Thermophysical Properties of 1-Propyronitrile-3-alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K

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In the present work, a series of 1-propyronitrile-3-alkylimidazolium bromide ionic liquids ([C_2CN $C_n$im]Br, where $n = 4$, 6, 8, and 10) were synthesized and characterized using Fourier transform infrared spectroscopy (FTIR), NMR, and elemental analysis. Physical properties such as density, viscosity, and refractive index are measured and reported for a temperature range of (293.15 to 353.15) K and at atmospheric pressure. The influence of the alkyl chain on these properties is discussed. The present synthesized ionic liquids show a weak temperature dependency on the thermal expansion coefficient.

Introduction

Ionic liquids (ILs) are typically defined as a new class of organic salts comprised of ions and have very low melting points with negligible vapor pressure.[1,2] ILs are exclusively composed of organic cations and inorganic or organic anions (making them markedly different from ionic solutions, which contain ions dissolved in a molecular medium) with different molecular sizes and can either be hydrophilic or hydrophobic, depending on the nature of the ionic combinations.[3,4] Unlike molecular liquids, the ionic nature of these compounds results in a typical combination of properties, namely, high thermal stability, long liquidous range, high electrical conductivity, and highly solvation capacity, for both polar and nonpolar compounds.[4,5] These exclusive properties of these compounds make them useful in many important areas of commercial applications such as solvents for reactions, absorption media for gas separations, separating agents in extractive distillation, heat transfer fluids, biomass processing, working fluids in a variety of electrochemical applications[6] (batteries, capacitors, solar cells, etc.), lubricants,[7,8] and in biocatalysts with unique advantages.[9] Both the cationic and anionic components of ILs can be varied and modified for specific application with desirable properties. Of a variety of these available liquids, most of the cations are monoquaternary species with only one quaternization center. However, just like conventional organic solvents, not all ILs are appropriate for a particular application, and at the same time a single IL will not always be the best in every respect. Hence, it is important to synthesize new ILs to facilitate the choice of IL with task-specific properties.[3] Recently, a series of new kind of ILs called task-specific ionic liquids (TSILs) have been introduced by incorporating additional functional groups to impart specific properties or reactivities.[10−12] The incorporation of a functional group (such as amine,[13] sulfonic acid,[14] ether, alcohol,[15−17] carboxylic, and fluorous chains[18,19]) facilitates the choice of ILs for interaction with dissolved substrates in specific ways, resulting in the wide range of applications.[20]

Owing to this inherent nature of ILs and among the TSILs, the nitrile-functionalized ILs have special properties and potential applications in many vital areas. When the nitrile group is introduced in the side chain of the IL, the architecture of the hydrogen bonding network will change. Besides, compared with conventional ILs, the ILs incorporated with the nitrile functionality showed several additional advantages, namely, suitable reaction media and ligands for catalytic reactions, electrolytes for lithium battery, dye-sensitized solar cells,[10,21,22] and also they find applications in the fields of organic synthesis and extraction.[23]

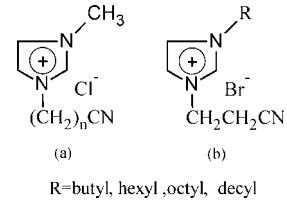

Figure 1. General structure for nitrile-functionalized ILs: (a) other studies, [C_nCN Mim]Cl; (b) this study, [C_2CN $C_n$im]Br.

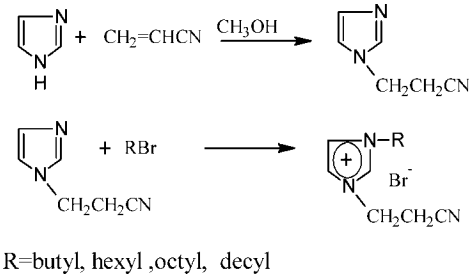

Figure 2. Synthesis route of the nitrile-functionalized ILs.

Even though many researchers have studied and reported the effect of the length of the alkyl chain unit linking the imidazolium ring and the nitrile group (Figure 1a) on the physiochemical properties, the effect of the length of alkyl chain in the third position of the imidazolium ring (Figure 1b) on the thermophysical properties has not been studied. This present study involves the synthesis of a new series of 1-propyronitrile-3-alkylimidazolium bromide ILs. They are synthesized by reacting imidazole with acrylonitrile, and then the product was reacted with alkyl bromides with C_4 to C_{10} hydrocarbon chain groups (Figure 2). The structure of the products was verified with ^{1}H NMR, Fourier transform infrared spectroscopy (FTIR), and elemental analysis. Despite their importance and interest

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in commercial applications, a detailed and systematic study on the physicochemical properties of these ILs has not been established. Hence in the present work an attempt was made to measure the important properties, namely, the density, viscosity, refractive index, and thermal expansion coefficient for the present synthesized ILs at different temperatures.

