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Basic ionic liquids based on monoquaternized 1,4-diazobicyclo[2.2.2]octane (dabco) and dicyanamide anion: Physicochemical and solvent properties*

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Abstract: In this paper, we report on the synthesis and application of monosubstituted diazabicyclo[2.2.2]octane (dabco) cations associated with a basic anion, dicyanamide. Key properties of these salts—phase transitions, density, and conductivity—were measured and compared to those of other common ionic liquids (ILs). Moreover, solvatochromic dyes were used to assess their solvation properties. The Heck cross-coupling reaction was evaluated in dabco-based ILs and compared with the behavior in common unfunctionalized ILs, evidencing good catalyst stability and a high recyclability in these basic ILs.

Keywords: basic ILs; dabco; ionic liquids; physicochemical properties; solvent properties.

INTRODUCTION

Room-temperature ionic liquids (RTILs) based on bulky asymmetric cations, such as 1,3-dialkylimidazolium salts, are currently attracting considerable attention as potentially benign media for a wide range of applications in chemistry, electrochemistry, and materials sciences [1]. This interest is mainly related to the alternative features of ILs to traditional solvents, such as nonvolatility, nonflammability, electrochemical and thermal stability, and high conductivity. Moreover, ILs possess physicochemical properties that make them improved media able to increase reactivity, selectivity, catalyst recyclability, and so on [2]. Like all molten salts, ILs are highly structured materials; much of the crystal lattice of the solid state is retained on melting [3]. The strong ion–ion interactions present in ILs lead to high-ordered three-dimensional supermolecular polymeric networks of anions and cations linked by H-bonds and/or Coulombic interactions [4]. The strength of the ion–ion interaction depends on the IL structure and may strongly affect the ability of the single components (anions and/or cations) to interact with dissolved species [5,13].

Recently, to maximize the advantages from using these new solvents, functionalized ILs (generally, defined task-specific ILs, TSILs) have been developed and applied [6]. TSILs are characterized by the presence of functional groups able to impart a particular reactivity, enhancing the capability for interaction with specific solutes (acids, bases, metals, nanoparticles, and so on). Among the functionalized anions and cations, those having a Lewis base character, have been recently proposed as promis-

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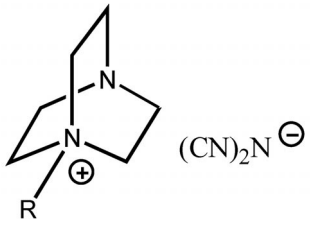
ing components of ILs able to act as solvents and catalysts and to enhance the acidity of dissolved acids [7].

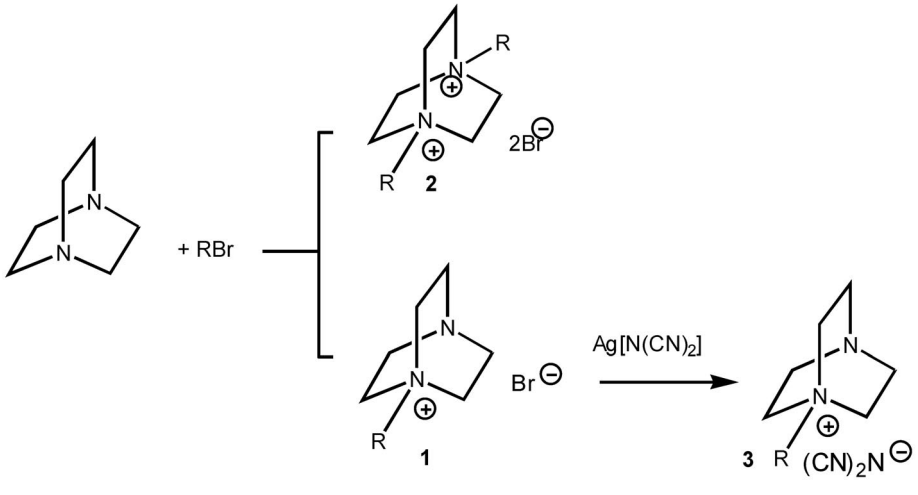
In this paper, we report on the synthesis and application of monosubstituted diazabicyclo[2.2.2]octane (dabco) cations associated with a basic anion, dicyanamide ($[N(CN)_2]^-$). Dabco-based ILs have been known for some time [7,8], but as far as we are aware, use of this class of ILs as a medium for catalyzed reactions is extremely limited.



