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PAPER

## Hydrophobic 1-allyl-3-alkylimidazolium dicyanamide ionic liquids with low densities†

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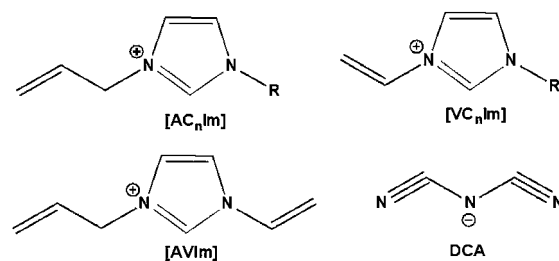
Nine 1-allyl-3-alkylimidazolium ([AC<sub>n</sub>Im]) or 1-vinyl-3-alkylimidazolium ([VC<sub>n</sub>Im]) dicyanamides (DCA) were prepared and characterized, and their physicochemical properties were studied in detail. Except for [AVIm]DCA and [AC<sub>4</sub>Im]DCA, the other dicyanamides with hexyl or longer alkyl chains on the cation exhibited the characteristic of hydrophobicity. Among them, [AC<sub>8</sub>Im]DCA and [AC<sub>10</sub>Im]DCA were found to possess similar densities to water, *i.e.* 1.007 g cm<sup>-3</sup> and 0.988 g cm<sup>-3</sup> at 25 °C, respectively. Interestingly, a reversible phase reversion of a [AC<sub>8</sub>Im]DCA/H<sub>2</sub>O mixture was observed as the temperature varied. These environmentally-friendly liquid materials have potential applications as precursors for syntheses of conducting polymeric materials.

Over the past decade, ionic liquids (ILs) have received great interest due to their potentially unique properties, such as negligible vapor pressure, high thermal stability, and high ionic conductivity, and their applications have been concentrated mainly on synthesis,<sup>1</sup> catalysis,<sup>2</sup> separation and extraction,<sup>3</sup> electrochemistry,<sup>4</sup> *etc.*, in which ILs mainly act as media or electrolytes. Recently, a new trend of IL application has been emerging along with rapid development of IL R&D, *i.e.* from environmentally-friendly media or electrolytes in traditional chemical processes to soft functional materials such as lubricants,<sup>5</sup> additives,<sup>6</sup> drugs,<sup>7</sup> heat transfer fluids,<sup>8</sup> luminescence materials,<sup>9</sup> *etc.* Thus, the current search for novel ILs is driven largely by the need to develop IL materials with special properties and functions. To date, a lot of ILs with unique features and performance have been developed, *e.g.* halogenated ILs with high density,<sup>10</sup> trialkylsulfonium dicyanamide salts with low viscosity,<sup>11</sup> trihalide anion based ILs with high refractive indices,<sup>12</sup> highly energetic ILs from azolate derivatives<sup>13</sup>, the immensely stable pyrrolidinium imide family of salts as excellent electrolytes,<sup>14</sup> amido functionalized ILs for CO<sub>2</sub> capture,<sup>15</sup> thiol functionalized ILs for nanoparticle modification,<sup>16</sup> *etc.*

Very recently, a new kind of hydrophobic and low-density amino acid IL was also been reported by Ohno *et al.*, with densities ranging from 0.886 to 0.945 g cm<sup>-3</sup>.<sup>17</sup> With our continuous efforts to develop novel ILs with special properties and performance,<sup>18–20</sup> in this work, nine allyl- or vinyl-functionalized RTILs, which are composed of 1-allyl-3-alkylimidazolium cation ([AC<sub>n</sub>Im]) or 1-vinyl-3-alkylimidazolium cation

([VC<sub>n</sub>Im]) and the dicyanamide anion (DCA), were synthesized and characterized (Scheme 1), and their physicochemical properties including thermal properties, surface properties, viscosity and density at different temperatures, refractive index, conductivity, electrochemical stability, *etc.* and the effect of the length of alkyl chain on these properties were also investigated in detail.

