

Densities, Viscosities, and Refractive Indices of 1-Hexyl-3-propanenitrile Imidazolium Ionic Liquids Incorporated with Sulfonate-Based Anions

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 Supporting Information

ABSTRACT: A new series of nitrile-functionalized room-temperature ionic liquids (RTILs), incorporating different anions, namely, dioctylsulfosuccinate, dodecylsulfate, benzenesulfonate, sulfobenzoate, and trifluoromethanesulfonate, have been prepared and characterized using FTIR-ATR, ¹H NMR, and elemental analysis. Their physical properties such as density, viscosity, refractive index, and thermal stability were measured and reported for a temperature range from (293.15 to 353.15) K at atmospheric pressure.

INTRODUCTION

In the recent years, ionic liquids (ILs) have attracted increasing attention and intensive investigation and witnessed a steady growth from the academics to industry due to their distinctive properties.^{1,2} ILs are organic salts with organic cations and inorganic or organic anions having melting points less than 100 °C and negligible vapor pressure.^{3,4} They often exhibit many unique advantages compared with conventional organic solvents, such as wide temperature range of application, high thermal stability, nonflammability, wide electrochemical window, high electrical conductivity, and highly favorable solubility of molecules (polar or nonpolar organic and inorganic compounds).^{5,6} These typical properties of ILs open up possible applications as solvents for reactions, absorption media for gas separation, heat transfer fluids, separating agents in extractive and azeotropic distillation, biomass processing fluids, working fluids in a variety of electrochemical applications (batteries, capacitors, solar cells, etc.), and also as lubricants.^{2,7,8} One of the most attractive features of these ILs is that they can be easily prepared for any specific application either by careful selection of the cation or anion or both,⁹ or by attaching new functional groups, such as amine, amide, nitrile,¹⁰ sulfonic acid, fluoros chains,¹¹ ether, alcohol,¹² carboxylic, and thiols,¹³ to the structure to impart the desired properties or reactivities.¹⁴ This ability results in an increasing number of applications.¹⁵ The ILs incorporated with functional groups are called task-specific or functionalized ILs. These relatively new type of ILs possess some distinctive features due to the presence of functional groups which are not present in the common ILs.¹⁶

Knowledge and understanding of the properties of ILs is indispensable for choosing a suitable liquid for each envisaged application. The physical properties such as density and viscosity are essential for the design of process equipment. Moreover, complete data sets are required for the validation and improvement of the property prediction methods, which can be applied for molecular simulation as well as design and development of the commercial process.¹⁷ Many researchers have synthesized

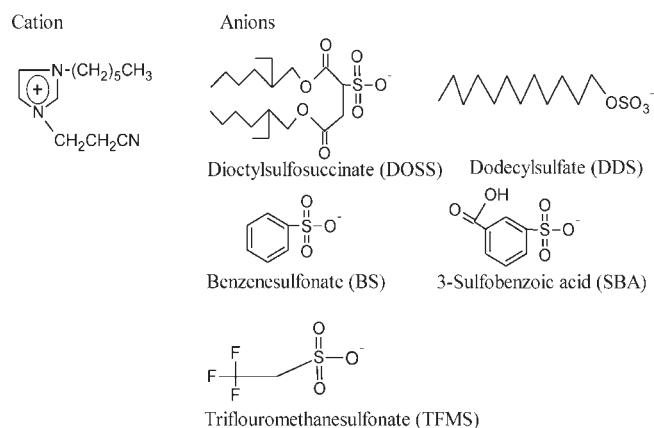


Figure 1. Structures of the cation and anions used in the present work.

and studied the physicochemical properties of 1-alkyl nitrile-3-methylimidazolium-based ILs incorporating chloride anions,^{18,19} but the physicochemical properties of 1-hexyl-3-propanenitrileimidazolium ILs incorporating anions such as dioctylsulfosuccinate (DOSS), dodecylsulfate (DDS), benzenesulfonate (BS), sulfobenzoate (SBA), and trifluoromethanesulfonate (TFMS) have not been studied yet. In continuance of our previous studies on the synthesis, characterization, and physicochemical properties measurements of novel ILs,^{18–20} the present work is proposed to synthesize a series of new nitrile-functionalized ILs incorporating different anions (Figure 1) and to measure their physicochemical properties. A series of 1-hexyl-3-propanenitrileimidazolium ILs (namely, 1-hexyl-3-propanenitrileimidazolium dioctylsulfosuccinate [C_2CNHim]DOSS, 1-hexyl-3-propanenitrileimidazolium dodecylsulfate [C_2CNHim]DDS, 1-hexyl-3-propanenitrileimidazolium benzenesulfonate [C_2CNHim]BS, 1-hexyl-3-propanenitrileimidazolium

