^{-3})$	1.6008	-0.0009	6.00×10^{-7}	0.9998
$\eta/(\text{mPa}\cdot\text{s})$	3852	-8.3106		0.9951
$ u/(\mathrm{mm}^2\cdot\mathrm{s}^{-1}) $	3779.1	-8.3056		0.9948
n _D	1.5382	-0.0004	2.00×10^{-7}	0.9999
$\sigma/(\mathrm{mN}~\mathrm{m}^{-1})$	97.428	-0.3570	0.0004	0.9987
$[C_{12}mim][NTf_2]$				
$ ho/(extrm{g}\cdot extrm{cm}^{-3})$	1.7418	-0.0011	2.00×10^{-6}	0.9992
$\eta/(\text{mPa}\cdot\text{s})$	3892.6	-8.2452		0.9969
$ u/(\mathrm{mm}^2\cdot\mathrm{s}^{-1}) $	3816.2	-8.2046		0.9968
n _D	1.5388	-0.0004	2.00×10^{-7}	0.9999
$\sigma/(\text{mN m}^{-1})$	65.406	-0.1556	0.0001	0.9990
[C ₁₄ mim][NTf <u>2]</u>				
$ ho/(extrm{g}\cdot extrm{cm}^{-3})$	1.4946	-0.0009	4.00×10^{-7}	0.9997
$\eta/(\text{mPa}\cdot\text{s})$	3896.4	-8.0508		0.9982
$ u/(\mathrm{mm}^2 \cdot \mathrm{s}^{-1}) $	3815.7	-7.9597		0.9981
n _D	1.5269	-0.0003	6.00×10^{-8}	0.9996
$\sigma/({ m mN}{\cdot}{ m m}^{-1})$	88.773	-0.3144	0.0004	0.9997

DIFFERENTIAL SCANNING CALORIMETRY

The melting points $T_{\rm m}$, for $[C_n {\rm mim}][{\rm Cl}]$ and $[C_n {\rm mim}][{\rm NTf}_2]$ $(n = 10, 12, {\rm and } 14)$, which were determined by differential scanning calorimetry are presented in Table 4, and DSC curves are given in Figure S7. Also the data from the literature are tabulated. The melting process results in an endothermic peak in the DSC curve.

Table 4. Phase Transition Temperatures of the Ionic Liquids at 101 kPa^{*a*}

$[C_n \min]$	[Cl]	$[NTf_2]$
n	$T_{\rm m}$ (K)	<i>T</i> _m (K)
10	302.11	276.19
	311.2 ⁵⁰	244.15 ⁵¹
		277.33 ⁵²
12	369.37	295.65
	369.78 ⁵³	292.4 ⁵⁴
	369.8 ⁵⁵	
14	467.20	307.5
		316.25 ⁵⁶
		308.77 ⁵²
^a Standard uncertainties	s u are $u(T) = 0.5$ K and	u(P) = 5 kPa.

Ionic liquids have melting points below 373 K. The diversity of anions and cations of ILs in size and interaction leads to different accumulation of ions. The melting point is a function of the molecular packing. The van der Waals interactions have a slight effect on the melting point.⁴⁶ In NTf₂ ionic liquids compared with chloride ILs, the ions are poorly coordinated, because of the bigger size and low symmetry. $[C_nmim][C1]$ ILs are more symmetric than NTf₂ based ILs and have a smaller

number of conformations of the cation—anion pairs. That is why they can organize more regularly ordered ionic networks with higher melting points.⁴⁷ On the other hand the lower melting point of the NTf₂ salt could be ascribed to the anion's inability in hydrogen bonding and electron delocalization.⁴⁸ Conversely, even in water free conditions the strong ability of hydrogen bonding of chloride leads to connecting cations and anions to form a hydrogen-bonded network in 1,3-dialkylimidazolium halides.⁴⁹

DENSITY AND THERMAL EXPANSION

The density experimental results are presented in Tables 2 and 3. They are also shown in graphical form in Figure 1a, along with comparisons with other experimental data sets taken from the literature (Figure 1b, c).

For $[C_{10}mim][Cl]$ and $[C_nmim][NTf_2]$ (n = 10, 12, and 14), densities were measured as a function of temperature over a range of melting points to 363.15 K in 10 K increments. The densities of the studied ILs decrease with increasing temperature, but at a rate less than that of organic solvents. In contrast with other ILs, the density of $[C_{10}mim][Cl]$ is lower than that of water at room temperature (0.982 g·cm⁻³) and similarly decreases with increasing temperature.