Nine dicyanamide salts with yields of 81–93% were obtained as transparent viscous liquids at room temperature. Except for [AVIm]DCA and [AC<sub>4</sub>Im]DCA, the other seven ILs exhibited hydrophobic characteristics. The chemical structure and purity of each IL was firstly identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy to check for residues of unreacted reactants or residual solvents (Fig. S1–S18†), and the analysis results indicated that each IL had a purity of >99 wt%. Since the impurities in ILs such as water and halogen ions also had great effects on the properties, the impurity content in each IL was first determined before every test of physicochemical properties. The content of bromide ion in each IL was determined by a Mettler–Toledo Seven Multi meter with a bromide ion selective electrode, and the values were less than 100 ppm. The water content of the ILs was determined by



R = butyl, [AC<sub>4</sub>Im]; hexyl, [AC<sub>6</sub>Im]; octyl, [AC<sub>8</sub>Im]; decyl, [AC<sub>10</sub>Im]; dodecyl, [AC<sub>12</sub>Im]; tetradecyl, [AC<sub>14</sub>Im]. R<sub>1</sub> = octyl, [VC<sub>8</sub>Im]; decyl, [VC<sub>10</sub>Im].

Scheme 1 Structures and abbreviations of the ILs prepared in this work.

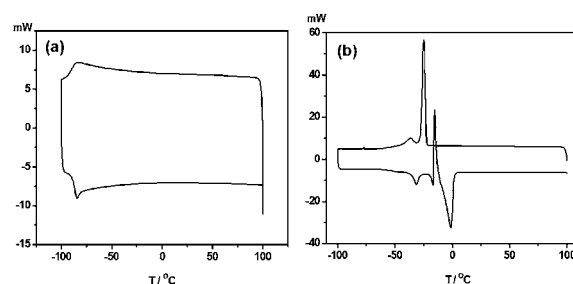
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means of a Karl-Fischer titration, and the water content in nine ILs ranged from 536 ppm to 1049 ppm (Table 1).

Firstly, the thermal properties of nine ILs were investigated. The DSC analysis showed that although [AC<sub>12</sub>Im]DCA (Fig. 1b) and [AC<sub>14</sub>Im]DCA exhibited melting points of  $-2.2\text{ }^{\circ}\text{C}$  and  $-14.5\text{ }^{\circ}\text{C}$ , respectively, only the glass-forming characteristic at a temperature of  $<-74\text{ }^{\circ}\text{C}$  and no melting or crystallization in the cooling and heating cycle were observed for the other dicyanamide salts (Fig. 1a, Table 1). Moreover, a solid–solid transition and a cold crystallization were observed from the DSC trace of [AC<sub>12</sub>Im]DCA (Fig. 1b), indicating that the mutual conversions between different crystalline structures occur in the interior of the IL as the temperature changes, which might be caused by dynamically disordered orientations of the IL constituents about the molecular axis.<sup>21</sup> However, no liquid crystal phenomenon was detected for [AC<sub>12</sub>Im]DCA (Fig. 1b) or [AC<sub>14</sub>Im]DCA. The heat capacity ( $C_p$ ) is a crucial parameter of an IL, which is very important in particular for ILs used in the fields of thermodynamics and thermochemistry. At  $25\text{ }^{\circ}\text{C}$ , the  $C_p$  values for the nine ILs range from  $1.9$  to  $2.5\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$  (Table 1), which are obviously much higher than those of common dicyanamide-based ILs (the  $C_p$  values of [BMIm]DCA and [BMIm]BF<sub>4</sub> are  $1.8$  and  $1.6\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$  at  $25\text{ }^{\circ}\text{C}$ , respectively<sup>22</sup>). A sensible heat storage density ( $E_s$ ) is a crucial quantity for thermal energy collection. The  $E_s$  values of the nine ILs ( $196.7$ – $257.1\text{ MJ cm}^{-3}$ ) are much higher than the  $1.9\text{ MJ m}^{-3}$  minimum specified by the American National Renewable Energy Laboratory<sup>23</sup> if a range of  $100\text{ }^{\circ}\text{C}$  is roughly chosen. This means that these hydrophobic dicyanamide salts are potential environmentally-friendly fluids for heat storage and heat transfer. The thermogravimetric analysis showed that these allyl or vinyl functionalized [DCA]<sup>−</sup>-based ILs exhibited slightly lower thermal stabilities ( $T_d = 228$ – $266\text{ }^{\circ}\text{C}$ ) than common dicyanamides (e.g. the  $T_d$  of [BMIm]DCA is ca.  $300\text{ }^{\circ}\text{C}$ <sup>22</sup>), mainly due to the incorporation of the allyl or the vinyl group into the cations.