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Table 1. Molecular Weight (mol wt.), Mass Fraction of Water ($w_{\text{H}_2\text{O}}$), Mass Fraction of Bromide (w_{Br}), Start Temperatures (T_s), and Decomposition Temperatures (T_d)

	[CNC ₂ Him]DOSS	[CNC ₂ Him]DDS	[CNC ₂ Him]BS	[CNC ₂ Him]SBA	[CNC ₂ Him]TFMS
mol wt. (g·mol ⁻¹)	628.88	472.70	364.48	408.49	355.38
$w_{\text{H}_2\text{O}}$ (10 ⁶ w)	219	198	206	235	243
w_{Br} (10 ⁶ w)	69	83	52	74	91
T_s /K	536	498	544	541	493
T_d /K	566	528	581	575	521

Table 2. Experimental Density, ρ , Values for [CNC₂Him]-Based Ionic Liquids As a Function of Temperature

T /K	ρ /(g·cm ⁻³)				
	[CNC ₂ Him]DOSS	[CNC ₂ Him]DDS	[CNC ₂ Him]BS	[CNC ₂ Him]SBA	[CNC ₂ Him]TFMS
293.15	1.0927	1.1011	1.2260	1.2481	1.2896
298.15	1.0890	1.0978	1.2227	1.2446	1.2857
303.15	1.0854	1.0945	1.2194	1.2412	1.2819
308.15	1.0818	1.0912	1.2161	1.2380	1.2783
313.15	1.0783	1.0880	1.2128	1.2347	1.2746
318.15	1.0748	1.0847	1.2096	1.2315	1.2710
323.15	1.0713	1.0815	1.2063	1.2282	1.2674
328.15	1.0679	1.0783	1.2030	1.2250	1.2638
333.15	1.0644	1.0751	1.1997	1.2218	1.2602
338.15	1.0610	1.0719	1.1965	1.2186	1.2566
343.15	1.0576	1.0688	1.1933	1.2154	1.2531
348.15	1.0542	1.0656	1.1901	1.2121	1.2492
353.15	1.0507	1.0626	1.1878	1.2089	1.2458

sulfobenzoate [C₂CNHim]SBA, and 1-hexyl-3-propanenitrileimidazolium trifluoromethanesulfonate [C₂CNHim]TFMS) were synthesized, and their densities and dynamic viscosities were measured at atmospheric pressure within a temperatures range of (293.15 to 353.15) K while their refractive indices were measured at a temperatures range of (293.15 to 333.15) K. The thermal expansion coefficients of the present ILs were calculated from the measured density as a function of temperature.

EXPERIMENTAL SECTION

Materials. The ILs used in the present study were synthesized using chemicals of analytical grade. The CAS number, source, and grades of the chemicals used are as follows: imidazole (288-32-4, Aldrich 99 %), acetone (67-64-1, Sigma-Aldrich 99.8 %), acrylonitrile (107-13-1, Aldrich 99 %), anhydrous methanol (67-56-1, Sigma-Aldrich 99.8 %), 1-bromohexane (111-15-1, Aldrich 99 %), anhydrous ethylacetate (141-78-6, Sigma-Aldrich 99.8 %), sodium dioctylsulfosuccinate (209-406-4, Aldrich 98 %), sodium dodecylsulfate (205-788-1, Sigma-Aldrich 99 %), sodium benzenesulfonate (515-42-4, Aldrich 97 %), sodium 3-sulfobenzoate (17625-03-5, Aldrich 97 %), sodium trifluoromethanesulfonate (2926-30-9, Aldrich 98 %), and diethyl ether (60-29-7, Sigma-Aldrich 99 %). All the chemicals were used without further purification.

Synthesis of Ionic Liquids. The syntheses of the ILs used in the present study were based on a metathesis reaction of 1-hexyl-3-propanenitrile imidazolium bromide ([C₂CNHim]Br) and alkali metal salts with different anions. [C₂CNHim]Br was synthesized by direct reaction of imidazole with acrylonitrile in methanol, and the product was then reacted with 1-bromohexane. The product

was washed with ethyl acetate, and the purification was accomplished using the standard procedure.²⁰

1-Hexyl-3-propanenitrile imidazolium dioctylsulfosuccinate [C₂CNHim]DOSS was synthesized by mixing [C₂CNHim]Br (0.03 mol) and sodium dioctylsulfosuccinate (0.03 mol) in 50 mL of acetone. The mixture was stirred at room temperature (25 °C) for 48 h, and then the solid precipitate was separated, and the solvent was removed under vacuum. The resulting pale yellow viscous compound was cooled to room temperature and washed with ethyl acetate and diethyl ether, and the remaining solvent was removed under vacuum at 80 °C for 48 h.

