

Insight into the Phase Equilibrium Phenomena of Systems Containing Dienes and Dicyanamide Ionic Liquids as a New Potential Application

Ewa Bogel-Łukasik,^{*,†} Catarina Lourenço,[†] Małgorzata E. Zakrzewska,[†] and Rafał Bogel-Łukasik[‡]

REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal, and Unit of Bioenergy, Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar 22, 1649-038, Lisboa, Portugal

Received: July 29, 2010; Revised Manuscript Received: October 22, 2010

This work presents a systematic investigation into liquid–liquid phase equilibria for systems containing three various ionic liquids and four dienes as they have not been reported yet. The systems employed in this study containing dicyanamide based ionic liquids and dienes reveal the phase envelopes that have a similar shape to binodal curves with the upper critical solution temperature. Generally, 1-methyl-3-octylimidazolium dicyanamide ([C₈mim][DCA]) was found to be a better solvent for nonpolar dienes. The 1-butyl-3-methylimidazolium dicyanamide ([C₄mim][DCA]) ionic liquid is a much worse solvent for 1,5-cyclooctadiene, 1,3-cyclooctadiene, 1,5-hexadiene, and 1,7-octadiene compared to other ionic liquids studied. The miscibility gaps shrink for a less polar [C₈mim][DCA] or even more for 1-dodecyl-3-methylimidazolium dicyanamide ([C₁₂mim][DCA]). In the range of the studied temperatures, the solubility of dienes is significantly higher compared to the solubility of the ionic liquids containing the shorter alkyl chain in the cation. The solubility of the presented dienes in ([C₄mim][DCA]) ionic liquid is also relatively high and may reach up to 0.19 mol fraction of the diene. The attained results demonstrate that nonpolar compounds can be dissolved to some extent in highly charged and polar solvents such as ionic liquids.

Introduction

Nowadays, ionic liquids (ILs) constitute a class of substances with a continuously growing number of compounds. Their various structures and properties offer wide possibilities for both fundamental studies and practical applications. Currently, ILs are defined as ionic compounds (salts) that possess glass transition and/or melting points below 100 °C. It is true that some of the “green” aspects of ionic liquids (toxicity and biodegradability) are still under discussion and are the origin of both problems and challenges.¹ A field of ionic liquids offers a phenomenal opportunity for new science and technology. For any application of an ionic liquid the physical properties and solvent behavior are a key feature. Properties of ILs such as low volatility² and outstanding thermal stability³ yet make them good candidates for alternative solvents⁴ and (co)catalysts.^{5,6} Based on the extraordinary properties of ILs, some industrial scale processes involving ionic liquids such as Basil,⁷ hydrosilylation process,⁸ or Difasol⁹ have been developed.¹⁰ Nevertheless, a global research on ILs seems to be still in its infancy employing mainly ILs based on alkylimidazolium as a cation and several inorganic anions such as [BF₄], [PF₆], and [CF₃SO₃].¹¹ Among the various groups of ionic liquids, dicyanamide ([N(CN)₂] = [DCA]) based ionic liquids are ones less studied. Apart from the general properties common for other ionic liquids, dicyanamide ILs have a huge advantage, which is their low viscosity.¹² Due to the low viscosity, dicyanamide ILs can be potentially used without any additional solvents that reduce viscosity in reactions requiring good mass transfer. Ionic

liquids due to their complex nature, existence of polar and nonpolar domains, have versatile solvent–solute properties and reveal broad variety of phase behaviors.^{13–17}

Liquid–liquid equilibria (LLE) of (ionic liquid + diene) solutions exhibit latent interest because dienes are important reagents in many chemical reactions in the presence of ILs. Dienes and ILs are very attractive compounds, mostly due to their prospective application. Employment of an ionic liquid in many classical processes results in production of the required compounds. Hydration of diene and dihydromyrcene in ionic liquids proceeded to a selective production of dihydromyrcenol.¹⁸ Use of ionic liquids in the hydrogenation of another diene, limonene¹⁹ in supercritical carbon dioxide, has driven the process toward the intermediate product.⁶ On the other hand, an interest in the telomerization processes has increased continuously. For example, the Kuraray telomerization of butadiene with water, with subsequent double bond reduction was reported to yield a linear 1-octanol.²⁰ The most often studied diolefin for telomerization with alcohols is 1,3-butadiene due to its low price and high reactivity.²¹ Isoprene (2-methyl-1,3-butadiene)²² has also been studied extensively due to the potential route to produce synthetic steroids. Furthermore, cyclic 1,3-dienes were investigated as well in the past.²³ Cyclopentadiene, 1,3-cyclohexadiene, 1,3-cyclooctadiene, and other cyclic olefins were employed in telomerization, which produce required compounds with a high yield and selectivity. Recently, a new trend has involved long-chain dienes²⁴ instead of popularly used 1,3-butadiene or isoprene. However, extending the telomerization reaction to long-chain dienes would open up new opportunities for building high molecular weight and value-added functionalized molecules. An attractive potential source of long-chain dienes is fatty acids obtained from renewable feedstocks.