Except for their hydrophobic characteristics, another special property of these [DCA]<sup>−</sup>-based ILs is that their densities are very close to that of water. From Table 2, the nine dicyanamide salts exhibited low densities ranging from  $0.963$  to  $1.118\text{ g cm}^{-3}$  at  $25\text{ }^{\circ}\text{C}$ , of which [AC<sub>8</sub>Im]DCA and [AC<sub>10</sub>Im]DCA were found to possess similar densities ( $1.007\text{ g cm}^{-3}$  and  $0.988\text{ g cm}^{-3}$ , respectively) to water ( $0.997\text{ g mL}^{-1}$  at  $25\text{ }^{\circ}\text{C}$ ). Fig. 2 shows pictures of the reversible phase reversion of an IL/H<sub>2</sub>O mixture as the temperature varied from  $25\text{ }^{\circ}\text{C}$  to  $35\text{ }^{\circ}\text{C}$ . To the best of our



**Fig. 1** DSC curves of [AC<sub>8</sub>Im]DCA (a) and [AC<sub>12</sub>Im]DCA (b) in a cooling and heating cycle.

knowledge, this is the first report about the hydrophobic RTILs with similar densities to water. Considering that the reversible phase reversion of the IL/H<sub>2</sub>O mixture as the temperature varied may be caused by both the density changes and the variation of water content, the saturated water contents of the ILs [AC<sub>8</sub>Im]DCA at different temperatures were measured using a Karl Fisher coulometer, and the corresponding values at  $10\text{ }^{\circ}\text{C}$ ,  $25\text{ }^{\circ}\text{C}$ , and  $35\text{ }^{\circ}\text{C}$  are  $2.99\text{ wt}\%$ ,  $3.12\text{ wt}\%$ , and  $3.40\text{ wt}\%$ , respectively.

Obviously, the ILs' densities decrease as the chain lengths of the substituents increase (Table 2), which may be attributed to the increased number of interstices between ions caused by the more bulky cations which cannot pack closely with the anion. Moreover, the electron deficiency of the allyl group is also partly responsible for the low density of the ILs. The effect of temperature on densities for these dicyanamide salts was also investigated. As expected, the densities of the ILs decreased linearly with increasing temperature (Fig. 3). As potential heat-storage or heat-transfer fluids, ILs possess many special advantages that traditional liquids do not, such as low volatility, good thermal stability, high heat storage density, good heat conductivity, etc. Thus, the coefficients of volume thermal expansion ( $\alpha$ ) of the ILs are very important data for IL application in many areas involving thermodynamics and engineering. However, up to now, the relative data are still deficient. Here, these coefficients of the studied ILs are calculated in this work. According to the definition of thermal expansion coefficient ( $\alpha$ ),

$$\alpha \equiv (1/V)(\partial V/\partial T)_p = -(\partial \ln \rho/\partial T)_p \quad (1)$$

where  $\alpha$  is the thermal expansion coefficient,  $V$  is the molar volume,  $\rho$  is the density,  $T$  is the temperature. The  $\alpha$  values of

**Table 1** Thermal properties of nine RTILs

ILs	H <sub>2</sub> O <sup>a</sup> (ppm)	$T_g^{b/\circ}\text{C}$	$C_p^{d/\text{J g}^{-1}\text{ }^{\circ}\text{C}^{-1}}$	$E_s^e/\text{MJ m}^{-3}$	$T_d^f/\text{ }^{\circ}\text{C}$
[AC <sub>4</sub> Im]DCA	536	-81.6	2.0	209.2	253
[AC <sub>6</sub> Im]DCA	684	-88.5	2.1	214.8	254
[AC <sub>8</sub> Im]DCA	842	-87.6	2.2	221.5	266
[AC <sub>10</sub> Im]DCA	987	-82.7	2.1	217.4	255
[AC <sub>12</sub> Im]DCA	1043	$-2.2^c$	2.5	243.5	256
[AC <sub>14</sub> Im]DCA	1016	$14.5^c$	2.5	240.8	265
[AVIm]DCA	572	-85.9	2.3	257.1	228
[VC <sub>8</sub> Im]DCA	1012	-75.4	1.9	196.7	232
[VC <sub>10</sub> Im]DCA	1049	-74.4	2.0	200.6	235