For all 1-alkyl-3-methylimidazolium salts, the density decreases as n is increased because addition of CH₂ to the alkyl chain on the cation decreases the density since the CH₂ group is less dense than the imidazolium ring.⁴⁹ Also increasing the volume occupied by aliphatic carbon chains leads to greater separation in polar and nonpolar regions.^{57,58} Interionic separation between the polar domains (cationic heads and anions) and nonpolar domains (aliphatic chains) results in the lower packing efficiency, which finally results in lower density.^{59,60} In this study, the halide salt has significantly lower density than the NTf₂ ILs with the same cation (0.9840



Figure 1. Comparison of the density data of (a) $[C_{10}mim][Cl]$ (blue triangles), $[C_{10}mim][NTf_2]$ (green triangles), $[C_{12}mim][NTf_2]$ (magenta triangles), and $[C_{14}mim][NTf_2]$ (red triangles) in this work. (b) $[C_{10}mim][NTf_2]$ in this work (green triangles), $[C_{10}mim][NTf_2]$ in Tome et al. (\times),⁶⁵ Jacquemin et al. (\diamond),⁶⁶ Tariq et al. (\bigcirc),⁴² Nann et al. (\bigstar),⁶⁷ Oliveira et al. (\blacksquare),⁶⁸ (c) $[C_{12}mim][NTf_2]$ in this work (magenta triangles), $[C_{12}mim][NTf_2]$ in this work (magenta triangles), $[C_{12}mim][NTf_2]$ in Tariq et al.⁴¹ (\triangle), Domanska et al.⁶⁹ (blue triangles), Santos et al.⁶⁴ (orange triangles), $[C_{14}mim][NTf_2]$ in this work (red triangles), $[C_{14}mim][NTf_2]$ in Tariq et al. (-).⁴²



Figure 2. (a) Plot of $\ln \eta$ as a function of temperature $[C_{10}mim][Cl]$ (blue triangles), $[C_{10}mim][NTf_2]$ (green triangles), $[C_{12}mim][NTf_2]$ (magenta triangles), and $[C_{14}mim][NTf_2]$ (red triangles) in this work. (b) Dependence of viscosity on alkyl chain length in NTf_2 ILs at 313.15 K for $[C_6mim][NTf_2]$,^{40,73} $[C_8mim][NTf_2]$,^{40,74} $[C_{10}mim][NTf_2]$, $[C_{12}mim][NTf_2]$, and $[C_{14}mim][NTf_2]$.

and 1.2784 g·cm⁻³, respectively). The density increases with increasing molecular weight of the anion. Here the molecular weights of the Cl and NTf₂ are 35.5 and 280.1 g/mol, respectively. Similar behavior was observed for different anions such as BF₄⁻ and PF₆⁻ with the same cation and alkyl chain in the ILs structure as documented in the literature.⁶¹⁻⁶³

It is necessary to say that some impurities, especially water and chloride ion, significantly affect volumetric and transport properties such as density and dynamic viscosity. As shown in Figure 1 for the synthesized $[C_{10}\text{mim}][\text{NTf}_2]$ and $[C_{12}\text{mim}]$ - $[\text{NTf}_2]$, deviations with the literature were less than 0.2% except for Santos et al.,⁶⁴ while in the case of $[C_{14}\text{mim}][\text{NTf}_2]$ the deviations with Tariq et al.⁴² was 1.1% through all the investigated temperature range. Although further purifications were carried out to achieve a chloride content less than 10 mg· kg⁻¹, however, an average deviation of 1% was observed due to the hygroscopic nature of these materials.

The coefficients of thermal expansion for the studied ILs are defined by the following equation.

$$\alpha_p = (-1/\rho)(\partial \rho/\partial T) \tag{3}$$

where α_p is the thermal expansion coefficient, ρ is density (g· cm⁻³), and *T* is temperature (K). The thermal expansion coefficients for each of the ILs at the measured temperatures are summarized in Table 2 and shown in Figure S8.

The values of the isobaric thermal expansion coefficient for $[C_{10}\text{mim}][\text{Cl}]$, $[C_{10}\text{mim}][\text{NTf}_2]$, and $[C_{12}\text{mim}][\text{NTf}_2]$ are 6.13, 6.80, and 8.14 × 10⁻⁴ g·cm⁻³ K⁻¹ and that for $[C_{14}\text{mim}][\text{NTf}_2]$ in 303.15 K is 7.32 × 10⁻⁴ g·cm⁻³ K⁻¹.