Experimental Section

Materials. Chemicals of analytical grade were used for the synthesis of the ILs. The CAS number, source, and grades of the chemicals used are as follows: imidazole (288-32-4, Aldrich 99 %), acrylonitrile (107-13-1, Aldrich 99 %), methanol (anhydrous, 67-56-1, Sigma-Aldrich 99.8 %), 1-bromohexane (111-15-1, Aldrich 99 %), 1-bromo-octane (111-81-1, Aldrich 99 %), 1-bromodecane (112-29-8, Aldrich 98 %), ethylacetate, (anhydrous, 141-78-6, Sigma-Aldrich 99.8 %), and 1-bromobutane (109-65-9, Merck 98 %). All of the chemicals were used without further purification.

Synthesis of ILs. 1-Propyronitrile-3-butylimidazolium Bromide, [C_2CN Bim]Br. Initially, imidazole (0.5 mol) was placed into a three-necked round-bottom flask, and the system was degassed with dry nitrogen. Methanol (1.0 mol) was added and stirred thoroughly, and then acrylonitrile (0.6 mol) was also added. The system was heated to 55 °C and stirred vigorously for 10 h under nitrogen atmosphere. The unreacted methanol and acrylonitrile were removed under vacuum at 70 °C. Then 1-bromobutane (0.5 mol) was then added, and the mixture was stirred and maintained at 70 °C under nitrogen atmosphere for 48 h. The resulting compound was cooled to room temperature and washed with ethyl acetate for three times, and the remaining solvent was removed at 80 °C under vacuum and then dried in a vacuum oven for 72 h. The yield was found to be 86 %.

Instead of 1-bromobutane (0.5 mol), 1-bromohexane (0.5 mol), 1-bromo-octane (0.5 mol), and 1-bromodecane (0.5 mol) were used to synthesize 1-propyronitrile-3-hexylimidazolium bromide [C_2CN Him]Br, 1-propyronitrile-3-octylimidazolium bromide [C_2CN Oim]Br, and 1-propyronitrile-3-decylimidazolium bromide [C_2CN Dim]Br, respectively, and a similar procedure was adopted. The yield of [C_2CN Him]Br, [C_2CN Oim]Br, and C_2CN Dim] was found to be 84 %, 85 %, and 79 %, respectively.

Characterization and Property Measurements. Millipore quality water with a known density, viscosity and refractive index was used to calibrate all of the instruments used for the present measurements of the physical properties. Accuracy and reproducibility of the instruments were validated using the ILs 1-butylpyridinium bis(trifluoromethylsulfonyl)imide, [C_4py]-Tf_2N, bis-(2-hydroxyethyl)ammonium acetate, BHEAA, and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_6Mim]Tf_2N, for which the data were established by our research group.[24−26]

FTIR, NMR, and Elemental Analysis. All of the ILs synthesized in this study were characterized using s Shimadzu FTIR-8400S spectrometer with a 4 cm^{-1} resolution and a wavenumber range of (350 to 7800) cm^{-1}. ^{1}H NMR spectra was taken in $CDCl_3$ solvent and recorded on a Bruker Avance 300 spectrometer, and CHNS-932 (LECO instruments) was used for elemental analysis. The details of the experimental procedures are presented in our recent work.[24,25]

Water Content. A coulometric Karl Fischer titrator, DL 39 (Mettler Toledo), was used to determine the water content of the synthesized ILs, using the Hydranal coulomat AG reagent (Riedel-de Haen). The measurement for each IL was made in triplicate, and the average values are reported in Table 1.