<sup>a</sup> Water content. <sup>b</sup> Glass transition temperature. <sup>c</sup> Melting point. <sup>d</sup> Heat capacity at  $25\text{ }^{\circ}\text{C}$ . <sup>e</sup> Sensible heat storage density ( $E_s$ ),  $E_s = \rho C_p > \Delta T$ ,  $\Delta T = 100\text{ }^{\circ}\text{C}$ . <sup>f</sup> Thermal decomposition temperature.

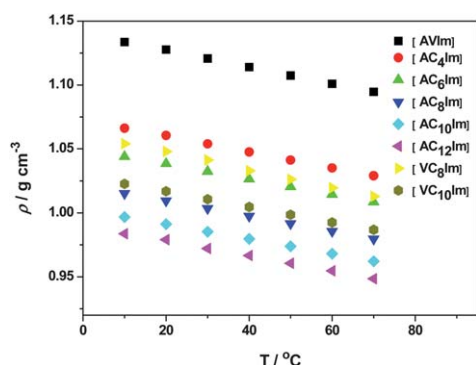
**Table 2** Part physicochemical properties of nine ILs at 25 °C

ILs	$\rho^a/\text{g cm}^{-3}$	$\alpha^b/10^{-4} \text{ K}^{-1}$	$\eta^c/\text{cP}$	$\sigma^d/\text{mN m}^{-1}$	$\kappa^e/\text{mS cm}^{-1}$	$n^f$
[AC <sub>4</sub> Im]DCA	1.046	5.97	24.3	42.1	7.50	1.514
[AC <sub>6</sub> Im]DCA	1.023	5.80	56.4	38.6	3.55	1.509
[AC <sub>8</sub> Im]DCA	1.007	5.95	87.6	32.7	1.85	1.505
[AC <sub>10</sub> Im]DCA	0.988	5.90	108.6	31.7	1.33	1.499
[AC <sub>12</sub> Im]DCA	0.974	6.14	167.4	31.1	0.87	1.495
[AC <sub>14</sub> Im]DCA	0.963	6.03	287.8	30.5	0.72	1.493
[AVIm]DCA	1.118	5.89	29.7	49.5	10.8	1.545
[VC <sub>8</sub> Im]DCA	1.045	6.75	114.2	32.8	2.91	1.506
[VC <sub>10</sub> Im]DCA	1.013	5.99	293.3	30.6	0.63	1.498
[BMIm]BF <sub>4</sub> <sup>26</sup>	1.260	—	104.2	46.6	3.46	1.4188
[BMIm]PF <sub>6</sub> <sup>26</sup>	1.368	—	352.2	48.8	1.63	1.4083

<sup>a</sup> Density. <sup>b</sup> The coefficient of volume thermal expansion. <sup>c</sup> Viscosity. <sup>d</sup> Surface tension. <sup>e</sup> Conductivity. <sup>f</sup> Refractive index.



**Fig. 2** Reversible phase reversion of a [AC<sub>8</sub>Im]DCA/H<sub>2</sub>O mixture as the temperature varies.



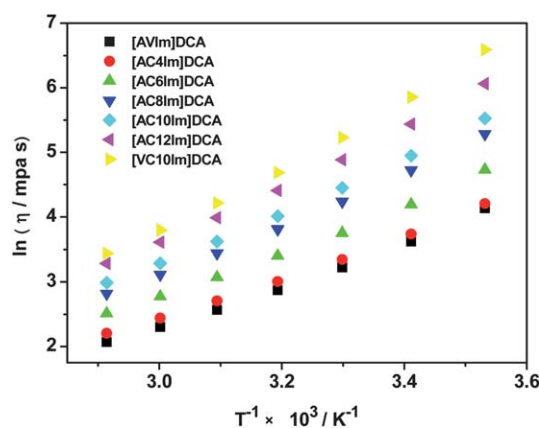
**Fig. 3** Densities of eight ILs as a function of temperature.