DYNAMIC AND KINEMATIC VISCOSITY

The influence of temperature on dynamic viscosity for $[C_{10}\text{mim}][Cl]$ and $[C_n\text{mim}][NTf_2]$ is tabulated in Table 2 and shown in Figure 2. Also the kinematic viscosity as a function of temperature is presented in Table 2 and Figure S9. In all samples the ILs viscosity tends to decrease as temperature increases. For $[C_n\text{mim}][NTf_2]$ ionic liquids, there is an increase in viscosity as cation size gets bulkier. Higher viscosities are due



Figure 3. Temperature dependence of the viscosity of (a) $[C_{10}\text{mim}][\text{NTf}_2]$ in this work (green triangles), Ahosseini et al. (\bigcirc),⁴³ Tariq et al. (-),⁴⁰ Fitchett et al. (\times),⁷¹ McHale et al. (\blacksquare).⁷² (b) $[C_{12}\text{mim}][\text{NTf}_2]$ in this work (magenta triangles), Tariq et al. (-),⁴⁰ Domanska et al.⁶⁸ (blue circles). (c) $[C_{14}\text{mim}][\text{NTf}_2]$ in this work (red triangles), Tariq et al. (-).⁴⁰



Figure 4. Temperature dependence of the refractive index of (a) $[C_{10}mim][Cl]$ (blue triangles), $[C_{10}mim][NTf_2]$ (green triangles), $[C_{12}mim][NTf_2]$ (green triangles), and $[C_{14}mim][NTf_2]$ (red triangles) in this work. (b) $[C_{10}mim][NTf_2]$ (green triangles), $[C_{12}mim][NTf_2]$ (magenta triangles), and $[C_{14}mim][NTf_2]$ (red triangles) in this work, $[C_{10}mim][NTf_2]$ (O) $[C_{12}mim][NTf_2]$ (×), and $[C_{14}mim][NTf_2]$ (•) Tariq et al.,⁴¹ and $[C_{10}mim][NTf_2]$ Lago et al.⁷⁷ (green circles), Branco et al. (black circles).⁷⁸

to increased van der Waals interaction between the alkyl chains. An almost linear descending (with the slope of 5.4 mPa·s per *n*) dependence of η as a function of the alkyl group length is observed for $[C_n \min][NTf_2]$, n = 6-14 (Figure 2b). The symmetry and molar mass of the anions have a strong influence on the viscosity of imidazolium based ionic liquids. Low symmetry NTf₂ anion can decrease the van der Waals forces between the cations and anions of ILs. The viscosity of the $[C_{10}mim]$ ILs increases with increasing the rigidity and the symmetry of the anion. The chloride-based ILs have a smaller number of conformations of the anion and of the cation-anion pairs because of the symmetry. Therefore, they can organize more regular ordered ionic networks.⁴⁷ Unfortunately a systematic study about most impurities was not performed by Tarig et al., but the water and chloride content of ILs was reported as major contamination. The experimental values for water and chloride were 70 mg·kg⁻¹ and 20-50 mg·kg⁻¹, respectively. These impurities have an inverse effect on viscosity values. The presence of water caused the viscosity values to decrease, while chloride has a positive effect, as previously reported by Seddon and other researchers. This is one of the reasons that our results are nearly lower than what is obtained by Tariq et al.⁴¹

Also the bulkier side chains reduce the rotational freedom of molecules, which leads to high viscosities for long alkyl chain ILs. These results suggest a complex relationship, as Watanabe and co-workers stated; differences observed in the transport properties may be due to different levels of "ionicity" (association/disassociation) that they explained from diffusion and ionic conductivity data. A high level of dissociation may result in a decrease of the free volume.⁷⁰ That is why $[C_{10}\text{mim}][Cl]$ was a highly viscous ionic liquid up to 353.15 K as stated in Table 2 and as it is heated the viscosity reduces more intensely compared with the other three. The viscosity is greater than that of most organic solvents and even greater than that of glycerin. Figure 2a shows a relationship between $\text{Ln } \eta$ and 1/T for all studied ILs. It was found that $[C_{10}\text{mim}][Cl]$ exhibited a slope of two times greater than that of the corresponding cation with NTf₂ anion.

Several measuring methods have been used earlier to determine the viscosity of $[C_n \text{mim}][\text{NTf}_2]$: concentric cylinders viscometry,⁴⁰ capillary tube,⁷¹ moving piston,^{43,72} and Stabinger⁴⁰ methods have been reported in the literature. The experimental data obtained from our studies by the Stabinger method for $[C_{10}\text{mim}][\text{NTf}_2]$, $[C_{12}\text{mim}][\text{NTf}_2]$, and $[C_{14}\text{mim}][\text{NTf}_2]$ were also compared with the literature as given in Figure 3. The results were adequately in agreement with previous reported works (Figure 3a, b, and c), so that their deviations were less than 1.0%. Obviously this was due to their impurities and differences in choice of measuring methods.