R = $CH_3(CH_2)_n$ n = 1-11, 15

RESULTS AND DISCUSSION

The synthetic route to synthesize dabco-based salts herein is shown in Scheme 1. In the first step, the appropriate alkyl bromide and dabco are reacted in ethyl acetate at temperatures lower than 50 °C to afford the mono-alkylation product, [$C_n$dabco]Br, **1**. Generally, an excess (ca. 10 %) of dabco was used to avoid bisalkylation. The use of an excess of alkyl bromide, or high temperatures (>100 °C), favor the formation of the bisalkylation product, [$C_nC_n$dabco]2Br, **2**. Subsequent metathesis of **1** with silver dicyanamide ($Ag[N(CN)_2]$), freshly prepared by reacting $AgNO_3$ and $Na[N(CN)_2]$ in equimolar quantities, afforded the corresponding dicyanamide **3**.



R = **a)** CH_3CH_2; **b)** $CH_3(CH_2)_2$; **c)** $CH_3(CH_2)_3$;**d)** $CH_3(CH_2)_4$;

e) $CH_3(CH_2)_5$; **f)** $CH_3(CH_2)_6$; **g)** $CH_3(CH_2)_7$; **h)** $CH_3(CH_2)_8$

i) $CH_3(CH_2)_9$; **l)** $CH_3(CH_2)_{10}$; **m)** $CH_3(CH_2)_{11}$; **n)** $CH_3(CH_2)_{15}$

Salts **1–3** were characterized using electrospray ionization mass spectroscopy (ESI-MS), IR, ^{1}H and ^{13}C NMR spectroscopy. The positive ion ESI mass spectra of **1** and **3** exhibit parent peaks corresponding to the cations $[C_n\ \text{dabco}]^+$, whereas in negative mode intense peaks corresponding to Br^- and $[N(CN)_2]^-$ were observed. In agreement with previous studies [5], aggregates based on cation–anion clusters were evidenced, which are reduced in relative intensity as the concentration of the IL solution is reduced in the cosolvent, or methanol is used as cosolvent instead of acetonitrile. At variance with salts **1** and **2**, most of the $[C_n\text{dabco}][N(CN)_2]$ salts **3** are liquid at room temperature. Salts **3a–c** show the characteristic behavior of supercooled fluids [9]: after removal of the solvent they did not solidify even on storage at –4 °C. If they are stored at lower temperatures (–50 °C), they solidify and do not melt at room temperature, they melt at the temperatures reported in Table 1. Glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures of $[C_n\text{dabco}][N(CN)_2]$ salts having a melting point higher than 0 °C were determined by differential scanning calorimeter (DSC). All of the salts **3** fall in the IL class since their melting points are below 100 °C. Furthermore, upon heating they decompose at temperatures higher than 300 °C, assuring a wide liquid region. The correlation between melting points and alkyl substituents of cations is clearly observed in Table 1. As the alkyl groups are changed from C2 to C3 to C4 the melting points vary from 65 to 41 to 36 °C. Lower melting points characterize ILs C5–C12, although an increasing trend can be observed comparing the melting points of ILs bearing alkyl groups changing from C10 to C16. This behavior suggests that for relatively short alkyl chains the increase of length and flexibility of the alkyl group result in lower melting point salts, probably a consequence of a poorer packing into the crystal lattice. In the presence of very long alkyl chains, however, stronger van der Waals interactions favor the formation of solid compounds having a wax-like appearance. It is noteworthy that these latter salts show clear evidence for the presence of several phase transitions upon increasing temperature; ILs **3m** and **3n** are characterized by three melting temperatures (T_m).