* Corresponding author. Tel: +351 212948353. Fax: +351 2948550. E-mail address: ewa@dq.fct.unl.pt.

[†] Universidade Nova de Lisboa.

[‡] Laboratório Nacional de Energia e Geologia.

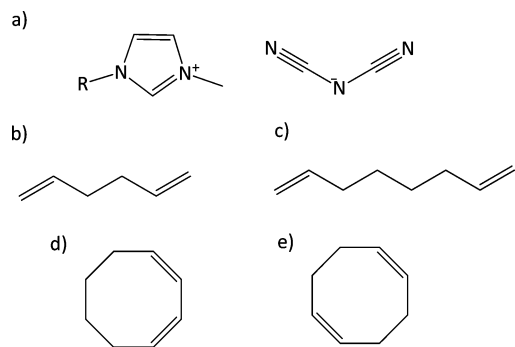


Figure 1. Structures of ionic liquids and dienes used in this investigation: (a) for $R = 4$, 1-butyl-3-methylimidazolium dicyanamide, for $R = 8$, 1-methyl-3-octylimidazolium dicyanamide, for $R = 12$, 1-dodecyl-3-methylimidazolium dicyanamide; (b) 1,5-hexadiene; (c) 1,7-octadiene; (d) 1,3-cyclooctadiene; (e) 1,5-cyclooctadiene.

A perspective in telomerization processes of dienes might be the use of low viscosity dicyanamide ionic liquids that could modify the selectivity of the process.^{6,18} To proceed successfully, the solubility data of dienes in the selected less viscous representatives of ionic liquids, which allows an easier operation of the processes, would be required. Investigations into the solubilities of systems containing diene and IL have been initiated recently⁶ by reporting data for *p*-mentha-1,8-diene (limonene, dipentene) at 323.15 K.

Our work presents a systematic study on influence of the temperature and a structural arrangement of ionic liquid and diene on solubility. Dienes as hydrocarbons are generally nonpolar compounds capable to form relatively weak van der Waals dispersive interactions. Conversely, ionic liquids due to their diverse nature present broad range of potential interactions such as Coulombic, dispersive, π - π , n - π , hydrogen bonding, dipolar, and ionic/charge-charge.^{3,13-16,25,26} A mutual interaction between these two different chemical species is interesting because even a subtle difference in unsaturated hydrocarbons leads to significant changes in solubility having a practical effect on chemical processes.⁶

In the current work, the mutual solubility in solutions of imidazolium-based ionic liquids, possessing dicyanamide anion ([C_n mim][DCA], $n = 4, 8$, or 12) and 1,5-hexadiene, 1,7-octadiene, 1,3-cyclooctadiene, or 1,5-cyclooctadiene, was investigated. Structures of ionic liquids and dienes referred to in this research are shown in Figure 1. In the cases of partial miscibility, the temperature-composition liquid-liquid equilibrium phase diagrams were determined.

Experimental Section

Materials. 1,5-Hexadiene was purchased from TCI Europe with the stated purity above 98% mass. 1,3-Cyclooctadiene was obtained from Fluka, with the purity $\geq 98\%$ mass; 1,7-octadiene and 1,5-cyclooctadiene were purchased from Sigma, with the stated purity of 98% mass and 99% mass, respectively. All dienes were additionally dried using 3 Å molecular sieves. Ionic liquids [C_4 mim][DCA], [C_8 mim][DCA], and [C_{12} mim][DCA] were obtained from Solchemar, Lisbon, Portugal, with the stated purity of 98% (mass). They were all further thoroughly degassed, dried, and freed from any small traces of volatile compounds by applying vacuum (0.1 Pa) at moderate temperature (60 °C). All drying procedures were carried out for 2 days, and fresh samples of components were used to prepare solutions, always immediately prior to measurements. The Karl-Fischer titrations revealed the water contents as follows: 1,5-hexadiene,

150 ppm; 1,3-cyclooctadiene, 180 ppm; 1,7-octadiene, 160 ppm; 1,5-cyclooctadiene, 210 ppm; [C_4 mim][DCA], 480 ppm; [C_8 mim][DCA], 400 ppm; [C_{12} mim][DCA], 620 ppm.