For the synthesis of 1-hexyl-3-propanenitrileimidazolium dodecylsulfate [C₂CNHim]DDS, [C₂CNHim]Br (0.04 mol) and sodium dodecylsulfate C₁₂H₂₅OSO₃Na (0.04 mol) were mixed in 40 mL of deionized water (60 °C). The mixture was stirred at room temperature for 48 h. The excess water was slowly removed under vacuum at 80 °C, and then 50 mL of CH₂Cl₂ was added to the precipitate and then filtered. The viscous extract was repetitively washed with deionized water until it was bromide-free. The remaining solvent was removed under vacuum at 80 °C for 48 h.

Instead of sodium dodecylsulfate (0.04 mol), sodium benzenesulfonate (0.04 mol), sodium 3-sulfobenzoate (0.04 mol), and sodium trifluoromethanesulfonate (0.04 mol) were used to synthesize 1-hexyl-3-propanenitrileimidazolium benzenesulfonate [C₂CNHim]BS, 1-hexyl-3-propanenitrileimidazolium sulfobenzoate [C₂CNHim]SBA, and 1-hexyl-3-propanenitrileimidazolium trifluoromethanesulfonate [C₂CNHim]TFMS, respectively, and a similar procedure was adopted.

Characterization and Properties Measurements. The instruments used for the measurements of the physical properties of the present synthesized ILs were calibrated using ultrapure Millipore quality water and validated with ILs of established

Table 3. Experimental Viscosity, η , Values for [CNC₂Him]-Based Ionic Liquids As a Function of Temperature

T/K	η /(mPa·s)				
	[CNC ₂ Him]DOSS	[CNC ₂ Him]DDS	[CNC ₂ Him]BS	[CNC ₂ Him]SBA	[CNC ₂ Him]TFMS
293.15	--	--	7079.4	19212.0	2243.6
298.15	19896.3	13769.7	4268.1	11463.0	1469.7
303.15	12117.4	8252.7	2865.6	7578.3	991.9
308.15	7571.4	5185.2	1795.1	4765.8	648.5
313.15	4586.7	3354.6	1170.4	3001.1	437.8
318.15	2939.5	2051.0	781.3	1953.3	301.9
323.15	1947.7	1301.8	537.6	1189.9	214.0
328.15	1264.7	846.3	359.9	830.5	155.1
333.15	848.3	566.9	274.2	557.3	102.7
338.15	579.4	390.1	181.0	352.1	77.4
343.15	411.4	274.9	133.6	225.5	54.8
348.15	278.6	189.5	94.6	133.6	40.1
353.15	191.2	133.6	70.0	92.8	29.4

Table 4. Experimental Refractive Index, n_D , Values for [CNC₂Him]-Based Ionic Liquids As a Function of Temperature

T/K	n_D				
	[CNC ₂ Him]DOSS	[CNC ₂ Him]DDS	[CNC ₂ Him]BS	[CNC ₂ Him]SBA	[CNC ₂ Him]TFMS
298.15	1.47970	1.48409	1.52700	1.52295	1.52975
303.15	1.47841	1.48269	1.52610	1.52221	1.52891
308.15	1.47709	1.48125	1.52499	1.52146	1.52774
313.15	1.47580	1.47991	1.52382	1.52029	1.52683
318.15	1.47447	1.47863	1.52266	1.51936	1.52590
323.15	1.47305	1.47702	1.52145	1.51800	1.52464
328.15	1.47171	1.47566	1.52025	1.51666	1.52334
333.15	1.47029	1.47422	1.51899	1.51502	1.52226

properties. The data established by our research group for the ILs 1-butyl-3-propanenitrileimidazolium bromide [C₂CNBim]Br, 1-butyl-

pyridinium bis(trifluoromethylsulfonyl) imide [C₄py][Tf₂N]ⁿ and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide [C₆Mim]Tf₂N were used for the validation of the reproducibility of the instruments.^{20–22}

FTIR-ATR, NMR, and Elemental Analysis. The present synthesized ILs were characterized using Fourier transformation infrared (FTIR) spectra. The spectra were recorded in a Shimadzu FTIR-8400S Fourier Transform Infrared Spectrometer (FTIR) in the mid region [(4000 to 400) cm⁻¹] using the Attenuated Total Reflectance (MIRacle ATR) measurement mode. A CHNS-932 (LECO instruments) elemental analyzer was used to determine the individual percentage of elements. A Bruker Avance 300 spectrophotometer was used to determine the ¹H NMR spectra of the present ILs. The estimated purities of the present synthesized ionic liquids, namely, [CNC₂Him]DOSS; [CNC₂Him]DDS; [CNC₂Him]BS; [CNC₂Him]SBA, and [CNC₂Him]TFMS, are 96.8 %, 97.0 %, 97.2 %, 96.7 %, and 96.4 %, respectively.