Table 1 Thermal properties of $[C_n\text{dabco}][N(CN)_2]$ salts.

	T_g		T_{cc1}		T_{m1}		T_{m2}		T_{cc2}		T_{m3}	
n	T (°C)	ΔC_p (J/gK)	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)
2			4	–76.0	65	85.0						
3			3	–39.0	41	45.4						
4					36							
10			0	–9.4	9	7.5	18	0.4				
12			–14	–17.3	2	3.7	11	7.0	15	–2	21	7.5
15	14	0.23			31	8.1	36	3.2			50	37.6

T_g: Glass transition temperature, T_{cc}: temperature of cold crystallization (crystallization during heating).

Other physical quantities characterizing ILs **3**, as liquid or supercooled fluids, are reported in Table 2.

Table 2 Physical properties of ILs **3**.[a]

Salt	d g cm^{-1}	C mol cm^{-1}	σ S cm^{-1}	Λ S cm^2 mol^{-1}
[C_2dabco][N(CN)$_2$]	1.13	5.46×10^{-3}	8.00×10^{-3}	1.46
[C_4dabco][N(CN)$_2$]	1.09	4.64×10^{-3}	3.11×10^{-3}	0.67
[C_5dabco][N(CN)$_2$]	1.07	4.30×10^{-3}	1.90×10^{-3}	0.44
[C_6dabco][N(CN)$_2$]	1.06	4.03×10^{-3}	0.79×10^{-3}	0.19
[C_7dabco][N(CN)$_2$]	1.05	3.79×10^{-3}	0.67×10^{-3}	0.17
[C_8dabco][N(CN)$_2$]	1.04	3.57×10^{-3}	0.54×10^{-3}	0.15
[C_9dabco][N(CN)$_2$]	1.03	3.40×10^{-3}	0.42×10^{-3}	0.12
[C_{10}dabco][N(CN)$_2$]	1.01	3.17×10^{-3}	0.32×10^{-3}	0.10
[C_{11}dabco][N(CN)$_2$]	1.01	3.03×10^{-3}	0.21×10^{-3}	0.07
[C_{12}dabco][N(CN)$_2$]	0.99	2.88×10^{-3}	0.40×10^{-3}	0.14

[a]d, density at 25 °C; C, molar concentration at 25 °C; σ, ionic conductivity at 25 °C; Λ, molar conductivity at 25 °C.

The density (d) decreases as the alkyl chain on cation elongates. In relation, the molar concentration (C) decreases significantly on going from [C_2dabco][N(CN)$_2$] to [C_{12}dabco][N(CN)$_2$]. A similar behavior was previously reported also for other imidazolium cation-based dicyanamide salts [10].

The variation of alkyl chain length exerts a drastic effect also on the ionic conductivity (σ). For the present salts, there is a pronounced decrease in conductivity with elongating of the alkyl chain in the cations. Their temperature dependencies seem to follow the Arrhenius equation, $\sigma = \sigma_0 \exp(-E_a(\sigma)/k_bT)$ ($R^2 > 0.998$), over the measured temperature range (25–100 °C), even if the longer chains salts show a slight upward curvature (Fig. 1). It is noteworthy that the ionic conductivity of [C_2dabco][N(CN)$_2$] is significantly higher than that of the other salts reported in Table 2, though this IL was in a supercooled state.