Experimental Procedure. A detailed description of experimental procedure was presented elsewhere.¹⁶ The liquid-liquid equilibrium (LLE) temperature-composition phase diagrams were obtained at an ambient pressure of 0.1 MPa and in the temperature range 295–418 K, using a visual method: an eye observation of turbidity (cloud point) that preceded the phase separation. An upper temperature limit was always determined by the boiling point of diene (1,5-hexadiene, 333.15 K; 1,7-octadiene, 387.15 K; 1,3-cyclooctadiene, 415.15 K; 1,5-cyclooctadiene, 422.15 K). Experiments were carried out in a Pyrex-glass cell equipped with a magnetic stirrer. The cell could be opened or closed by a Teflon valve placed at the end of the neck. It allowed the cell to be deeply immersed in a temperature controlled bath, while at the same time diminished losses caused by evaporation. A 2 L glass beaker used as a thermostat bath was filled with thermostatic liquid, water (293–333 K), or silicon oil (333–418 K). A temperature was monitored using a Pt100 temperature probe having an accuracy of ± 0.03 K. The solutions were prepared in the cell using the gravimetric method. The compositions were measured using a Mettler AT201 analytical semimicrobalance with a stated accuracy (repeatability) of $\pm 2 \times 10^{-5}$ in mass fraction.

In each LLE experiment, a heterogeneous solution was continuously heated with a constant stirring from room temperature until it (eventually) became homogeneous. Then, starting from the one-phase region, the solution was cooled off continuously and the temperature at which it became turbid was taken as a cloud point. The experiments were performed in three to four runs with the last run being carried out very slowly (the rate of temperature change near the expected cloud point was no more than 5 K h⁻¹).

Results and Discussion

ILs have been investigated for a wide variety of reaction, separation and extraction processes that require knowledge on phase behavior. The imidazolium (1-butyl-3-methylimidazolium, 1-methyl-3-octylimidazolium, and 1-dodecyl-3-methylimidazolium) dicyanamide ionic liquids and dienes (1,5-hexadiene, 1,7-octadiene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene) have been chosen as systems studied in this work. The mentioned ionic liquids are one of the most popular ionic liquids studied among numerous dicyanamide ILs. Selected dienes were examined to demonstrate an effect of the alkyl chain length of diene and cyclization of the molecule on solubility in ionic liquids. The liquid-liquid equilibrium diagrams present shapes typical for diagrams with upper critical solution temperature (UCST). The phase envelope for systems containing [C_4 mim][DCA] and investigated dienes is shown in Figure 2, while Figures 3 and 4 illustrate mutual solubility of the examined dienes in [C_8 mim][DCA] and [C_{12} mim][DCA] ionic liquid. Comparison of phase diagrams for systems containing [C_4 mim][DCA] or [C_8 mim][DCA] or [C_{12} mim][DCA] and 1,5-cyclooctadiene or 1,3-cyclooctadiene is presented in Figure 5.

The experimental technique used in this research allowed us to obtain the ionic liquid-rich side of the binodal curve. Solubility of ionic liquid in the diene-rich phase was found to be below the detection limit of the technique used. Nevertheless, the aim of this study was to examine the solubility (LLE) of dienes in ILs as a potentially data interested for designing the reaction (e.g., telomerization) conditions. From results achieved it can be concluded that generally 1,7-octadiene is the least

