

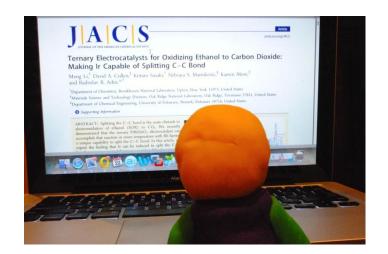
ACS ActiveView PDF



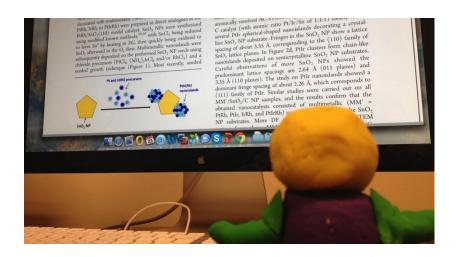


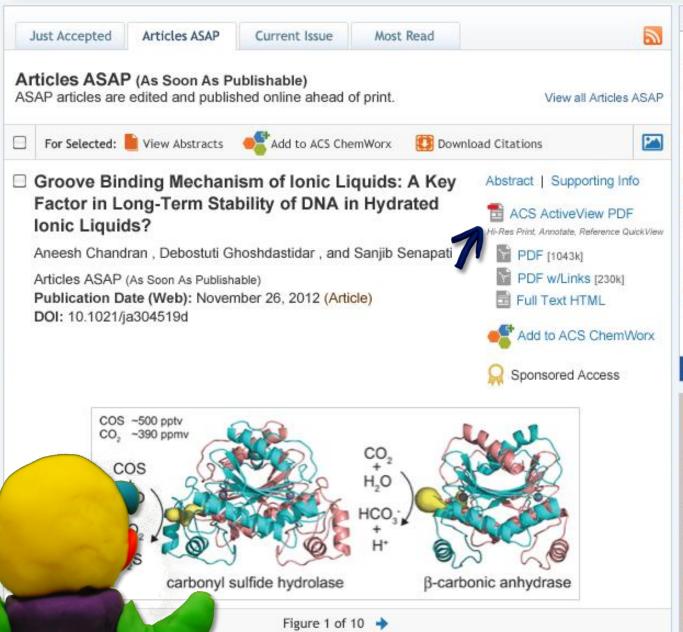
Joel Penner - http://www.flickr.com/photos/featheredtar/2302651444/











JACS Research in C&EN

JACS Research in **C&EN**

Low Temperature Process To Make Crystalline Silicon February 05, 2013

Matyjaszewski Wins AkzoNobel North America Science Award January 28, 2013

Enzymes Steer Toward High Substrate Concentrations January 25, 2013

More Stories »

C&EN Latest News

Peter J. Stang named Priestley Medalist

Congratulations to JACS Editor Peter J. Stang, who will receive the 2013 Priestley Medal



















With ACS ActiveView PDF, you can:

Learn more about ACS ActiveView PDF.

Cite this article while you write.



Add this article to your ACS ChemWorx Library Find it again in your ACS ChemWorx library or return to this page.

Automatically sync your annotations as you work.

Find out more about this and other ACS ChemWorx features.

browser or the ACS ChemWorx apps.