Table 1. Water Content (mass fraction) for [C_2CN $C_n$im]Br

[C_2CN Bim]Br	[C_2CN Him]Br	[C_2CN Oim]Br	[C_2CN Dim]Br
$406\cdot10^{-6}$	$385\cdot10^{-6}$	$369\cdot10^{-6}$	$341\cdot10^{-6}$

Table 2. Start Temperatures T_s and Decomposition Temperatures T_d for [C_2CN $C_n$im]Br

property	[C_2CN Bim]Br	[C_2CN Him]Br	[C_2CN Oim]Br	[C_2CN Dim]Br
T_s/K	481	474	467	464
T_d/K	524	518	513	511

Thermogravimetry Measurements. The decomposition temperatures were measured using a Perkin-Elmer, Pyris V-3.81 thermal gravimetric analyzer. The samples were placed in an aluminum pan under nitrogen atmosphere at a heating rate of 10 °C·min^{-1}. The measured start temperature (T_s) and decomposition temperature (T_d) are presented in Table 2.

Density and Viscosity Measurements. The density and viscosity measurements of the present synthesized ILs were carried out at a temperature range of (293.15 to 353.15) K using an Anton Paar viscometer (model SVM3000).[27] The temperature was controlled to within ± 0.01 °C. The reproducibility of the measurements were 0.35 % and $\pm 5\cdot10^{-4}$ g·cm^{-3} for viscosity and density, respectively.[24−26]

Refractive Index Measurements. The refractive indices were measured in the temperature range from (298.15 to 333.15) K using an ATAGO programmable digital refractometer (RX-5000 α) with a measuring accuracy of $\pm 4\cdot10^{-5}$. The temperature of the apparatus was controlled to within ± 0.05 °C. The apparatus was calibrated before each series of measurements and checked using pure organic solvents with known refractive indices.[24,25] Dried samples kept in desiccators were directly placed into the measuring cell. The reproducibility of the results was confirmed by performing at least three experiments for each sample in the whole temperature range.

Results and Discussion

The structures of all ILs synthesized in the present study were characterized using FTIR, NMR, and elemental analysis (CHNS), and the results confirmed the desired structures. The main feature in the FTIR spectra was the characteristic absorption of a C≡N group in the range from (2245 to 2260) cm^{-1} and also for C═N at (1550 to 1660) cm^{-1}. The FTIR exhibit C—H bond and weaker C—H bond stretches from (2920 to 3140) cm^{-1} and from (2840 to 2870) cm^{-1}, respectively.[10,22]

Since the present synthesized [C_2CN $C_n$im]Br ILs are highly hygroscopic in nature, the compounds were considered mostly as an intermediate instead of an end product.

The start temperatures for weight loss (T_s) and decomposition temperatures (T_d) of 1-propyronitrile-3-alkylimidazolium bromide are reported in Table 2. Decomposition temperatures of this series of ILs are affected slightly by the size of the alkyl chain of the cation; the decomposition temperature decreases as the alkyl chain increases. The T_d of ILs with the incorporation of a CN group were less in comparison with the corresponding ILs without a CN group (T_d of [C_4Mim]Cl, [C_6Mim]Cl, and [C_8Mim]Cl are (254, 253, and 243) °C, respectively).[28]

Table 3 presents the experimental densities of nitrile-functionalized ILs in the temperature range from (293.15 to 353.15) K. The density values are found to increase after the incorporation of a nitrile group due to the nature of the structural arrangement of cations and anions in the IL molecule which may result in the strong dipole moment of the nitrile group.[22] The densities of the present synthesized ILs are lower compared to the other nitrile-functionalized ILs reported by Zhao et al.[10]

Table 3. Experimental Densities ρ for [C_2CN $C_n$im]Br as a Function of Temperature

	ρ/(g·cm^{-3})			
T/K	[C_2CN Bim]Br	[C_2CN Him]Br	[C_2CN Oim]Br	[C_2CN Dim]Br
293.15	1.3085	1.2324	1.1801	
298.15	1.3047	1.2290	1.1766	
	1.2991[30]	1.2281[30]	1.1780[30]	
303.15	1.3011	1.2256	1.1732	
308.15	1.2977	1.2223	1.1698	1.1342
313.15	1.2943	1.2190	1.1664	1.1295
318.15	1.2910	1.2157	1.1630	1.1256
323.15	1.2876	1.2124	1.1596	1.1212
328.15	1.2844	1.2091	1.1562	1.1182
333.15	1.2812	1.2058	1.1529	1.1150
338.15	1.2779	1.2025	1.1495	1.1117
343.15	1.2747	1.1992	1.1461	1.1085
348.15	1.2714	1.1959	1.1428	1.1052
353.15	1.2682	1.1927	1.1396	1.1019

Table 4. Experimental Dynamic Viscosities η for [C_2CN $C_n$im]Br as a Function of Temperature