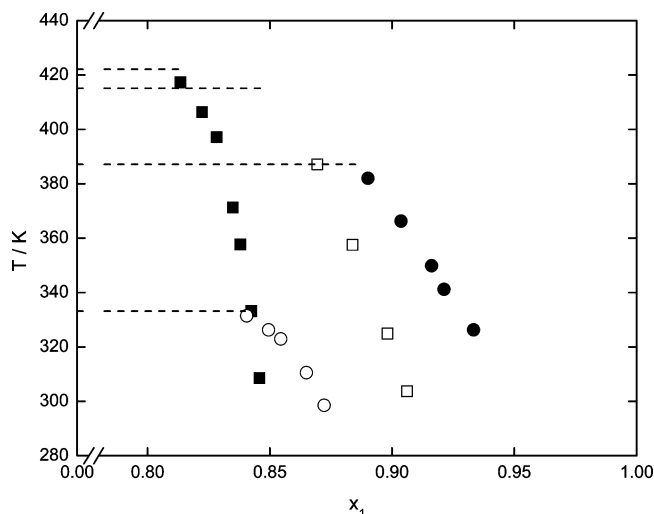


Figure 2. Phase envelopes for systems containing [C₄mim][DCA] and dienes: 1,5-hexadiene (○); 1,7-octadiene (●); 1,3-cyclooctadiene (□); 1,5-cyclooctadiene (■). The dashed lines designate boiling temperatures of the dienes.

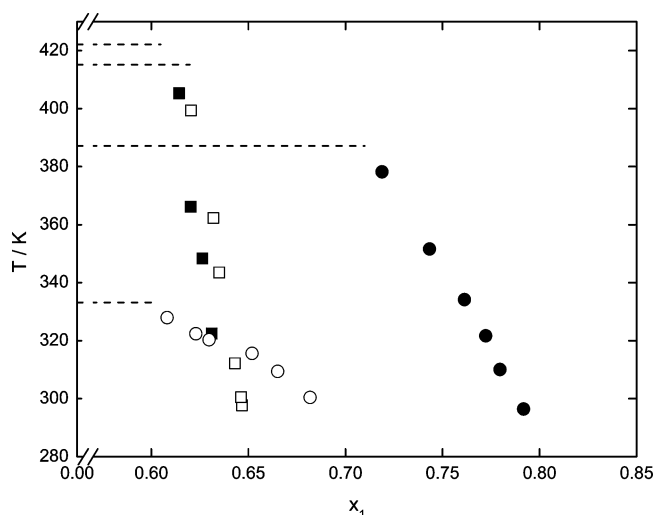


Figure 3. Phase diagrams of systems consisting of [C₈mim][DCA] and dienes: 1,5-hexadiene (○); 1,7-octadiene (●); 1,3-cyclooctadiene (□); 1,5-cyclooctadiene (■). The dashed lines represent the boiling points of the dienes.

soluble in ionic liquids used in this investigation. Next, it can be assumed that solubility is higher for 1,3-cyclooctadiene and even more for 1,5-cyclooctadiene. Analysis of solubility of 1,5-hexadiene in ionic liquids shows that it is significantly higher than the solubility of the 1,7-octadiene; however, a low boiling point of 1,5-hexadiene has limited studies to the temperature of 328 K.

Summarizing, from the solubility data it can be concluded that for all ionic liquids the system with 1,5-hexadiene exhibits a lower miscibility gap contrary to systems with 1,7-octadiene. This feature might be caused by the difference in size of molecules of solute and solvent (diene and ionic liquid) that leads to a larger entropic effect. This usually leads to a negative deviation from the ideal solubility that might explain why 1,5-hexadiene (smaller molecular mass) is more soluble in dicyanamide ionic liquids than 1,7-octadiene. Furthermore, considering length of the alkyl chain in the cation of the ionic liquid it can be assumed that a larger cation of ionic liquid (C₁₂ versus C₈ and C₄) is also responsible for an improvement of solubility of dienes in ionic liquids.

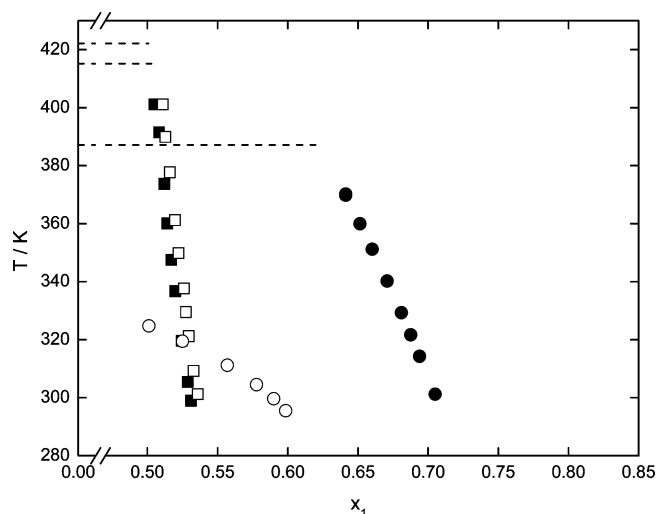


Figure 4. LLE phase diagram for systems containing [C₁₂mim][DCA] and dienes: 1,5-hexadiene (○); 1,7-octadiene (●); 1,3-cyclooctadiene (□); 1,5-cyclooctadiene (■). The dashed lines represent the boiling points of the dienes.