· Access your article and annotations from anywhere, with a









References

- 1. Kutzler, M. A.; Weiner, D. B. Nat. Rev. Genet. 2008, 9, 776-788 [CrossRef] [PubMed] [CAS]
- 2. Jobling, M. A.; Gill, P. Nat. Rev. Genet. 2004, 5, 739-751 [CrossRef] [PubMed] [CAS]
- 3. Krishnan, Y.; Simmel, F. C. Angew. Chem., Int. Ed. 2011, 50, 3124-3156 [CrossRef] [CAS]
- 4. Lukin, M.; de los Santos, C. Chem. Rev. 2006, 106, 607-686 [CrossRef] [PubMed] [CAS]
- 5. Roder, B.; Fruhwirth, K.; Vogl, C.; Wagner, M.; Rossmanith, P. J. Clin. Microbiol. 2010, 48, 4260-4262 [CAS]
- 6. Bonnet, J.; Colotte, M.; Coudy, D.; Couallier, V.; Portier, J.; Morin, B.; Tuffet, S. Nucleic Acids Res. 2010, 38, 1531-1546 [CrossRef] [PubMed] [CAS]
- 7. Kokorin, A., Ed. Ionic Liquids: Applications and Perspectives; InTech: Rijeka, Croatia, 2011.
- Qin, W.; Li, S. F. Y. Analyst 2003, 128, 37-41 [CrossRef] [PubMed] [CAS]
- 9. Nishimura, N.; Nomura, Y.; Nakamura, N.; Ohno, H. Biomaterials 2005, 26, 5558-5563 [CrossRef] [PubMed] [CAS]
- 10. Wang, J. H.; Cheng, D. H.; Chen, X. W.; Du, Z.; Fanq, Z. L. Anal. Chem. 2007, 79, 620-625 [CrossRef] [PubMed] [CAS]
- de Zoysa, R. S. S.; Jayawardhana, D. A.; Zhao, Q.; Wang, D.; Armstrong, D. W.; Guan, X. J. Phys. Chem. B 2009, 113, 13332-13336 [CrossRef] [PubMed] [CAS]
- 12. Vijayaraghavan, R.; Izgorodin, A.; Ganesh, V.; Surianarayanan, M.; MacFarlane, D. R. Angew. Chem., Int.

JACS

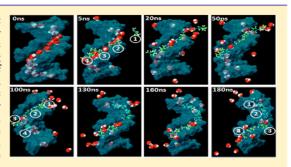
Groove Binding Mechanism of Ionic Liquid Term Stability of DNA in Hydrated Ionic L

Aneesh Chandran, Debostuti Ghoshdastidar, and Sanjib Senapati*

Department of Biotechnology, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

ABSTRACT: Nucleic acid sample storage is of paramount importance in biotechnology and forensic sciences. Very recently, hydrated ionic liquids (ILs) have been identified as ideal media for long-term DNA storage. Hence, understanding the binding characteristics and molecular mechanism of interactions of ILs with DNA is of both practical and fundamental interest. Here, we employ molecular dynamics simulations and spectroscopic experiments to unravel the key factors that stabilize DNA in hydrated ILs. Both simulation and experimental results show that DNA maintains the native B-conformation in ILs. Simulation results further suggest that, apart from the electrostatic association of IL cations with the DNA backbone, groove binding of IL cations through



hydrophobic and polar interactions contributes significantly to DNA stability. Circular dichroism spectral measurements and fluorescent dye displacement assay confirm the intrusion of IL molecules into the DNA minor groove. Very interestingly, the IL ions were seen to disrupt the water cage around DNA, including the spine of hydration in the minor groove. This partial dehydration by ILs likely prevents the hydrolytic reactions that denature DNA and helps stabilize DNA for the long term. The detailed understanding of IL-DNA interactions provided here could guide the future development of novel ILs, specific for nucleic acid solutes.

1. INTRODUCTION

DNA, apart from being a natural biological information carrier,

utilizes the basic natural principles of anhydrobiosis, is becoming a more attractive alternative to the conventional

View Supporting Information

← Page

1 of 10 →















References

16. Perez, A.; Marchan, I.; Svozil, D.; Sponer, J.; Cheatham, T. E., III; Laughton, C. A.; Orozco, M. Biophys. J. 2007, 92, 3817-3829 [CrossRef] [PubMed] [CAS]