these ILs ranged between  $5.80 \times 10^{-4} \text{ K}^{-1}$  and  $6.75 \times 10^{-4} \text{ K}^{-1}$  (Table 2), which are obviously larger than the  $\alpha$  value of mercury ( $1.8 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ ). Therefore, these novel RTILs with low densities may have potential utility as thermosensitive fluids in temperature sensors and other fields involving thermal expansion.

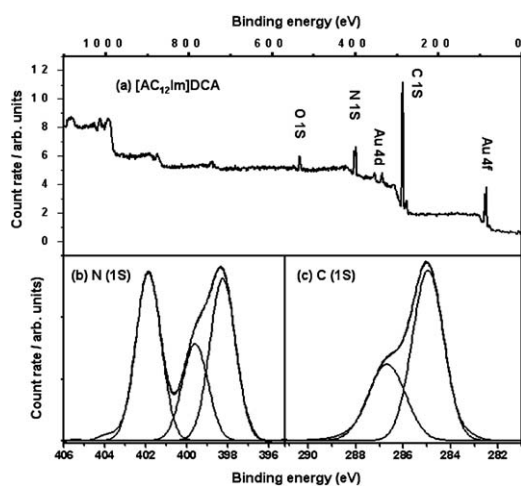
The viscosities of the nine ILs were measured on a Stabinger Viscosimeter SVM 3000/GR. From Table 2, it can be seen that these dicyanamide salts exhibited relatively low viscosities (24.3–293.3 cP at 25 °C), although the ILs possess long chain lengths in the cations. Among them, [AC<sub>4</sub>Im]DCA gave the lowest viscosity (24.3 cP at 25 °C), which is much lower than that of [BMIm]BF<sub>4</sub> (219 cP at 25 °C) but is still much higher than that of [EMIm]DCA (21 cP at 25 °C). The relationship between cation structure and viscosity was also noticeable. That is, the viscosities of the ILs obviously increased as the chain lengths of the cations increased, which might be caused by the increased hydrogen bonding interactions derived from the more bulky cation. It is

obvious that the content of residual water in ILs is also related to the viscosities of ILs, since the removal of water from highly viscous ILs is more difficult under the same conditions. Moreover, the effect of temperature on the viscosities were also investigated, and the Arrhenius plots of viscosity showed that the seven salts were approximately fit by the Arrhenius model over the temperature range 10 °C to 70 °C (Fig. 4).

In comparison with the physico-chemical “bulk” properties of ILs, the studies on the surface properties of ILs are relatively limited. Recently, the XPS technique was proven as a very powerful tool in surface science of ILs, *e.g.* to obtain information about the composition and molecular arrangement of the surface ILs.<sup>24,25</sup> Therefore, here the surface studies of four selected ILs (*i.e.* [AC<sub>*n*</sub>Im]DCA, *n* = 8, 10, 12, 14) utilizing XPS were also performed. Under our analysis conditions, four hydrophobic ILs all showed well-defined characteristic emissions (Fig. 5, Fig. S20–28†), and no obvious degradation of the ILs was observed during or after measuring, which indicated that these ILs appeared to be very stable during exposure to the X-ray source and ultra-high vacuum conditions. Fig. 5 shows the overview scan of [AC<sub>12</sub>Im]DCA film and the high resolution spectra for N 1s and C 1s. From the survey spectrum in Fig. 5a, a small amount of elemental O (O 1s) as a contaminant and elemental Au (Au 4d and Au 4f) as the film substrate were detected, the expected elements N and C were detected, and no evidence of other element impurities could be found, indicating that the surface



**Fig. 4** Arrhenius plots of viscosity for seven dicyanamide ILs.



**Fig. 5** XPS spectra of [AC<sub>12</sub>Im]DCA: survey spectrum (a) and high-resolution spectra dealing with the N 1s (b) and C 1s (c) photoemission.

concentration of other impurities is under the detectable level of XPS.