REFRACTIVE INDEX

The refractive index (n_D) of a material is a dimensionless number that describes how light propagates through that medium. It can be used as a measure of the electronic polarizability of a molecule and can provide useful information when studying the forces between molecules or their behavior in solution.^{75,76}

The refractive index measurement data for the ILs are given in Table 2 and they also are presented in Figure 4 along with

Article



Figure 5. Surface tension as a function of temperature (a) $[C_{10}\text{mim}][Cl]$ (blue triangles), $[C_{10}\text{mim}][NTf_2]$ (green triangles), $[C_{12}\text{mim}][NTf_2]$ (magenta triangles), and $[C_{14}\text{mim}][NTf_2]$ (red triangles) in this work. (b) $[C_{10}\text{mim}][NTf_2]$ in this work (green triangles), $[C_{10}\text{mim}][NTf_2]$ Tariq et al. (\Box) ,⁴⁴ $[C_{10}\text{mim}][NTf_2]$ Kolbeck et al. (\bullet) ,⁷⁹ (c) $[C_{12}\text{mim}][NTf_2]$ in this work (magenta triangles), $[C_{14}\text{mim}][NTf_2]$ Kolbeck et al. (\bullet) ,⁷⁹ (d) $[C_{14}\text{mim}][NTf_2]$ in this work (red triangles), $[C_{14}\text{mim}][NTf_2]$ $[C_{10}\text{mim}][NTf_2]$ Tariq et al. (\diamond) ,⁴¹

data from the literature. In all of the studied ILs and the whole studied temperature range the refractive index is higher than 1.41 which is above the range of most common organic materials. Such materials with a high refractive index are required for antireflective coating and photonic devices. It can be observed that the refractive index (n_D) of the ILs can be ordered as $[C_{10}mim][NTf_2] < [C_{12}mim][NTf_2] < [C_{14}mim][NTf_2] < [C_{10}mim][Cl]$. Refractive index increases with increasing alkyl chain length because of the increasing electronic polarizability of the molecule, which results in variation of intermolecular interactions.

For a comparison of the refractive index of the ILs, only for $[C_{10}mim][NTf_2]$, $[C_{12}mim][NTf_2]$ and $[C_{14}mim][NTf_2]$ data are presented by Tariq et al.⁴¹ who studied in 4 temperatures (293.15, 283.15, 313.15, and 333.15 K) by standard Abbe refractometry. The data for $[C_{10}mim][NTf_2]$ are in a good correlation with Tariq et al. The impurities such as water and chloride are different in the samples that is why the data for $[C_{12}mim][NTf_2]$ investigated within this work is about 0.7% higher than Tariq et al. and for $[C_{14}mim][NTf_2]$ it is 0.4% lower. To best of our knowledge, only one single point at 293.15 K was found by Sigma-Aldrich company (USA) for refractive index of $[C_{10}mim][Cl]$ with a purity grade of 0.960. The related experimental value was reported 1.501 with a relative deviation of <0.051% in comparison with our studies.

The molar polarizability (R_m) was calculated from molar volume (V_m) and refractive index (n_D) experimental data using the Lorentz-Lorenz relation eq 4.

$$R_m = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) V_m \tag{4}$$

where V_m is the molar volume (cm³·mol⁻¹). The calculated R_m and V_m values of the ILs are presented in Table S1 in the Supporting Information along with molar free volume (f_m).

Molar free volume (f_m) is the unoccupied fraction of the molar volume of an IL, which can be predicted by eq 5.

$$f_m = V_m - R_m \tag{5}$$

Molar free volumes are related to the solubilities of different types of solutes in the ILs. 41

SURFACE PROPERTIES

Surface tension of ILs was measured by the ring method as a function of temperature from 283.15 to 363.15 K. Experiments were performed in a homemade heating system. The cell containing 10 mL of sample was placed in a water circulating heating system. Temperature was stable (better than 1 K) which was monitored with an alumel-chromel thermocouple.