17. Lopes, J. N. C.; Padua, A. A. H. J. Phys. Chem. B 2006, 110, 19586-19592 [PubMed]

18. Sambasivarao, S. V.; Acevedo, O. J. Chem. Theory Comput. 2009, 5, 1038-1050 [CrossRef] [CAS]

19. Case, D. A.; AMBER 11; University of California: San Francisco, 2010.

20. El Hassan, M. A.; Calladine, C. R. J. Mol. Biol. 1998, 282, 331-343 [CrossRef] [PubMed] [CAS]

21. Altona, C.; Sundaralingam, M. J. Am. Chem. Soc. 1972, 94 (23) 8205-8212 [CrossRef] [PubMed] [CAS]

22. Kollman, P. A.; Massova, I.; Reyes, C.; Kuhn, B.; Huo, S.; Chong, L.; Lee, M.; Lee, T.; Duan, Y.; Wang, W.; Donini, O.; Cieplak, P.; Srinivasan, J.; Case, D. A.; Cheatham, T. E., III. Acc. Chem. Res. 2000, 33, 889-897 [CrossRef] [PubMed] [CAS]

23a. Wang, J.; Morin, P.; Wang, W.; Kollman, P. A. J. Am. Chem. Soc. 2000. 123, 5221-5230

23b. Mascarenhas, N. M.; Kastner, J. BMC Struct. Biol. 2012, 12, 8 [CrossRef] [CAS]

24a. Huang, M.-M.; Jiang, J.; Sasisanker, P.: Driver, G. W.: Weingartner, H. J. Chem. Eng. Data 2011, 56, 1494-1499 [CrossRef] [CAS]

24b. Dielectric constants used for MMPBSA calculations are as follows: [BMIM][CI], 15; [BMIM][NO3], 15; [BMIM][lactate], 40; [choline]NO3], 44; JACS

pubs.acs.org/JACS

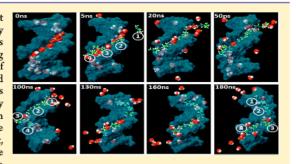
Groove Binding Mechanism of Ionic Liquids: A Key Factor in Long-Term Stability of DNA in Hydrated Ionic Liquids?

Aneesh Chandran, Debostuti Ghoshdastidar, and Sanjib Senapati*

Department of Biotechnology, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

ABSTRACT: Nucleic acid sample storage is of paramount importance in biotechnology and forensic sciences. Very recently, hydrated ionic liquids (ILs) have been identified as ideal media for long-term DNA storage. Hence, understanding the binding characteristics and molecular mechanism of interactions of ILs with DNA is of both practical and fundamental interest. Here, we employ molecular dynamics simulations and spectroscopic experiments to unravel the key factors that stabilize DNA in hydrated ILs. Both simulation and experimental results show that DNA maintains the native B-conformation in ILs. Simulation results further suggest that, apart from the electrostatic association of IL cations with the DNA backbone, groove binding of IL cations through



hydrophobic and polar interactions contributes significantly to DNA stability. Circular dichroism spectral measurements and fluorescent dye displacement assay confirm the intrusion of IL molecules into the DNA minor groove. Very interestingly, the IL ions were seen to disrupt the water cage around DNA, including the spine of hydration in the minor groove. This partial dehydration by ILs likely prevents the hydrolytic reactions that denature DNA and helps stabilize DNA for the long term. The detailed understanding of IL-DNA interactions provided here could guide the future development of novel ILs, specific for nucleic acid solutes.

1. INTRODUCTION

DNA, apart from being has also been recognize and forensic realms and advanced molecular d reported that DNA vaccination confers protective immunity

al information carrier, nent in pharmaceutical in the development of xample, it has been

utilizes the basic natural principles of anhydrobiosis, is becoming a more attractive alternative to the conventional cold storage of DNA.6 Nonetheless, there is a continuous inquest to develop suitable media for long-term preservation of

Ionic liquids (ILs) have found a wide range of applications in various fields, including organic synthesis, extraction/separa-