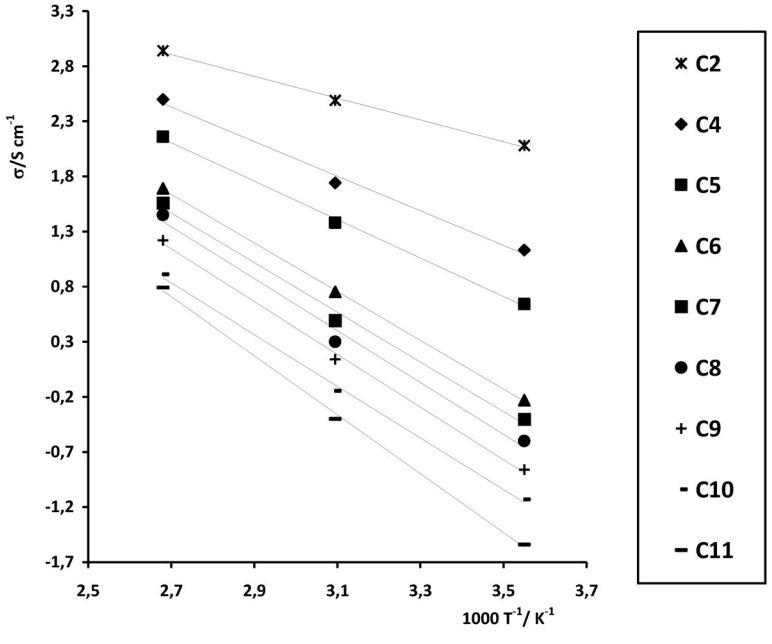


Fig. 1 Temperature dependence of conductivity for [$C_n$dabco][N(CN)$_2$].

Although a wide range of solvatochromic dyes has been used to estimate IL polarity by comparison to well-known polarity scales based on molecular solvents [11], E_T^N and Kamlet–Taft parameters are probably the most extensively employed to classify ILs [12]. Therefore, E_T^N and Kamlet–Taft parameters have been determined for RTILs **3** using Reichardt's betaine dye, *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline [13]. Table 3 presents the $E_{T(30)}$, π^*, α, and β values of the [$C_n$dabco][$N(CN)_2$] salts. By comparison, the corresponding values of the other two dicyanamide salts (1-butyl-3-methyl imidazolium dicyanamide, [bmim]$N(CN)_2$, and methyl-ethylpyrrolidium dicyanamide, [emPyr][$N(CN)_2$]) and some molecular solvents have been inserted.

Table 3 Solvatochromic parameters of the [$C_n$dabco][$N(CN)_2$] salts.

Salt	$E_{T(30)}$	E_T^N	π^*	α	β
[bmim][$N(CN)_2$][a,b]	51.4	0.639	1.05	0.51	nd
		(0.629)	(1.13)	(0.46)	(0.70)
[emPyr][$N(CN)_2$][a]	48.7	0.556	1.03	0.37	nd
[C_5dabco][$N(CN)_2$]	48.4	0.546	1.11	0.31	0.55
[C_6dabco][$N(CN)_2$]	48.5	0.549	1.08	0.32	0.56
[C_7dabco][$N(CN)_2$]	48.7	0.557	1.06	0.35	0.60
[C_8dabco][$N(CN)_2$]	48.7	0.557	1.05	0.36	0.60
[C_9dabco][$N(CN)_2$]	48.5	0.549	1.02	0.34	0.57
[C_{10}dabco][$N(CN)_2$]	48.5	0.549	1.06	0.34	0.55
Water[c]		1.000	1.13	1.12	0.50
Methanol[c]		0.760	0.73	1.05	0.61
Acetone[c]		0.350	0.70	0.20	0.54
Acetonitrile[c]		0.460	0.75	0.19	0.40
DMSO[c]		0.444	1.00	0.00	0.76

[a]From ref. [10].
[b]From ref. [15].
[c]From ref. [16].