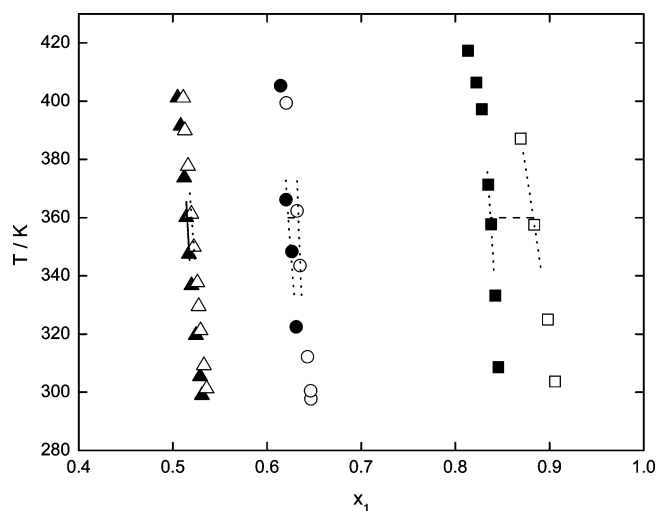


Figure 5. Comparison of phase diagrams for systems containing [C₈mim][DCA] + 1,5-cyclooctadiene (●) or 1,3-cyclooctadiene (○); [C₄mim][DCA] + 1,5-cyclooctadiene (■) or 1,3-cyclooctadiene (□); and [C₁₂mim][DCA] + 1,5-cyclooctadiene (▲) or 1,3-cyclooctadiene (△). The dotted lines represent the trend of the bimodal lines, while the horizontal dashed lines illustrate differences in solubility between 1,5-cyclooctadiene and 1,3-cyclooctadiene in dicyanamide ILs studied.

Observed differences in solubility can be caused by the entropic effect and by a polarity of the investigated ionic liquids; because [C₄mim][DCA] is more polar than [C₈mim][DCA] and such a difference is more visible when [C₁₂mim][DCA] is considered. The additional carbons in the side alkyl chain reduce the hydrogen bond acidity (α) and dipolarity/polarizability effect (π^*), which are the most sensitive on polarity of the cation among all of the Kamlet–Taft parameters.^{27–30} Moreover, additional carbons in the alkyl chain generate a possibility for formation of dispersive van der Waals interactions between less polar domains of the IL cation and nonpolar alkyl chains of dienes. For these reasons, the solubility of all dienes studied in less polar [C₁₂mim][DCA] ionic liquid was found to be higher compared to those in [C₈mim][DCA] and [C₄mim][DCA].

The results obtained for systems with both cyclooctadienes are particularly interesting. In systems with all employed ionic liquids, 1,5-cyclooctadiene is more soluble than 1,3-cyclooctadiene. Comparing differences between the solubility of 1,3-