View Supporting Information

1 of 10 → ← Page























References

- 1. Kutzler, M. A.; Weiner, D. B. Nat. Rev. Genet. 2008, 9, 776-788 [CrossRef] [PubMed] [CAS]
- 2. Jobling, M. A.; Gill, P. Nat. Rev. Genet, 2004, 5, 739-751 [CrossRef] [PubMed] [CAS]
- 3. Krishnan, Y.; Simmel, F. C. Angew. Chem., Int. Ed. 2011, 50, 3124-3156 [CrossRef] [CAS]
- 4. Lukin, M.; de los Santos, C. Chem. Rev. 2006, 106, 607-686 [CrossRef] [PubMed] [CAS]
- 5. Roder, B.; Fruhwirth, K.; Vogl, C.; Wagner, M.; Rossmanith, P. J. Clin. Microbiol. 2010, 48, 4260-4262 [CAS]
- Bonnet, J.; Colotte, M.; Coudy, D.; Couallier, V.; Portier, J.; Morin, B.; Tuffet, S. Nucleic Acids Res. 2010, 38, 1531-1546 [CrossRef] [PubMed] [CAS]
- 7. Kokorin, A., Ed. Ionic Liquids: Applications and Perspectives; InTech: Rijeka, Croatia, 2011.
- 8. Qin, W.; Li, S. F. Y. Analyst 2003, 128, 37-41 [CrossRef] [PubMed] [CAS]
- 9. Nishimura, N.; Nomura, Y.; Nakamura, N.; Ohno, H. Biomaterials 2005, 26, 5558-5563 [CrossRef] [PubMed] [CAS]
- 10. Wang, J. H.; Cheng, D. H.; Chen, X. W.; Du, Z.; Fang, Z. L. Anal. Chem. 2007, 79, 620-625 [CrossRef] [PubMed] [CAS]
- 11. de Zoysa, R. S. S.; Jayawardhana, D. A.; Zhao, Q.; Wang, D.; Armstrong, D. W.; Guan, X. J. Phys. Chem. B 2009, 113, 13332-13336 [CrossRef] [PubMed] [CAS]
- 12. Vijayaraghavan, R.; Izgorodin, A.; Ganesh, V.; Surianarayanan, M.; MacFarlane, D. R. Angew. Chem., Int.

JACS

pubs.acs.org/JACS

Groove Binding Mechanism of Ionic Liquids: A Key Factor in Long-



1. DNA vaccines: ready for prime time?

Kutzler, Michele A.; Weiner, David B.

Nature Reviews Genetics (2008), 9(10), 776-788CODEN: NRGAAM; ISSN: 1471-0056. English.

A review. In the past 16 years, there has been much excitement in the area of DNA vaccine development for a range of medical conditions. The recent licensure of DNA vaccines for veterinary use bodes well for applications in humans, in which progress has been slower. Since the discovery, over a decade and a half ago, that genetically engineered DNA can be delivered in vaccine form and elicit an immune response, there has been much progress in understanding the basic biol. of this platform. A large amt. of data has been generated in preclin. model systems, and more sustained cellular responses and more consistent antibody responses are being obsd. in the clinic. Four DNA vaccine products have recently been approved, all in the area of veterinary medicine. These results suggest a productive future for this technol. as more optimized constructs, better trial designs and improved platforms are being brought into the clinic.









ectral measurements and Very interestingly, the inor groove. Thi A for the l of novel I

1. INTRODUCTION

» More from SciFinder®

DNA, apart from being a natural biological information carrier, has also been recognized as a key component in pharmaceutical and forensic realms and a crucial material in the development of advanced molecular devices. 1-3 For example, it has been reported that DNA vaccination confers protective immunity

utilizes the basic natural principles of an becoming a more attractive alternative to the cold storage of DNA.6 Nonetheless, there is a inquest to develop suitable method for long-term pr DNA.