Water and Bromide Content. A coulometric Karl Fischer titrator (DL 39 Mettler Toledo) with CombiCoulomat fritless Karl Fischer reagent (Merck)^{20,21} was used to determine the water content of the ILs. The measurement for each IL was made in triplicate, and the average values are reported.

Bromide content measurements were conducted by ion chromatography (Metrohm model 761 Compact IC) with

(150 × 4.0) mm analytical column (Metrosep A Supp 5-150) and (5.0 × 4.0) mm guard column (Metrosep A Supp 4/5).²¹ The measurements were analyzed using Metrodata IC Net 2.3 software.

Thermogravimetry Measurements. The start and onset temperatures of the present synthesized ILs were determined using Perkin-Elmer, Pyris V-3.81. The samples were placed in aluminum pans under nitrogen atmosphere at a heating rate of 10 °C·min⁻¹. The estimated water and bromide content, the start temperature (T_g), and the decomposition temperature (T_d) are presented in Table 1.

Densities and Viscosities Measurements. Density and viscosity of all ionic liquids were measured in a temperature range (293.15 to 353.15) K at atmospheric pressure using a Stabinger viscometer (Anton-Paar model SVM3000).^{20,21} The temperature was controlled to within ± 0.01 °C. The repeatability of measurements were ± 5 · 10⁻⁴ g·cm⁻³ and 0.75 % for density and viscosity, respectively.^{20,21} The standard calibration fluid provided by the supplier was used for the calibration of the viscometer followed by the validation of the measurements using ionic liquids with known densities and viscosities.^{20,22} The measured densities and viscosities are presented in Table 2 and Table 3, respectively.

Refractive Indices Measurements. An ATAGO programmable digital refractometer (RX-5000 alpha) with a measuring accuracy of ± 4 · 10⁻⁵ was used to measure the refractive index of various ILs in a temperature range of (298.15 to 333.15) K. The

Table 5. Fitting Parameters of Equation 1 for the Density of the ILs

Ionic liquid	A_0	$A_1 \cdot 10^4$	$SD \cdot 10^4$
[CNC ₂ Him]DOSS	1.296715	-6.97	1.44
[CNC ₂ Him]DDS	1.289327	-6.43	1.46
[CNC ₂ Him]BS	1.415283	-6.46	2.87
[CNC ₂ Him]SBA	1.438327	-6.50	1.14
[CNC ₂ Him]TFMS	1.502418	-7.27	1.30

Table 6. Fitting Parameters of Equation 2 for the Refractive Index of the ILs

ionic liquid	A_2	$A_3 \cdot 10^4$	$SD \cdot 10^4$
[CNC ₂ Him]DOSS	1.559855	-2.69	1.30
[CNC ₂ Him]DDS	1.568024	-2.81	1.55
[CNC ₂ Him]BS	1.596133	-2.31	1.19
[CNC ₂ Him]SBA	1.590568	-2.25	3.34
[CNC ₂ Him]TFMS	1.594194	-2.16	2.16

Table 7. Fitting Parameters of Equation 3 for the Viscosity of the ILs

ionic liquid	A_4	$A_5 \cdot 10^{-3}$	$SD \cdot 10^2$
[CNC ₂ Him]DOSS	-8.60621	3.84509	0.83
[CNC ₂ Him]DDS	-8.83420	3.86561	1.11
[CNC ₂ Him]BS	-7.93228	3.44860	1.32
[CNC ₂ Him]SBA	-9.22432	3.97177	3.47
[CNC ₂ Him]TFMS	-7.72063	3.24659	0.75

temperature was controlled with an accuracy of ± 0.05 °C. The apparatus was calibrated and checked before each series of measurements using pure organic solvents (methanol, ethylacetate) with known refractive indices.^{20,21} Dried samples (water contents are given in Table 1) kept in desiccators were directly placed into the measuring cell, and the measurements were made in triplicate. The average values are reported in Table 4.