The surface tension measurement data are presented in Table 2, and the plots of σ vs temperature are shown in Figure 5. In general, with increases in temperature surface tension decreases because cohesive forces decrease with an increase of molecular thermal activity. The measured data present surface tension values well above those of conventional organic solvents, but still lower than the surface tension of water (72.86 mN m⁻¹). In NTf₂ ILs, the surface tension decreases with a rise in temperature, almost linearly. [C₁₀mim][Cl], with

Tab	le 5.	Impurities	of	the	Synt	thesized	Ionic	Liquids

Species	[C ₁₀ mim][Cl]	[C ₁₂ mim][Cl]	[C ₁₄ mim][Cl]	$[C_{10}mim][NTf_2]$	$[C_{12}mim][NTf_2]$	$[C_{14}mim][NTf_2]$
Water content ^{<i>a</i>} , $mg \cdot kg^{-1}$	117	184	119	260	249	230
Chloride ^b , mg·kg ⁻¹	137200	123700	112700	<10	<10	<10
Bromide ^b , mg·kg ⁻¹	<10	<10	<10	<10	<10	<10
Sulfate ^c , mg·kg ⁻¹	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Heavy metals ^{c} (as Pb), mg·kg ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ash content ^d , mass %	< 0.001	<0.001	<0.001	<0.001	<0.001	< 0.001

^{*a*}The water content results are obtained by Karl Fischer titration after the drying treatment described in the Experimental Section. ^{*b*}Test method = potentiometry. ^{*c*}Test method = turbidimetry. ^{*d*}Test method = electric furnace and gravimetry.

a high viscosity, has a lower surface tension than that of water. Different types of arrangements of ions at the surface of liquid, such as the ratio of the polar to nonpolar moieties of the ionic liquids changing by chain length increasing, result in reduction in surface tension. The major source of error in the measurement of surface tension of ILs is the water content and other impurities, which is normally reduced to a large extent prior to experimental session by mild heating under vacuum. Figure 5 also shows the data from Tariq et al.,⁴² Kolbeck et al.,⁷⁹ Carvalho et al.⁴⁴ They used the pendant drop shape method for measurements.

The fact that the surface tension is a property sensitive to the presence of small amounts of impurities and measurement method explains the differences between the literature and our measurements. In the case of $[C_{10}mim][NTf_2]$, Carvalho et al.⁴⁴ measurements are 2.4 mN m⁻¹ mean higher than that of our study and those of Tariq et al.⁴² and Kolbeck et al.⁷⁹

It must be noted that impurities can have dramatic effects on the chemistry and physical properties of the ionic liquids. In the synthesis of ILs the impurities either need to be eliminated completely during synthesis or a material with a clearly defined amount of impurities needs to be investigated. So that the impurities should be prevented or removed as far as possible during the preparation of the ionic liquid.

The level of the main impurities in the ionic liquids is summarized in Table 5.

CONCLUSION

In this work synthesis of six imidazolium based ionic liquids containing $[C_n \text{mim}][\text{Cl}]$ and $[C_n \text{mim}][\text{NTf}_2]$ (n = 10, 12, and 14) was reported. As $[C_{12}\text{mim}][\text{Cl}]$ and $[C_{14}\text{mim}][\text{Cl}]$ are solid, other ILs were characterized in the range 283.15 to 363.15 K. The effect of temperature on physicochemical properties, density and thermal expansion, refractive index dynamic and kinematic viscosity, and surface properties at atmospheric pressure was investigated. Also the alkyl chain and anion effect on them was discussed.

The refractive index and viscosity of the studied ionic liquids increases with the increase of the alkyl chain length, whereas the densities show the opposite trend. An increase in the alkyl chain length of the imidazolium cation produces a decrease in the surface tension of the ionic liquid.

The densities of $[C_{10}\text{mim}][\text{Cl}]$ and $[C_{10}\text{mim}][\text{NTf}_2]$ in 298.15 K are 0.9840 and 1.2784 m³·kg⁻¹, respectively. Because the higher the molecular weight of the anion, the greater the density.

Viscosity decreases with decreasing symmetry of the anion can reduce the van der Waals forces between cations and anions of ILs, which explains the dramatic difference between the viscosities of $[C_{10}\text{mim}][\text{Cl}]$ and $[C_{10}\text{mim}][\text{NTf}_2]$ (3716 and 50.864 mPa·s in 313.15 K, respectively). The density and

refractive index data were used to calculate the molar refraction of the ionic liquids using Lorentz–Lorenz equations.

The experimental data of each were correlated with the expected equation, and the parameters were calculated. Reported values from data available in the literature were compared with the measured data. Deviations between reported values from different researchers are mostly a consequence of both the presence of impurities and poor temperature control. The stated information can be used for theoretical and experimental studies with considering the impurities and their quantity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00242.

NMR spectra (Figures S1–6) and DSC curve (Figure S7), thermal expansion coefficient (α_p) (Figure S8), kinematic viscosity (ν) (Figure S9), molar polarizability (R_m) , molar volume (V_m) , and molar free volume (f_m) (Table S1) as a function of temperature (PDF)

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Notes

The authors declare no competing financial interest.

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