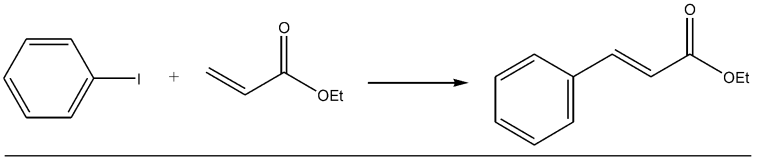
At 25 °C, the polarities of our six dabco-based ILs, as expressed by E_T^N values, are higher than those of acetone, acetonitrile, and dimethyl sulfoxide (DMSO); however, they are slightly lower than that of the corresponding imidazolium salt, [bmim][$N(CN)_2$], of water and methanol. On the other hand, π^* parameters evidence a high dipolarity–polarizability; they are higher than those for methanol and acetone and are close to that for imidazolium IL and for water. At variance, dabco-based ILs show a hydrogen-bond acidity, as expressed by α parameter, significantly lower than that of [bmim][$N(CN)_2$], but comparable to that of the reported pyrrolidinium salt. Finally, the β values for our ILs are close to those for methanol and acetone, evidencing a significant hydrogen-bond basicity. Unlike α, at least for imidazolium ILs, β depends mainly on the nature of the anion. Because all investigated dabco-based ILs have the same anion ([$N(CN)_2$]$^-$), β parameters do not vary significantly inside this class of salts. Nevertheless, we observe that the nature of cation influences the parameter β. At 25 °C, parameters β for [$C_n$dabco][$N(CN)_2$] are lower than that of [bmim][$N(CN)_2$], suggesting a correlation with the cation polarity and hydrogen-bond acidity.

Interestingly, the stretching CN modes of the $N(CN)_2$ anion show a blue shift by ca. 20 cm^{-1} in going from imidazolium to dabco-based ILs, whereas they are practically unaffected by the alkyl chain length both in imidazolium [10] and dabco salts. Since in molecular solvents it has been found that the stretching C N modes of the $N(CN)_2$ anion shows a noticeable red shift [16], in going from aprotic DMSO to protic methanol, the comparison between imidazolium and dabco-based ILs confirms this behavior also in ionic media.

PALLADIUM-CATALYZED HECK CROSS-COUPLING REACTIONS IN DABCO-BASED IONIC LIQUIDS

The Heck reaction has been studied extensively in ILs, where Pd(II) complexes or Pd(0) nanoparticles act as catalysts [17]. Generally, a base such as K_2CO_3, $NaHCO_3$, and choline acetate must be added. Although the consumption of one equivalent of base is inevitable, it has been recently shown that a basic IL acting as both the solvent and base can make the synthetic procedure much easier to handle [18]. In this study, the Heck cross-coupling reaction was evaluated using three dabco-based ILs. Reactions were stopped after 2 h, avoiding complete conversion, to evaluate the efficiency of the selected dabco-based ILs. Moreover, for comparison the reaction in two unfunctionalized imidazolium-based ILs was also performed. The coupling reaction of iodobenzene and ethyl acrylate in the selected ILs at 90 °C, was performed using 1 mol % palladium acetate as the catalyst, $HCOONH_4$ (10 mol %) as reducing agent and cholinium acetate (equimolar with iodobenzene) as base. In all investigated ILs, base was added exclusively in the first reaction. *trans*-Ethyl cinnamate was formed as the only product in all reactions (no biphenyl could be detected), and it was easily separated from the catalyst and IL solvent by simple extraction with hexane. After extracting the products from the catalytic solution, the resulting solution was dried under vacuum before new substrates were charged. It is noteworthy that, after the product extraction, reuse of the IL systems (without re-addition of the base and reducing agent) gave positive results only in the case of ILs bearing a basic anion and/or cation (runs 2–6), (Table 4). As previously evidenced [17i], the catalytic system in [bmim][BF_4] cannot be easily reused probably due to the depletion of the base due to its consumption. At variance, in dabco-based ILs, not only the reuse of the catalytic system is possible, but also significantly higher yields have been always found starting from the first recycle.