	η/(mPa·s)			
T/K	[C_2CN Bim]Br	[C_2CN Him]Br	[C_2CN Oim]Br	[C_2CN Dim]Br
298.15	19103.0			
303.15	11304.0	15893.0		
308.15	7058.4	9029.8	19620.3	
313.15	4502.1	5610.4	13044.0	16702.3
318.15	2953.0	3602.1	8302.7	10314.5
323.15	1989.7	2379.9	5136.1	6813.4
328.15	1377.5	1618.2	3291.8	4573.6
333.15	975.6	1128.4	2160.4	3016.4
338.15	705.8	805.1	1459.8	2051.2
343.15	520.5	639.6	1019.6	1426.6
348.15	390.7	465.7	727.9	1014.6
353.15	298.1	359.3	530.5	737.0

(the densities of [C_2CN Mim]BF_4, [C_3CN Mim]BF_4, and [C_4CN Mim]Cl are (2.15, 1.87, and 1.61) g·cm^{-3}, respectively) and Zhang et al.[22] (the densities of [C_3CN Mim]BF_4 and [C_3CN Mim]NTf_2 are (1.319 and 1.519) g·cm^{-3}, respectively). These results might be due to the presence of a long alkyl chain compared to the other nitrile-functionalized ILs,[10,22] and in general the density decreases as the alkyl chain length increases.[29] The densities of this series of ILs are in good agreement with that calculated using Ye and Shreeve method:[30] the calculated density values at 298.15 K are (1.2991, 1.2281, and 1.1780) g·cm^{-1} for [C_2CNBim]Br, [C_2CN Him]Br, and [C_2CN Oim]Br, respectively, when compared with the present values of (1.3047, 1.2290, and 1.1766) g·cm^{-1}, respectively. The density decreases linearly with increasing temperature and also decreases as the alkyl chain length increases.[31]

Table 4 shows the effect of the alkyl chain length and temperature on the viscosity of imidazolium cations incorporated with the nitrile functionality for a fixed anionic species [Br] at atmospheric pressure. The results indicate that an increase in the alkyl chain length of the cation tends to increase the viscosity (Table 4), as observed by Tokuda et al.[31]

Experimental results of the temperature dependency of the refractive indices, n_D, for nitrile-functionalized ILs are presented in Table 5. The measured refractive indices of the present ILs at 298.15 K are in the range of (1.54540 to 1.50279), and the values are comparable to other nitrile functionalized ILs (1.4188 to 1.5453) but higher than those of the corresponding ILs without a nitrile group, which could be due to the high electron mobility around the nitrile group.[22] Refractive indices decrease linearly with increasing temperature for each of the ILs and also decrease with increasing the alkyl chain length.

Table 5. Experimental Refractive Indices n_D for [C_2CN $C_n$im]Br as a Function of Temperature

	n_D			
T/K	[C_2CN Bim]Br	[C_2CN Him]Br	[C_2CN Oim]Br	[C_2CN Dim]Br
298.15	1.54540	1.52872	1.51473	
303.15	1.54454	1.52823	1.51362	
308.15	1.54346	1.52719	1.51266	1.50786
313.15	1.54229	1.52600	1.51149	1.50696
318.15	1.54111	1.52479	1.51024	1.50606
323.15	1.53992	1.52354	1.50891	1.50502
328.15	1.53869	1.52229	1.50757	1.50388
333.15	1.53748	1.52117	1.50604	1.50279

Table 6. Fitting Parameters of Equation 1 and the SDs Calculated Using Equation 4

IL	A_0	A_1	SD	R^2
[C_2CN Bim]Br	1.503132	−0.000666	$2.51\cdot10^{-4}$	0.9996
[C_2CN Him]Br	1.426100	−0.000661	$8.76\cdot10^{-5}$	0.9999
[C_2CN Oim]Br	1.378105	−0.000676	$8.49\cdot10^{-5}$	0.9999
[C_2CN Dim]Br	1.348755	−0.000701	$7.38\cdot10^{-4}$	0.9958

Table 7. Fitting Parameters of Equation 2 and the SDs Calculated Using Equation 4

IL	A_2	A_3	SD	R^2
[C_2CN Bim]Br	1.614128	−0.000230	$1.41\cdot10^{-4}$	0.9981
[C_2CN Him]Br	1.598682	−0.000233	$1.96\cdot10^{-4}$	0.9981
[C_2CN Oim]Br	1.588503	−0.000247	$2.24\cdot10^{-4}$	0.9956
[C_2CN Dim]Br	1.570713	−0.000204	$6.50\cdot10^{-2}$	0.9974