Ionic liquids (ILs) have fo various fields, including org

View Supporting Information

← Page 1 of 10 ->

















pubs.acs.org/JACS

References

16. Perez, A.; Marchan, I.; Svozil, D.;

16. Perez, A.; Marchan, I.; Svozil, D.; Sponer, J.; Cheatham, T. E., III; Laughton,

C. A.; Orozco, M. Biophys. J. 2007, 92,

3817-3829 [CrossRef] [PubMed] [CAS]

linding Mechanism of Ionic Liquids: A Key Factor in Longbility of DNA in Hydrated Ionic Liquids?

dran, Debostuti Ghoshdastidar, and Sanjib Senapati*

iotechnology, Indian Institute of Technology Madras, Chennai 600036, India

1038-1050 [CrossRef] [CAS]

19. Case, D. A.; AMBER 11; University of California: San Francisco, 2010.

20. El Hassan, M. A.; Calladine, C. R. J. Mol. Biol. 1998, 282, 331-343 [CrossRef] [PubMed] [CAS]

21. Altona, C.; Sundaralingam, M. J. Am. Chem. Soc. 1972, 94 (23) 8205–8212 [CrossRef] [PubMed] [CAS]

22. Kollman, P. A.; Massova, I.; Reyes, C.; Kuhn, B.; Huo, S.; Chong, L.; Lee, M.; Lee, T.; Duan, Y.; Wang, W.; Donini, O.; Cieplak, P.; Srinivasan, J.; Case, D. A.; Cheatham, T. E., III. Acc. Chem. Res. 2000, 33, 889-897 [CrossRef] [PubMed] [CAS]

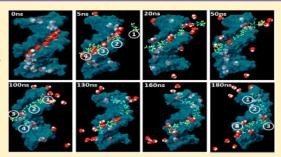
23a. Wang, J.; Morin, P.; Wang, W.; Kollman, P. A. J. Am, Chem. Soc. 2000. 123, 5221-5230

23b. Mascarenhas, N. M.; Kastner, J. BMC Struct. Biol. 2012, 12, 8 [CrossRef] [CAS]

24a. Huang, M.-M.; Jiang, J.; Sasisanker, P.: Driver, G. W.: Weingartner, H. J. Chem. Eng. Data 2011, 56, 1494-1499 [CrossRef] [CAS]

24b. Dielectric constants used for MMPBSA calculations are as follows: [BMIM][CI], 15; [BMIM][NO3], 15; [BMIM][lactate], 40; [choline]NO3], 44; Supporting Information

ABSTRACT: Nucleic acid sample storage is of paramount importance in biotechnology and forensic sciences. Very recently, hydrated ionic liquids (ILs) have been identified as ideal media for long-term DNA storage. Hence, understanding the binding characteristics and molecular mechanism of interactions of ILs with DNA is of both practical and fundamental interest. Here, we employ molecular dynamics simulations and spectroscopic experiments to unravel the key factors that stabilize DNA in hydrated ILs. Both simulation and experimental results show that DNA maintains the native B-conformation in ILs. Simulation results further suggest that, apart from the electrostatic association of IL cations with the DNA backbone, groove binding of IL cations through



hydrophobic and polar interactions contributes significantly to DNA stability. Circular dichroism spectral measurements and fluorescent dye displacement assay confirm the intrusion of IL molecules into the DNA minor groove. Very interestingly, the IL ions were seen to disrupt the water cage around DNA, including the spine of hydration in the minor groove. This partial dehydration by ILs likely prevents the hydrolytic reactions that denature DNA and helps stabilize DNA for the long term. The detailed understanding of IL-DNA interactions provided here could guide the future development of novel ILs, specific for nucleic acid solutes.