Table 4 Heck coupling of iodobenzene with ethylacetate at 90 °C.[a]



Run	Salt	Product				
		yield %[b]	Recycles (yields %)			
			1	2	3	4
1	[bmim][BF_4]	55	36	20	12	14
2	[bmim][N(CN)$_2$]	38	33	35	30	35
3	[C_4dabco][N(CN)$_2$]	18	32	38	43	43
4	[C_6dabco][N(CN)$_2$]	20	37	33	35	37
5	[C_8dabco][N(CN)$_2$]	24	40	38	35	38
6	[C_8dabco][BF_4]	22	40	37	30	38

[a]0.5 mmol iodobenzene, 0.6 mmol ethyl acrylate, 10 mol % $HCCONH_4$, 0.5 mmol choline acetate, 1 mol % Pd(OAc)$_2$.
[b]Determined by GC using mesitylene as internal standard.

CONCLUDING REMARKS

In conclusion, ILs based on monosubstituted dabco cation and having dicyanamide as anion have been studied. Key physicochemical properties of these salts have been determined, evidencing that these ILs represent an interesting class of functionalized nonaromatic ILs. The application in Pd-catalyzed Heck cross-coupling reaction is evidence of the ability of these ILs to immobilize Pd catalysts working as

both solvents and ligands. Moreover, these ILs can act as internal base during the recycles, avoiding the progressive decrease in conversion, generally observed in common ILs due to the consumption of the base.

EXPERIMENTAL SECTION

Measurements

^{1}H NMR measurements were conducted on a Bruker Advance II 250 spectrometer operating at 250 MHz, and D_2O was used as solvent. Fourier transform-infrared (FT-IR) spectra were taken on pure compounds using a Perkin Elmer Spectrum One FTIR-ATR (400–4000 cm^{-1}). Glass transition (T_g), crystallization (T_c), melting (T_m), and decomposition (T_d) temperatures were determined from DSC thermograms during the heating scans (10 °C min^{-1}) on a Mettler Toledo 822e instrument. The samples were sealed in aluminum pans under an inert atmosphere, and the temperature was calibrated by water and indium. Density values were obtained using an AP PAAR DMA calculating density meter. Conductance measurements were performed using a CON 510 bench meter supplied with conductivity/TDS electrode. His electrode comes with stainless steel ring, a cell constant of K = 1.0 and a built-in temperature sensor for automatic temperature compensation. UV–vis absorption spectra of Reichardt's betaine dye, *N*,*N*-diethyl-4-nitroaniline, and 4-nitroaniline dissolved in ILs were taken in a quartz cell with light path length of 1 mm on a Cary 2200 spectrophotometer (300–800 nm). Individual stock solutions of Reichardt's betaine dye, 4-nitroaniline, and *N*,*N*-diethyl-4-nitroaniline were prepared in dichloromethane. To prepare a given dye/IL solution, the appropriate amount of the dye stock solution was micropipetted into a clean dry quartz cuvette. Residual dichloromethane was evaporated under a gentle stream of argon gas. The IL was then added to the cuvette, the cuvette was capped and sealed, and the sample was mixed for an appropriate time prior to experimental measurements. Gas chromatography (GC) analyses were carried out using an ECONOCAP EC-5 column (30 m). ESI-MS analyses were performed on a Finnigan LCQ Advantage (Thermo Finnigan, San Jose, CA, USA) ion trap instrument equipped with Excalibur software.

Heck reaction

Reactions were carried out in a screw cup with Teflon-faced rubber septum vials under magnetic stirring. In a typical procedure, iodobenzene (0.5 mmol) was mixed with the IL (0.5 ml) under a nitrogen atmosphere. Anhydrous cholinium acetate (0.5 mmol), $Pd(OAc)_2$ (1 mol %) and $HCCONH_4$ (10 mol %), were added. After the flask was flushed with dry nitrogen, ethyl acrylate (0.6 mmol) was injected. The mixture was heated to 90 °C for 2 h. After the reaction, the mixture was cooled and the product extracted with hexane. The combined extracts were washed with brine and water, dried with $MgSO_4$, and analyzed by GC after addition of mesitylene, as an internal standard.

SUPPLEMENTARY INFORMATION

Electronic supplementary information (ESI) available: Ionic liquids synthesis and characterization. Supplementary information is available online (doi: 10.1351/PAC-CON-08-11-01).

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