RESULTS AND DISCUSSIONS

Figure 1 shows the structure of the cation and anions used. The FTIR spectra (Figure 1 in Supporting Information) of the present ILs show the characteristic absorption bands of the nitrile group in the range (2248 to 2256) cm^{-1} for C=N at (1560 to 1665) cm^{-1} and exhibit C-H bond at (3080 to 3145) cm^{-1} , and a weaker C-H bonds stretches from (2854 to 2933) cm^{-1} , which are similar to that reported for other nitrile-functionalized ILs.¹⁸⁻²⁰ In addition, these ILs show a S-O stretching band in the range (1181 to 1195) cm^{-1} and the strong peak at 1730 cm^{-1} for the [CNC₂Him]DOSS, which is due to the presence of the C=O group in the dioctylsulfosuccinate anion.

The results of ¹H NMR and elemental analysis of the ionic liquids are as follows:

[CNC₂Him]DOSS: ¹H NMR 300 MHz, D₂O; δ 0.88 (t, 15H), 1.28 (br, 20H), 1.59 (m, 4H), 1.92 (m, 2H), 2.30 (m, 4H), 3.17 (m, 2H), 4.01 (t, 2H), 4.16 (t, 2H), 4.25 (t, 2H), 4.71 (m, 1H), 7.30 (s, 1H), 7.80 (s, 1H), 9.63 (s, 1H).

Analysis (% calculated): C 61.03 (61.12), H 9.41 (9.30), N 6.52 (6.68), S 5.13 (5.10).

[CNC₂Him]DDS: ¹H NMR 300 MHz, D₂O; δ 0.87 (t, 6H), 1.30 (br, 20H), 1.81 (br, 4H), 1.93 (m, 2H), 3.18 (t, 2H), 4.19 (t, 2H), 4.63 (m, 2H), 7.51 (t, 2H), 7.75 (t, 2H), 9.20 (s, 2H), 9.92 (s, 1H).

Analysis (% calculated): C 61.09 (60.98), H 9.92 (9.81), N 8.81 (8.89), S 6.73 (6.78).

[CNC₂Him]BS: ¹H NMR 300 MHz, D₂O; δ 0.81 (t, 3H), 1.26 (m, 6H), 1.84 (m, 2H), 3.15 (t, 2H), 4.19 (t, 2H), 4.56 (t, 2H), 7.50 (d, 3H), 7.57 (s, 1H), 7.61 (s, 1H), 7.75 (s, 1H), 8.96 (d, 2H).

Analysis (% calculated): C 51.35 (59.31), H 7.14 (7.19), N 11.57 (11.53), S 8.72 (8.80).

[CNC₂Him]SBA: ¹H NMR 300 MHz, D₂O; δ 0.77 (t, 3H), 1.21 (m, 6H), 1.80, (m, 2H), 3.13 (t, 2H), 4.16 (t, 2H), 4.53 (t, 2H), 7.53 (s, 1H), 7.59 (s, 1H), 7.96 (d, 2H), 8.06 (s, 1H), 8.27 (d, 2H), 9.93 (s, 1H).

Analysis (% calculated): C 55.93 (55.86), H 6.45 (6.42), N 10.35 (10.29), S 7.89 (7.85).

[CNC₂Him]TFMS: ¹H NMR 300 MHz, D₂O; δ 0.81 (t, 3H), 1.26 (m, 2H), 1.84 (m, 6H), 3.14 (t, 2H), 4.21 (t, 2H), 4.55 (t, 2H), 7.56 (s, 1H), 7.60 (s, 1H), 7.92 (s, 1H).

Analysis (% calculated): C 43.98 (43.94), H 5.78 (5.67), N 11.70 (11.82), S 9.13 (9.02).

The thermal stability of the present ILs is reported as the start and decomposition temperatures. The decomposition temperature depends on alkyl chain of the cation and mainly on the type of the anion.²¹ The thermogravimetric results show that the present ILs exhibited short-term thermal stability up to 536 K at a scan rate of 10 °C·min⁻¹, except for [CNC₂Him]DDS and [CNC₂Him]TFMS up to (498 and 493) K, respectively (Table 1).