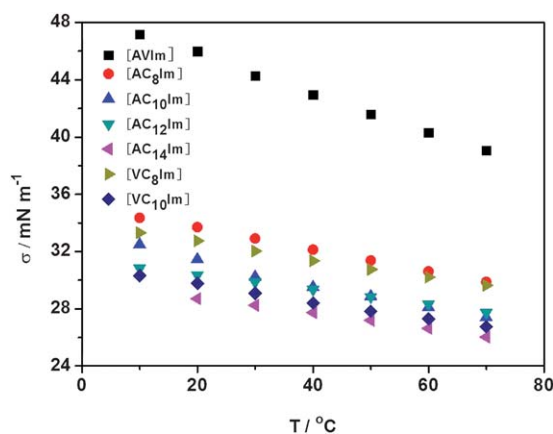
The electron emissions from N 1s and C 1s emissions all displayed well-resolved spectral features (Fig. 5b and c). For N 1s, the signals originate from the three chemically different types of nitrogen atoms in [AC<sub>12</sub>Im]DCA, *i.e.* the signal at 401.9 eV from two nitrogen atoms of the imidazolium cation, the signal at 399.6 eV from two nitrile groups, and the signal at 398.3 eV from the nitrogen ion with a negative charge (Fig. 5b). The ratio of peak areas corresponding to the nitrogen of the imidazolium cation and the nitrile groups is 0.99 : 1 (the theoretical ratio is 1 : 1), suggesting that the actual distribution of the imidazolium cation and the dicyanamide anion at the IL surface is very close to 1 : 1. Moreover, the ratio of peak areas corresponding to the nitrogen ion with a negative charge and the nitrile groups is 1.1 : 2 (the theoretical ratio is 1 : 2), suggesting that the assignment of molecular configuration of the dicyanamide anion is not linear, and the nitrogen ion with a negative charge tends to direct or move toward the interface. As shown in the C 1s spectrum (Fig. 5c), at least two peaks are clearly distinguishable by their binding energies: one peak at 286.6 eV originating from the carbon atoms covalently linked to the seven nitrogen atoms with strong electronegativity, and another peak at 284.9 eV that can be assigned to the thirteen carbon atoms which can not form a covalent bond with the nitrogen atom. The ratio of two peak areas is 13.5 : 7, which is close to the theoretical ratio (13 : 7). This also further proved that the actual distribution of the imidazolium cation and the dicyanamide anion at the IL surface is close to 1 : 1. The survey spectrum and high-resolution spectra dealing with the N 1s and C 1s photoemission for other three ILs are provided in Fig. S20–S28.†

Moreover, the surface tensions ( $\sigma$ ) of nine ILs were also measured, and their  $\sigma$  values at 25 °C ranged from 30.5 mN m<sup>-1</sup> to 49.5 mN m<sup>-1</sup>. Except for [AVIm]DCA, the  $\sigma$  values of the other ILs are obviously lower than those of common [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> based ILs (Table 2). The results also showed that the surface tensions of the ILs strongly depended on their chain lengths, and the  $\sigma$  values increased as the chain lengths of the cations increased. Moreover, the effect of temperature on the

surface tension was also studied, and the  $\sigma$  values decreased linearly with increased temperature (Fig. 6).

Finally, the refractive indices, the ion conductivities and the electrochemical stability of these ILs were studied. As the results in Table 2 show, the refractive indices ranged from 1.493 to 1.545, which are slightly higher than those of traditional [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> based ILs (*e.g.*  $n = 1.4188$  for [BMIm][BF<sub>4</sub>]<sup>-</sup> and  $n = 1.4083$  for [BMIm][PF<sub>6</sub>]<sup>-</sup> at 25 °C). Among them, [AVIm]DCA gave the highest refractive index (1.545) mainly due to the high electron mobility around the allyl and vinyl groups. The ion conductivities ( $\kappa$ ) of the nine ILs ranged from 0.63 mS cm<sup>-1</sup> to 10.8 mS cm<sup>-1</sup>, in which [AVIm][DCA] gave the highest conductivity (Table 2). Obviously, the conductivities of the studied ILs strongly depended on their viscosities, and the  $\kappa$  values decreased as the viscosities increased. According to the conclusions drawn by Grätzel *et al.*,<sup>4b</sup> the ionic conductivity of an IL is mainly determined by its viscosity and ionic size. Therefore, the increased cation size might decrease the rate of ion mobility and increase the viscosity, thereby resulting in the low conductivities of the ILs. Since these ILs exhibited good ionic conductivities, their electrochemical stability of the ILs were evaluated by cyclic voltammetry. Under the same measurement conditions, four selected ILs exhibited the same oxidative potential at *ca.* 1.1 V (Fig. S29–S33†), and their reductive potentials (from -1.7 V to -2.0 V) were obviously different due to the electrochemical stability of the four cations. The low electrochemical stabilities of these ILs are mainly attributed to the high electrochemical activity of the [DCA]<sup>-</sup> anion.