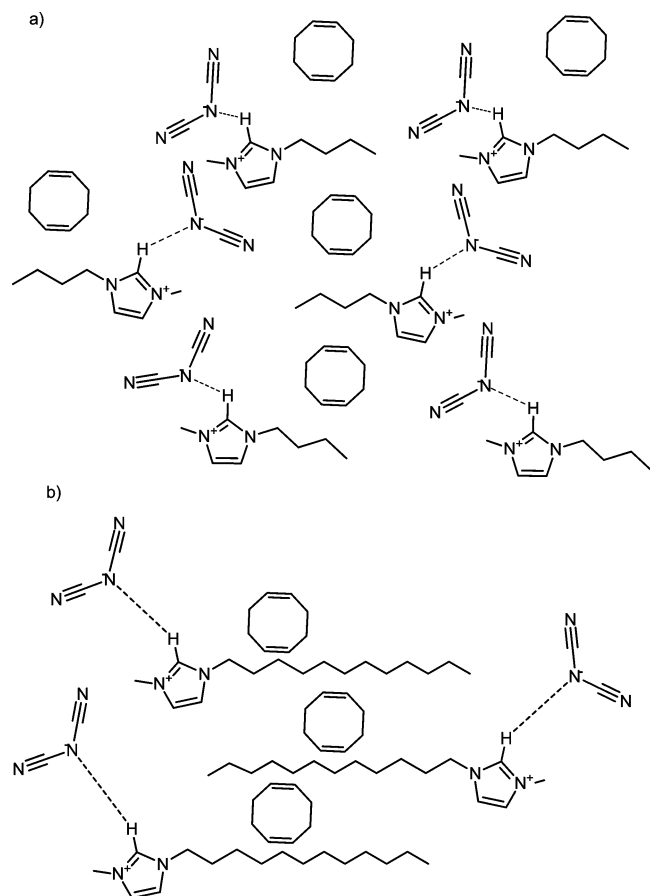


Figure 6. Structural arrangement of ionic liquids and cyclooctadienes. (a) illustrates a system with $[C_4mim][DCA]$, where dotted bonds represent short-distance, strong hydrogen bonds. 1,5-Cyclooctadiene is presented as an example of a dissolved olefin molecule in the compact ionic liquid structure. (b) discloses a system containing $[C_{12}mim][DCA]$ and 1,5-cyclooctadiene as a representative of dienes dissolved. The less constrained structure of the diene and cation of $[C_{12}mim][DCA]$ is an effect of the short-distance van der Waals forces between these two species and weak, long-distance, hydrogen bond interactions between the cation and anion of ionic liquid represented by long dashed bonds. The acidity of the H(4) and H(5) protons and other less significant specific and nonspecific interactions between the cation and anion of the ionic liquid are omitted to improve the clarity of the figure.

cyclooctadiene and 1,5-cyclooctadiene in $[C_4mim][DCA]$ and $[C_8mim][DCA]$, one can see that it diminishes from 0.05 to 0.01 at 360 K for $[C_4mim][DCA]$ and $[C_8mim][DCA]$ ionic liquids, respectively. For $[C_{12}mim][DCA]$ such a difference is even smaller and equals 0.005 of mole fraction; however, 1,5-cyclooctadiene still remains more soluble than 1,3-cyclooctadiene. The aforementioned differences between solubilities are demonstrated in Figure 6 as horizontal dashed lines.

Results on the solubility of 1,3-cyclooctadiene and 1,5-cyclooctadiene are intriguing. A careful analysis of structures of ionic liquids and dienes might disclose a possible reason of these differences. The position of C=C double bonds in 1,5-cyclooctadiene immobilizes a structure almost completely, making it a quasi-plane, which does occur partially in the 1,3-cyclooctadiene skeleton. The quasi-plane structure of 1,5-cyclooctadiene allows forming channels for dienes in a very compact and strong “sandwich” structure of ionic liquids, where the ionic liquid cation and solute interrelate in an alternating structure through π and $n-\pi$ interactions with the ionic liquid anions arranged around this complex. The illustration of this structure arrangement is shown in Figure 6a. A structural

organization for $[C_1mim][PF_6]$ and benzene³¹ confirms the aforesaid hypothesis regarding $[C_4mim][DCA]$ + 1,5-cyclooctadiene. Formation of a similar complex structure for the second isomer (1,3-cyclooctadiene) is not entirely possible because the alkyl chain of 1,3-cyclooctadiene is flat only in the domain of the C=C double bonds. The remaining part of the chain might form a spacious skeleton and consequently the strong and compact ionic liquid structure would be less accessible for 1,3-cyclooctadiene that can lead to a decrease of 1,3-cyclooctadiene solubility in a certain ionic liquid. The aforementioned structural organization can be considered as the most pronounced for good proton donor ionic liquid such as $[C_4mim][DCA]$, in which H(2) proton exhibits a strong acidic character. The H(4) or H(5) protons were reported to reveal weak but measurable acidity.^{32–34} The structural arrangement of $[C_4mim][DCA]$ ionic liquid could be governed by strong hydrogen bonds (presented as short and bolded dotted bonds in Figure 6a) as well as other specific and nonspecific interactions (i.e., $n-\pi$, dipole–dipole, ionic/charge–charge). Since a strong and packed structure of ionic liquid is more constrained for a spacious 1,3-cyclooctadiene, solubility is lower than in $[C_8mim][DCA]$ or even in $[C_{12}mim][DCA]$.