The density of the ILs (Table 2) shows a linear decrease with increasing temperature. It was found that the densities of the present ILs are higher when paired with the trifluoromethanesulfonate anion followed by sulfobenzoic acid, benzenesulfonate, and then by dodecylsulfate anion. The lowest densities were observed with the dioctylsulfosuccinate anion. These results showed that an increase in the anion molecular weight does not directly correspond to the rise in the density values for the present ILs, and a similar behavior for other imidazolium-based ILs was observed by Sánchez et al.¹⁷ and Gardaset al.²³ The measured densities of the present ILs incorporating the anions DOSS, DDS, BS, SBA, and TFMS at 298.15 K are (1.0890, 1.0978, 1.2227, 1.2446, and 1.2857) $\text{g} \cdot \text{cm}^{-3}$, respectively. The present ILs showed lower densities compared to other nitrile-functionalized ILs reported by Zhang et al.¹⁹ (the densities of [C₃CNMim]BF₄ and [C₃CNMim]NTf₂ are (1.319 and 1.519) $\text{g} \cdot \text{cm}^{-3}$) and Zhao et al.¹⁸ (the densities of [C₂CNMim]BF₄, [C₃CNMim]BF₄, and [C₄CNMim]Cl are (2.15, 1.87, and 1.61) $\text{g} \cdot \text{cm}^{-3}$, respectively). The lower density of these ILs might be due to the presence of a long alkyl chain compared to the other nitrile-functionalized ILs.²⁰

The measured viscosities are higher for the IL with DOSS anion, while it was the lowest for the IL with TFMS anion. The viscosities of [CNC₂Him]DOSS and [CNC₂Him]TFMS at 298.15 K are (19896.3 and 4268.1) mPa·s, respectively. As can be observed, a rise in temperature caused a significant reduction in the viscosities of the present synthesized ILs. However, as can be seen in Table 3, the viscosity values of the ILs show functional group and alkyl chain length dependency.²⁴ An addition of functional group or increasing alkyl chain length has been found to give higher viscosity values. The viscosity values of the present ionic liquids are much higher compared with the reported similar nitrile-functionalized ILs. For [C₂CNMim]BF₄, [C₃CNMim]BF₄, and [C₄CNMim]Cl the

Table 8. Thermal Expansion Coefficients α_p for [CNC₂Him]-Based Ionic Liquids

T/K	$\alpha_p \cdot 10^4 / (\text{K}^{-1})$				
	[CNC ₂ Him]DOSS	[CNC ₂ Him]DDS	[CNC ₂ Him]BS	[CNC ₂ Him]SBA	[CNC ₂ Him]TFMS
293.15	6.41	5.67	5.21	5.31	5.81
298.15	6.43	5.68	5.22	5.32	5.83
303.15	6.45	5.70	5.24	5.34	5.84
308.15	6.48	5.71	5.25	5.35	5.86
313.15	6.50	5.73	5.26	5.36	5.88
318.15	6.52	5.75	5.28	5.38	5.89
323.15	6.54	5.76	5.29	5.39	5.91
328.15	6.56	5.78	5.31	5.41	5.93
333.15	6.58	5.80	5.32	5.42	5.95
338.15	6.60	5.81	5.33	5.44	5.97
343.15	6.63	5.83	5.35	5.45	5.98
348.15	6.65	5.85	5.36	5.47	6.00
353.15	6.67	5.87	5.38	5.48	6.02

viscosities are (65.5, 352, and 5222) mPa·s, respectively.^{18,19} Furthermore, the present ILs except [C₂CNHim]DOSS show lower viscosities than the similar ILs with bromide anion (for [C₂CNHim]Br at 303.15 K is 15893.0 mPa·s).²⁰

The measured data of the refractive indices of the ILs [C₂CNHim]DOSS, [C₂CNHim]DDS, [C₂CNHim]BS, [C₂CNHim]SBA, and [C₂CNHimM]TFMS are presented in Table 4. The refractive index values of the present ionic liquids are in good agreement with that reported by Zhang et al.¹⁹ for other nitrile-functionalized ILs; for [C₃CNMMim]N(CN)₂, [C₃CNMMim]N(CN)₂, and [C₃CNPy]N(CN)₂, the refractive indices are 1.5258, 1.5255, and 1.5453, respectively. Moreover, the present ILs show similar refractive index values as compared with similar nitrile ILs incorporating the bromide anion.²⁰ As can be seen in Table 4, the functional group and alkyl chain length attached to the anion have a large effect on the refractive index values, and also the refractive indices decrease linearly with increasing temperature.

The measured densities, viscosities, and refractive indices were correlated as a function of temperature T using the following form of equations^{20,25}

$$\rho / (\text{g} \cdot \text{cm}^{-3}) = A_0 + A_1 T \quad (1)$$

$$n_D = A_2 + A_3 T \quad (2)$$

$$\log \eta / (\text{mPa} \cdot \text{s}) = A_4 + A_5 / T \quad (3)$$

The coefficients A_0 , A_1 , A_2 , A_3 , A_4 , and A_5 are estimated using the method of least-squares and are listed in Tables 5, 6, and 7, respectively, together with the standard deviations (SD) calculated as follows^{20,21}

$$\text{SD} = \sqrt{\frac{\sum_j^{n_{\text{DAT}}} (z_{\text{exp}} - z_{\text{cal}})^2}{n_{\text{DAT}}}} \quad (4)$$

where z_{exp} and z_{cal} are the experimental and calculated values (using eqs 1, 2, and 3), respectively, and n_{DAT} is the number of experimental points.