In summary, nine 1-allyl-3-alkylimidazolium ([AC<sub>*n*</sub>Im]) or 1-vinyl-3-alkylimidazolium ([VC<sub>*n*</sub>Im]) dicyanamides (DCA) have been synthesized and characterized. All the salts are liquids at room temperature, and are moisture stable. When the alkyl chains on the cations were hexyl or longer, the resulting dicyanamides exhibited the characteristic of hydrophobicity. Among them, [AC<sub>8</sub>Im]DCA and [AC<sub>10</sub>Im]DCA were found to possess similar densities to water, *i.e.* 1.007 g cm<sup>-3</sup> and 0.988 g cm<sup>-3</sup>, respectively. Interestingly, a reversible phase reversion of a [AC<sub>8</sub>Im]DCA/H<sub>2</sub>O mixture was observed as the temperature varied. Moreover, their physicochemical properties including thermal properties, surface properties, density, viscosity, refractive index, and electrochemical properties, *etc.* and the effect of



**Fig. 6** Surface tensions of seven ILs as a function of temperature.

temperature and alkyl chains on these properties were also comprehensively studied. These functional ILs displayed low glass transition temperatures of below  $-88\text{ }^{\circ}\text{C}$ , high heat capacities of  $1.9\text{--}2.5\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$ , as well as viscosities of  $24.3\text{--}293.3\text{ cP}$  at  $25\text{ }^{\circ}\text{C}$ . Considering these properties and the characteristic of easily polymerized cations, these hydrophobic allyl- or vinyl-functionalized ILs are potential precursors for syntheses of conducting polymeric materials with special functionality and applications.