1. INTRODUCTION

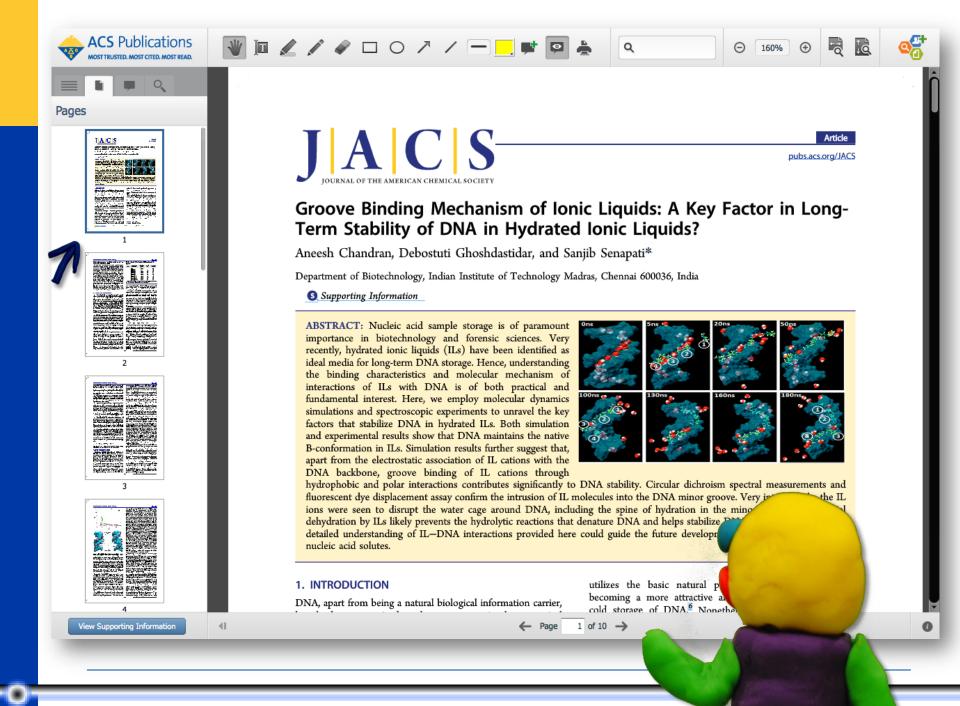
DNA, apart from being a natural biological information carrier, has also been recognized as a key component in pharmaceutical and forensic realms and a crucial material in the development of advanced molecular devices. 1-3 For example, it has been reported that DNA vaccination confers protective immunity

utilizes the basic natural principles of anhydrobiosis, is becoming a more attractive alternative to the conventional cold storage of DNA.6 Nonetheless, there is a continuous inquest to develop suitable media for long-term preservation of

Ionic liquids (ILs) have found a wide range of applications in various fields, including organic synthesis, extraction/separa-

View Supporting Information

1 of 10 → ← Page

















References

16. Perez, A.; Marchan, I.; Svozil, D.; Sponer, J.; Cheatham, T. E., III; Laughton, C. A.; Orozco, M. Biophys. J. 2007, 92, 3817-3829 [CrossRef] [PubMed] [CAS]

17. Lopes, J. N. C.; Padua, A. A. H. J. Phys. Chem. B 2006, 110, 19586-19592 [PubMed]

18. Sambasivarao, S. V.; Acevedo, O. J. Chem. Theory Comput. 2009, 5, 1038-1050 [CrossRef] [CAS]

19. Case, D. A.; AMBER 11; University of California: San Francisco, 2010.

20. El Hassan, M. A.; Calladine, C. R. J. Mol. Biol. 1998, 282, 331-343 [CrossRef] [PubMed] [CAS]

21. Altona, C.; Sundaralingam, M. J. Am. Chem. Soc. 1972, 94 (23) 8205-8212 [CrossRef] [PubMed] [CAS]

22. Kollman, P. A.; Massova, I.; Reyes, C.; Kuhn, B.; Huo, S.; Chong, L.; Lee, M.; Lee, T.; Duan, Y.; Wang, W.; Donini, O.; Cieplak, P.; Srinivasan, J.; Case, D. A.; Cheatham, T. E., III. Acc. Chem. Res. 2000, 33, 889-897 [CrossRef] [PubMed] [CAS]

23a. Wang, J.; Morin, P.; Wang, W.; Kollman, P. A. J. Am. Chem. Soc. 2000, 123, 5221-5230

23b. Mascarenhas, N. M.; Kastner, J. BMC Struct. Biol. 2012, 12, 8 [CrossRef] [CAS]

24a. Huang, M.-M.; Jiang, J.; Sasisanker, P.; Driver, G. W.; Weingartner, H. J. Chem. Eng. Data 2011, 56, 1494-1499 [CrossRef] [CAS]

24b. Dielectric constants used for

w Supporting Information

View Supporting Information

JACS

pubs.acs.org/JACS

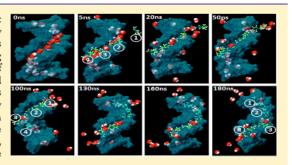
Groove Binding Mechanism of Ionic Liquids: A Key Factor in Long-Term Stability of DNA in Hydrated Ionic Liquids?