The changes in the liquid volume with temperature were evaluated using the thermal expansion coefficient. Since the

densities of the present ILs decrease linearly with temperature, the coefficients of volume expansion at constant pressure were easily obtained from linear fits of the density data using the following equation^{20,21}

$$\begin{aligned} \alpha_p / (\text{K}^{-1}) &= -(1/\rho) \cdot (\partial \rho / \partial T)_p \\ &= -(A_1)(A_0 + A_1 T) \end{aligned} \quad (5)$$

where α_p is the thermal expansion coefficient in K^{-1} . A_0 and A_1 are the fitting parameters of eq 1. The variation of the volumetric expansion with temperature shows that ILs have less expansion capacity than regular organic solvents.²⁴ The thermal expansion coefficients of the present ILs vary between $(5.21 \cdot 10^{-4}$ and $6.67 \cdot 10^{-4}) \text{K}^{-1}$, which is lower than that for traditional organic solvents. The calculated expansivities are similar to those reported for [C₂CNBim]Br, [C₂CNHim]Br, [C₂CNOim]Br, and [C₂CNDim]Br, which are in the range of $(5.09$ to $6.36) \cdot 10^{-4} \text{K}^{-1}$.²⁰ Similar ranges of thermal expansion coefficients have been earlier reported for the imidazolium-, pyridinium-, phosphonium-, and ammonium-based ILs, $(5.0$ to $6.5) \cdot 10^{-4} \text{K}^{-1}$.²⁵ As can be seen in Table 8, the thermal expansion coefficients of this series of ILs increases with increasing alkyl chain length of the anion with the exception of the TFMS anion.

CONCLUSION

A series of new nitrile-functionalized ILs incorporating different anions were synthesized, and their properties, namely, density, dynamic viscosity, and refractive index, were measured. Furthermore thermogravimetry measurements show that the present ILs feature higher thermal stability than their pure counterparts incorporating bromide anion. Density and refractive index show linear behavior with temperature. Empirical correlations (eqs 1, 2, and 3) were proposed to represent the present experimental results. Finally, these ILs show weak temperature dependency for the thermal expansion coefficient.