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## Notes and references

- 1 P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, VCH, Weinheim, 2003.
- 2 (a) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789; (b) T. J. Geldbach and P. J. Dyson, *J. Am. Chem. Soc.*, 2004, **126**, 8114–8115; (c) R. A. Sheldon, *Green Chem.*, 2005, **7**, 267–278; (d) D. Zhao, M. Wu, Y. Kou and E. Min, *Catal. Today*, 2002, **74**, 157–189.
- 3 (a) J. G. Huddlestou, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766; (b) A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz and P. Wasserscheid, *Chem. Commun.*, 2001, 2494–2495.
- 4 (a) H. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, Inc., New Jersey, 2005; (b) B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740; (c) M. Forsyth, J. Huang and D. R. MacFarlane, *J. Mater. Chem.*, 2000, **10**, 2259–2265.
- 5 C. Ye, W. Liu, Y. Chen and L. Yu, *Chem. Commun.*, 2001, 2244.
- 6 B. Weyershausen and K. Lehmann, *Green Chem.*, 2005, **7**, 15–19.
- 7 W. L. Hough, M. Smiglak, H. Rodríguez, R. P. Swatloski, S. K. Spear, D. T. Daly, J. Pernak, J. E. Grisel, R. D. Carliss, M. D. Soutullo, J. D. Davis and R. D. Rogers, *New J. Chem.*, 2007, **31**, 1429–1436.
- 8 (a) H. G. Joglekar, I. Rahman and B. D. Kulkarni, *Chem. Eng. Technol.*, 2007, **30**, 819–828; (b) M. E. V. Valkenburg, R. L. Vaughn, M. Williams and J. S. Wilkes, *Thermochim. Acta*, 2005, **425**, 181–188.
- 9 (a) A. J. Boydston, C. S. Pecinovskiy, S. T. Chao and C. W. Bielawski, *J. Am. Chem. Soc.*, 2007, **129**, 14550–14551; (b) S. Tang, A. Babai and A. Mudring, *Angew. Chem., Int. Ed.*, 2008, **47**, 7631–7634.
- 10 C. Ye and J. M. Shreeve, *J. Org. Chem.*, 2004, **69**, 6511.
- 11 D. Gerhard, S. C. Alpaslan, H. J. Gores, M. Uerdingen and P. Wasserscheid, *Chem. Commun.*, 2005, 5080–5081.
- 12 M. Deeltf, K. R. Seddon and M. Shara, *New J. Chem.*, 2006, **30**, 317–326.
- 13 (a) H. Xue and J. M. Shreeve, *Adv. Mater.*, 2005, **17**, 2142–2146; (b) A. R. Katritzky, S. Singh, K. Kirichenko, M. Smiglak, J. D. Holbrey, W. M. Reichert, S. K. Spear and R. D. Rogers, *Chem.–Eur. J.*, 2006, **12**, 4630–4641.
- 14 D. R. MacFarlane, P. Meakin, J. Sun, N. Amini and M. Forsyth, *J. Phys. Chem.*, 1999, **103**, 4164–4170.
- 15 E. D. Bates, R. D. Mayton, I. Ntai and J. H. Davis, Jr, *J. Am. Chem. Soc.*, 2002, **124**, 926–927.
- 16 H. Itoh, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 2004, **126**, 3026–3027.
- 17 J. Kagimoto, S. Taguchi, K. Fukumoto and H. Ohno, *J. Mol. Liq.*, 2010, **153**, 133–138.
- 18 Q. Zhang, S. Liu, Z. Li, J. Li, Z. Chen, R. Wang, L. Lu and Y. Deng, *Chem.–Eur. J.*, 2009, **15**, 765–778.
- 19 J. Yang, Q. Zhang, L. Zhu, S. Zhang, J. Li, X. Zhang and Y. Deng, *Chem. Mater.*, 2007, **19**, 2544–2550.
- 20 Z. Du, Z. Li, S. Guo, J. Zhang, L. Zhu and Y. Deng, *J. Phys. Chem. B*, 2005, **109**, 19542–19546.
- 21 (a) D. R. MacFarlane, J. Huang and M. Forsyth, *Nature*, 1999, **402**, 792–794; (b) C. M. Forsyth, D. R. MacFarlane, J. J. Golding, J. Huang, J. Sun and M. Forsyth, *Chem. Mater.*, 2002, **14**, 2103–2108.
- 22 A. Diedichs and J. Gmehling, *Fluid Phase Equilib.*, 2006, **244**, 68–77.
- 23 Thermanol VP-1 Heat-transfer fluid by Solutia. Technical Bulletin 7239115B; on Thermanol Reference Disk available from Solutia Inc.; <http://www.therminol.com/>.
- 24 (a) E. F. Smith, I. J. V. Garcia, D. Briggs and P. Licence, *Chem. Commun.*, 2005, 5633–5635; (b) D. S. Silvester, T. L. Broder, L. Aldous, C. Hardacre, A. Crossley and R. G. Compton, *Analyst*, 2007, **132**, 196–198; (c) F. Maier, J. M. Gottfried, J. Rossa, D. Gerhard, P. S. Schulz, W. Schwieger, P. Wasserscheid and H.-P. Steinrück, *Angew. Chem., Int. Ed.*, 2006, **45**, 7942–7944.
- 25 (a) O. Höfft, S. Bahr, M. Himmerlich, S. Krischok, J. A. Schaefer and V. Kempter, *Langmuir*, 2006, **22**, 7120–7123; (b) V. Lockett, R. Sedev, C. Bassell and J. Ralston, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1330–1335.
- 26 (a) J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156–164; (b) Q. Zhang, Z. Li, J. Zhang, S. Zhang, L. Zhu, J. Yang, X. Zhang and Y. Deng, *J. Phys. Chem. B*, 2007, **111**, 2864–2872.