Solubilities of 1,3-cyclooctadiene in ionic liquids with a longer alkyl chain in the cation, $[C_8mim][DCA]$ or $[C_{12}mim][DCA]$, can be attributed to the van der Waals forces responsible for formation of organized structure due to presence of a long alkyl chain of the cation. The hydrogen bond (long dotted bonds in Figure 6b) and other types of aforementioned interactions are weak and do not play a crucial role in this alignment. The van der Waals forces, which might be dominant, are less sparsely constrained and enhance solubility for both 1,3- and 1,5-cyclooctadiene. In other words, a longer alkyl chain of cation diminishes differences in solubility of both cyclooctadiene isomers, making the ionic liquid no longer selective toward one of the dienes. A schematic visualization of the discussed possible structural arrangement of $[C_4mim][DCA]$ and $[C_{12}mim][DCA]$ solutions is presented in Figure 6.

The presented LLE phase diagrams show that the structural isomers of octadienes differentiate solubility in ionic liquids. Systems with aliphatic 1,7-octadiene exhibit much lower solubility compared to either 1,3-cyclooctadiene or 1,5-cyclooctadiene systems. From this information the conclusion about the cyclization impact on solubility can be withdrawn. The results allow us to assume that closing of the aliphatic ring enhances solubility and reduces a miscibility gap. It can be explained by differences in the molecular volume of aliphatic and cyclic isomers of octadiene. Cyclooctadiene molecules have molecular volumes smaller than a linear octadiene, and thus, cyclooctadienes have higher solubilities than their aliphatic analogue. This observation finds the confirmation in the work of Domańska et al.³⁵ who elucidated this by a packing effect.

Conclusions

Summarizing, this work showed that imidazolium ionic liquids exhibit very distinct solvent abilities toward dienes studied. The $[C_4mim][DCA]$ ionic liquid is a much worse solvent for 1,5-cyclooctadiene, 1,3-cyclooctadiene, 1,5-hexadiene, and 1,7-octadiene compared to other ILs tested. The miscibility gaps shrink for a less polar $[C_8mim][DCA]$ or more for $[C_{12}mim][DCA]$. In the range of temperatures studied, the solubility of dienes is significantly higher compared to that of the ionic liquids consisting of the shorter alkyl chain in the cation. Dissimilarities in solubility of 1,3- and 1,5-cyclooctadiene in the three studied ILs indicate the existence of significant

forces leading to dramatic differences in solubility. A structure of diene and the ability of the cation of an ionic liquid to form the “sandwich” form seem to play an important role in directing the solubility. The quasi-plane structure of 1,5-cyclooctadiene favors the solubility of this diene in ionic liquid in contrast to more movable 1,3-cyclooctadiene that can ruin the structural organization of the ionic liquid sandwich form. The weak van der Waals interactions dominating the long side alkyl chain of the [C₁₂mim][DCA] cation reduce differences between solubilities of 1,3- and 1,5- isomers of cyclooctadiene due to the less formalized net created by the mentioned ionic liquid. Additionally, this weak interaction can explain the fact that [C₁₂mim][DCA] is no longer selective toward the solubility of both cyclooctadienes.

The attained results demonstrate that nonpolar compounds can be dissolved to some extent in highly charged and polar solvents such as ionic liquids. The achieved solubility results provide crucial data that are important for design of conditions of the future reactions with dienes in ionic liquids as solvents; for example, a telomerization of dienes accompanied by the use of an ionic liquid as a solvent.

Acknowledgment. This work was supported by the Fundação para a Ciência e a Tecnologia (FCT, Portugal) through the grant SFRH/BPD/26356/2006.