Table 8. Fitting Parameters of Equation 3 and the SDs Calculated Using Equation 4

IL	A_4	A_5	SD	R^2
[C_2CN Bim]Br	−7.329316	3445.3359	$2.920\cdot10^{-2}$	0.9973
[C_2CN Him]Br	−7.378833	3488.2439	$3.898\cdot10^{-2}$	0.9943
[C_2CN Oim]Br	−8.254749	3867.7933	$1.588\cdot10^{-2}$	0.9990
[C_2CN Dim]Br	−7.759077	3747.1494	$9.308\cdot10^{-3}$	0.9995

The present experimental results on density, refractive index, and viscosity could be represented by the following empirical equations as a function of temperature.[24−26]

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

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

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

where ρ, n_D, and η are the density, refractive index, and viscosity, respectively. T is the absolute temperature; A_0, A_1, A_2, A_3, A_4, and A_5 are correlation coefficients. The correlation coefficients are estimated using linear regression analysis, and the values are reported in Tables 6, 7, and 8 together with the standard deviations (SD). The SDs were calculated by applying the following expression:

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

where n_{DAT} is the number of experimental points and z_{exp} and z_{cal} are the experimental and calculated values, respectively.

Since the temperature−density relationship for ILs is linear, density values as a function of temperature were used to calculate the thermal expansion coefficient (Table 9). The thermal expansion coefficients (α), also known as volume expansivity, as a function of temperature at atmospheric pressure were estimated using the following equation.[32]

$$\alpha_P/(\mathrm{K^{-1}}) = -(1/\rho)(\partial\rho/\partial T)_P = -(A_1)/(A_0 + A_1 T) \quad (5)$$

where α is the thermal expansion coefficient in K^{-1}, ρ is the density, and A_0 and A_1 are the fitting parameters of eq 1. The

Table 9. Thermal Expansion Coefficients (α) for [C_2CN $C_n$im]Br as a Function of Temperature

	$\alpha \cdot 10^4/(K^{-1})$			
T/K	[C_2CN Bim]Br	[C_2CN Him]Br	[C_2CN Oim]Br	[C_2CN Dim]Br
293.15	5.09	5.36	5.73	
298.15	5.10	5.38	5.75	
303.15	5.12	5.39	5.76	
308.15	5.13	5.41	5.78	6.18
313.15	5.15	5.42	5.80	6.21
318.15	5.16	5.44	5.81	6.23
323.15	5.17	5.45	5.83	6.25
328.15	5.19	5.47	5.85	6.27
333.15	5.20	5.48	5.86	6.29
338.15	5.21	5.50	5.88	6.31
343.15	5.22	5.51	5.90	6.32
348.15	5.24	5.53	5.92	6.34
353.15	5.25	5.54	5.93	6.36

thermal expansion coefficients of this series of ILs do not appreciably change with temperature for the range from (293.15 to 353.15) K studied in the present work. The studied ILs show a weak temperature dependency for the thermal expansion coefficient, $\alpha = (5.09 \cdot 10^{-4}$ to $6.17 \cdot 10^{-4}) K^{-1}$, which is higher than those of high-temperature molten salts, but is noticeably smaller than those for molecular organic liquids. Also, these values are similar to those reported for imidazolium-, pyridinium-, phosphonium-, and ammonium-based ILs, ($5.0 \cdot 10^{-4}$ to $6.5 \cdot 10^{-4}) K^{-1}$.[33] ILs having a shorter alkyl chain on the cation show a lower expansion coefficient when compared with those having a longer alkyl chain which might be due to the coiling of the chain.

Conclusion

The experimental values of density and dynamic viscosity at a temperature range from (293.15 to 353.15) K and refractive index from (298.15 to 343.15) K were measured and reported for the 1-propyronitrile-3-alkylimidazolium bromide ILs. Empirical correlations (eqs 1, 2, and 3) were proposed to represent the present experimental results. The density, dynamic viscosity, and refractive index values decrease with increasing temperature. The present measured decomposition temperature, density, and refractive index values deceased with the increase in the length of the alkyl chain in the third position of the imidazolium ring. The thermal expansion coefficients of the present synthesized ILs are less than those of the molecular organic liquids.

Supporting Information Available:

Plots of FTIR and NMR spectra, densities, refractive indices, and log η versus T^{-1} for the nitrile-functionalized ILs studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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