Aneesh Chandran, Debostuti Ghoshdastidar, and Sanjib Senapati*

Department of Biotechnology, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

ABSTRACT: Nucleic acid sample storage is of paramount importance in biotechnology and forensic sciences. Very recently, hydrated ionic liquids (ILs) have been identified as ideal media for long-term DNA storage. Hence, understanding the binding characteristics and molecular mechanism of interactions of ILs with DNA is of both practical and fundamental interest. Here, we employ molecular dynamics simulations and spectroscopic experiments to unravel the key factors that stabilize DNA in hydrated ILs. Both simulation and experimental results show that DNA maintains the native B-conformation in ILs. Simulation results further suggest that, apart from the electrostatic association of IL cations with the DNA backbone, groove binding of IL cations through



hydrophobic and polar interactions contributes significantly to DNA stability. Circular dichroism spectral measurements and fluorescent dye displacement assay confirm the intrusion of IL molecules into the DNA minor groove. Very interestingly, the IL ions were seen to disrupt the water cage around DNA, including the spine of hydration in the minor groove. This partial dehydration by ILs likely prevents the hydrolytic reactions that denature DNA and helps stabilize DNA for the long term. The detailed understanding of IL-DNA interactions provided here could guide the future development of novel ILs, specific for nucleic acid solutes.

1. INTRODUCTION

DNA, apart from being a natural biological information carrier, has also been recognized as a key component in pharmaceutical and forensic realms and a crucial material in the development of vanced molecular devices. 1-3 For example, it has been orted that DNA vaccination confers protective immunity

utilizes the basic natural principles of anhydrobiosis, is becoming a more attractive alternative to the conventional cold storage of DNA.6 Nonetheless, there is a continuous inquest to develop suitable media for long-term preservation of

Ionic liquids (ILs) have found a wide range of applications in various fields, including organic synthesis, extraction/separa-

1 of 10 -> ← Page

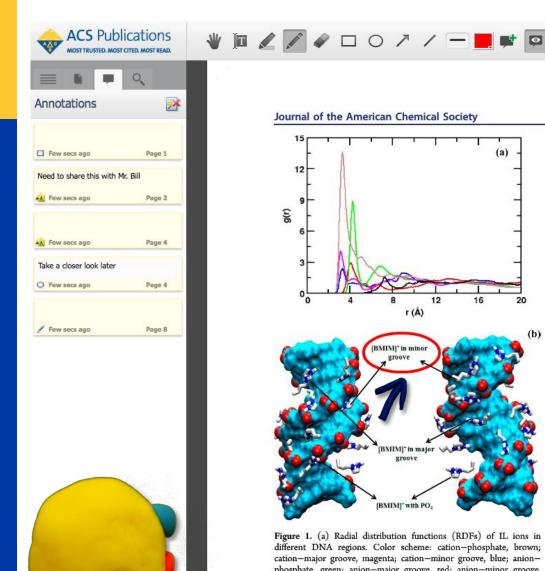


Figure 1. (a) Radial distribution functions (RDFs) of IL ions in different DNA regions. Color scheme: cation-phosphate, brown; cation-major groove, magenta; cation-minor groove, blue; anionphosphate, green; anion-major groove, red; anion-minor groove, black. The following sites were considered for calculating the RDFs: center-of-mass (COM) of the imidazolium ring for the cation, Cl for the anion. P for the phosphate group, electronegative sites N3 and O2.