References and Notes

- (1) Stark, A.; Behrend, P.; Braun, O.; Müller, A.; Ranke, J.; Ondruschka, B.; Jastorff, B. *Green Chem.* **2008**, *10*, 1152–1161.
- (2) Paulechka, Y. U.; Kabo, G. J.; Blokhin, A. V.; Vydrov, O. A.; Magee, J. W.; Frenkel, M. J. *J. Chem. Eng. Data* **2003**, *48*, 457–462.
- (3) Domańska, U.; Bogel-Lukasik, R. *J. Phys. Chem. B* **2005**, *109*, 12124–12132.
- (4) Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasik, R. *Energy Fuels* **2010**, *24*, 737–745.
- (5) Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasik, R. *Chem. Rev.* **2010**, doi: 10.1021/cr100171a.
- (6) Bogel-Lukasik, E.; Santos, S.; Bogel-Lukasik, R.; Nunes da Ponte, M. J. *Supercrit. Fluids* **2010**, *54*, 210–217.
- (7) Freemantle, M. *Chem. Eng. News* **2003**, *81*, 9.
- (8) Weyershausen, B.; Hell, K.; Hesse, U. *Green Chem.* **2005**, *7*, 283–287.
- (9) Olivier-Bourbigou, H.; Hugues, F. In *Green Industrial Applications of Ionic Liquids*; Rogers, R. D., Seddon, K. R., Volkov, S., Eds.; NATO Science Series II: Mathematics, Physics and Chemistry; Kluwer: Dordrecht, The Netherlands, 2002; No. 92, p 67.
- (10) Seddon, K. R. *Nat. Mater.* **2003**, *2*, 363–364.
- (11) Perissi, I.; Bardi, U.; Caporali, S.; Lavachi, A.; Pucci, S.; Tolstoguzov, A. *Corros. Sci.* **2006**, *28*, 2349–2362.
- (12) MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G. B. *Chem. Commun.* **2001**, 1430–1431.
- (13) Domańska, U.; Bogel-Lukasik, R. *Fluid Phase Equilib.* **2005**, *233*, 220–227.
- (14) Domańska, U.; Bogel-Lukasik, E.; Bogel-Lukasik, R. *J. Phys. Chem. B* **2003**, *107*, 1858–1863.
- (15) Domańska, U.; Bogel-Lukasik, E.; Bogel-Lukasik, R. *Chem.—Eur. J.* **2003**, *9*, 3033–3041.
- (16) Trindade, C. A. S.; Visak, Z. P.; Bogel-Lukasik, R.; Bogel-Lukasik, E.; Nunes da Ponte, M. *Ind. Eng. Chem. Res.* **2010**, *49*, 4850–4857.
- (17) Domańska, U.; Bogel-Lukasik, E. *Fluid Phase Equilib.* **2004**, *218*, 123–129.
- (18) Davey, P. N.; Earle, M. J.; Hamill, J. T.; Katdare, S. P.; Rooney, D. W.; Seddon, K. R. *Green Chem.* **2010**, *12*, 628–6321.
- (19) Bogel-Lukasik, E.; Fonseca, I.; Bogel-Lukasik, R.; Tarasenko, Y. A.; Nunes da Ponte, M.; Paiva, A.; Brunner, G. *Green Chem.* **2007**, *9*, 427–430.
- (20) Yoshimura, N. In *Applied Homogeneous Catalysis with Organometallic Complexes*; Cornils, B., Herrmann, W. A., Eds.; VCH-Weinheim: Weinheim, Germany, 1996; p 351.
- (21) Jackstell, R.; Harkal, S.; Jiao, H. J.; Spannenberg, A.; Borgmann, C.; Rottger, D.; Nierlich, F.; Elliott, M.; Niven, S.; Cavell, K.; Navarro, O. S.; Viciu, M.; Nolan, S. P.; Beller, M. *Chem.—Eur. J.* **2004**, *10*, 3891–3900.
- (22) Gordillo, A.; Duran Pachon, L.; de Jesus, E.; Rothernberg, G. *Adv. Synth. Catal.* **2009**, *351*, 325–330.
- (23) Afanas'ev, I. B.; Samokhvalov, G. I. *Russ. Chem. Rev.* **1969**, *38*, 318–329.
- (24) Torrente-Murciano, L.; Lapkin, A.; Nielsen, D. J.; Fallis, I.; Cavell, K. J. *Green Chem.* **2010**, *12*, 866–869.
- (25) Bogel-Lukasik, R.; Matkowska, D.; Zakrzewska, M. E.; Bogel-Lukasik, E.; Hofman, T. *Fluid Phase Equilib.* **2010**, *295*, 177–185.
- (26) Bogel-Lukasik, R.; Matkowska, D.; Bogel-Lukasik, E.; Hofman, T. *Fluid Phase Equilib.* **2010**, *293*, 168–174.
- (27) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377–383.
- (28) Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 2886–2894.
- (29) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 3233–3237.
- (30) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027–6038.
- (31) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. *Chem. Commun.* **2003**, 476–477.
- (32) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168–1178.
- (33) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591–595.
- (34) Seddon, K. R.; Stark, A.; Torres, M.-J. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.
- (35) Domańska, U.; Pobudkowska, A.; Eckert, F. *Green Chem.* **2006**, *8*, 268–276.

JP107094N