ASSOCIATED CONTENT

S Supporting Information. Additional figure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Pereira, A. B.; Veiga, H. I. M.; Esperança, J.; Rodríguez, A. Effect of temperature on the physical properties of two ionic liquids. *J. Chem. Thermodyn.* **2009**, *41* (12), 1419–1423.
- (2) Saha, S.; Hamaguchi, H. Effect of water on the molecular structure and arrangement of nitrile-functionalized ionic liquids. *J. Phys. Chem. B* **2006**, *110* (6), 2777–2781.
- (3) Earle, M. J.; Seddon, K. R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391–1398.
- (4) Newington, I.; Perez-Arlandis, J. M.; Welton, T. Ionic liquids as Designer Solvents for Nucleophilic Aromatic Substitutions. *Org. Lett.* **2007**, *9*, 5247–5250.
- (5) Freire, M. G.; Carvalho, P. J.; Fernandes, A. M.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Surface tensions of imidazolium based ionic liquids: Anion, cation, temperature and water effect. *J. Colloid Interface Sci.* **2007**, *314*, 621–630.
- (6) Chiappe, C.; Pieraccini, D. Kinetic Study of the Addition of Trihalides to Unsaturated Compounds in Ionic Liquids. Evidence of a Remarkable Solvent Effect in the Reaction of ICl_2^- . *J. Org. Chem.* **2004**, *69*, 6059–6064.
- (7) Vila, J.; Ginés, P.; Pico, J. M.; Franjo, C.; Jiménez, E.; Varela, L. M.; Cabeza, O. Temperature dependence of the electrical conductivity in EMIM based ionic liquids. Evidence of Vogel-Tamman-Fulcher behavior. *Fluid Phase Equilib.* **2006**, *242*, 141–146.
- (8) Ye, C.; Liu, W.; Chen, Y.; Yu, L. Room-temperature ionic liquids: a novel versatile lubricant. *Chem. Commun.* **2001**, *21*, 2244–2245.
- (9) Torrecilla, J. S.; Palomar, J.; Garcá, J. n.; Rodríguez, F. Effect of Cationic and Anionic Chain Lengths on Volumetric, Transport, and Surface Properties of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids at (298.15 and 313.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1297–1301.
- (10) Zhang, S.; Chen, Y.; Li, F.; Lu, X.; Dai, W.; Mori, R. Fixation and conversion of CO₂ using ionic liquids. *Catal. Today* **2006**, *115*, 61–69.
- (11) Liu, X.-M.; Song, Z.-X.; Wang, H.-J. Density Functional Theory Study on the $-\text{SO}_3\text{H}$ Functionalized Acidic Ionic Liquids. *Struct. Chem.* **2009**, *20*, 509–515.
- (12) Fei, Z.; Ang, W. H.; Zhao, D.; Scopelliti, R.; Zvereva, E. E.; Katsyuba, S. A.; Dyson, P. J. Revisiting Ether-Derivatized Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 10095–10108.
- (13) Nockemann, P.; Thijs, B.; Parac-Vogt, T. N.; Hecke, K. V.; Meervelt, L. V.; Tinant, B.; Hartenbach, I.; Schleid, T.; Ngan, V. T.; Nguyen, M. T.; Binnemans, K. Carboxyl-Functionalized Task-Specific Ionic Liquids for Solubilizing Metal Oxides. *Inorg. Chem.* **2008**, *47*, 9987–9999.
- (14) Davis, J. H. Task-Specific Ionic Liquids. *Chem. Lett.* **2004**, *33*, 1072–1077.
- (15) Mazille, F.; Fei, Z.; Kuang, D.; Zhao, D.; Zakeeruddin, S. M.; Grätzel, M.; Dyson, P. J. Influence of Ionic Liquids Bearing Functional Groups in Dye-Sensitized Solar Cells. *Inorg. Chem.* **2006**, *45*, 1585–1590.
- (16) Fei, Z.; Zhao, D.; Pieraccini, D.; Ang, W. H.; Geldbach, T. J.; Scopelliti, R.; Chiappe, C.; Dyson, P. J. Development of Nitrile-Functionalized Ionic Liquids for C-C Coupling Reactions: Implication of Carbene and Nanoparticle Catalysts. *Organometallics* **2007**, *26* (7), 1588–1598.
- (17) Sanchez, L. G.; Espel, J. R.; Onink, F.; Meindersma, G. W.; Haan, A. B. Density, viscosity, and surface tension of synthesis grade imidazolium, pyridinium, and pyrrolidinium based room temperature ionic liquids. *J. Chem. Eng. Data* **2009**, *54* (10), 2803–2812.
- (18) Zhao, D.; Fei, Z.; Scopelliti, R.; Dyson, P. J. Synthesis and Characterization of Ionic Liquids Incorporating the Nitrile Functionality. *Inorg. Chem.* **2004**, *43*, 2197–2205.
- (19) Zhang, Q.; Li, Z.; Zhang, J.; Zhang, S.; Zhu, L.; Yang, J.; Zhang, X.; Deng, Y. Physicochemical Properties of Nitrile-Functionalized Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 2864–2872.
- (20) Ziyada, A. K.; Wilfred, C. D.; Bustam, M. A.; Man, Z.; Murugesan, T. Thermophysical Properties of 1-Propyrronitrile-3-alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K. *J. Chem. Eng. Data* **2010**, *55*, 3886–3890.
- (21) Yunus, N. M.; Mutalib, M. I. A.; Man, Z.; Bustam, M. A.; Murugesan, T. Thermophysical properties of 1-alkylpyridinium bis-(trifluoromethylsulfonyl)imide ionic liquids. *J. Chem. Thermodyn.* **2010**, *42*, 491–495.
- (22) Muhammad, A.; Mutalib, M. I. A.; Wilfred, C. D.; Murugesan, T.; Shafeeq, A. Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions. *J. Chem. Thermodyn.* **2008**, *40*, 1433–1438.
- (23) Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. High-pressure densities and derived thermodynamic properties of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2007**, *52* (1), 80–88.
- (24) Hasse, B.; Lehmann, J.; Assenbaum, D.; Wasserscheid, P.; Leipertz, A.; Froba, A. P. Viscosity, Interfacial Tension, Density, and Refractive Index of Ionic Liquids [EMIM][MeSO₃], [EMIM][MeOHPO₂], [EMIM][OCSO₄], and [BBIM][NTf₂] in Dependence on Temperature at Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, *54* (9), 2576–2583.
- (25) Gu, Z.; Brennecke, J. F. Volume expansivities and isothermal compressibilities of imidazolium and pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47* (2), 339–345.