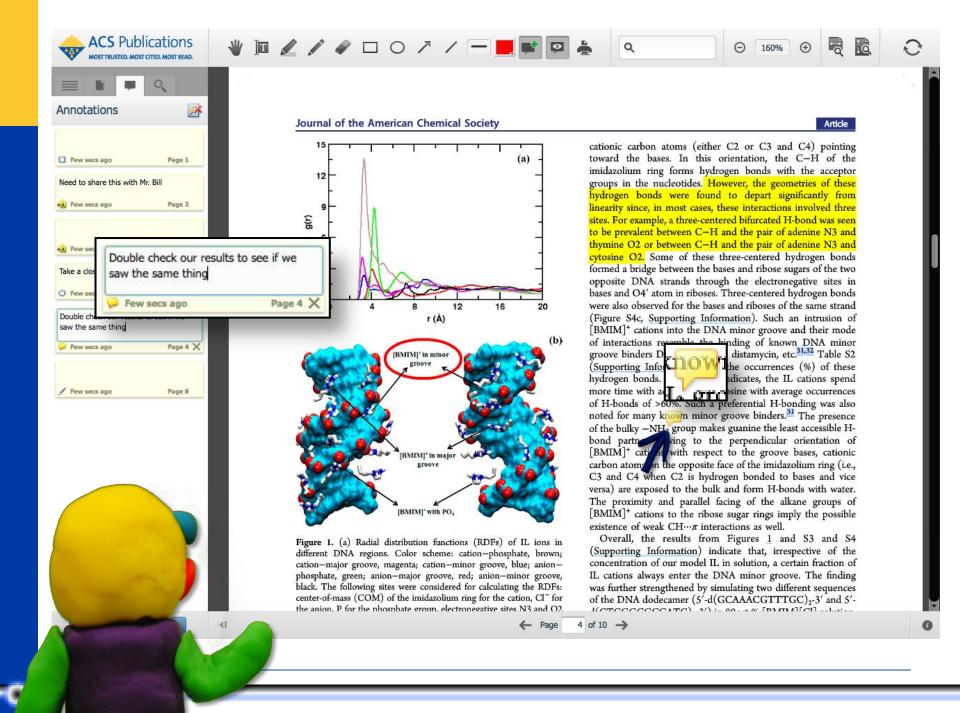
Synced

Article

cationic carbon atoms (either C2 or C3 and C4) pointing toward the bases. In this orientation, the C-H of the imidazolium ring forms hydrogen bonds with the acceptor groups in the nucleotides. However, the geometries of these hydrogen bonds were found to depart significantly from linearity since, in most cases, these interactions involved three sites. For example, a three-centered bifurcated H-bond was seen to be prevalent between C-H and the pair of adenine N3 and thymine O2 or between C-H and the pair of adenine N3 and cytosine O2. Some of these three-centered hydrogen bonds formed a bridge between the bases and ribose sugars of the two opposite DNA strands through the electronegative sites in bases and O4' atom in riboses. Three-centered hydrogen bonds were also observed for the bases and riboses of the same strand (Figure S4c, Supporting Information). Such an intrusion of [BMIM]+ cations into the DNA minor groove and their mode of interactions resemble the binding of known DNA minor groove binders DAPI, netropsin, distamycin, etc. 31,32 Table S2 (Supporting Information) lists the occurrences (%) of these hydrogen bonds. As the table indicates, the IL cations spend more time with adenine and cytosine with average occurrences of H-bonds of >60%. Such a preferential H-bonding was also noted for many known minor groove binders.31 The presence of the bulky -NH2 group makes guanine the least accessible Hbond partner. Owing to the perpendicular orientation of [BMIM]+ cations with respect to the groove bases, cationic carbon atoms on the opposite face of the imidazolium ring (i.e., C3 and C4 when C2 is hydrogen bonded to bases and vice versa) are exposed to the bulk and form H-bonds with water. The proximity and parallel facing of the alkane groups of [BMIM]+ cations to the ribose sugar rings imply the possible existence of weak $CH \cdot \cdot \cdot \pi$ interactions as well.

Overall, the results from Figures 1 and S3 and S4 (Supporting Information) indicate that, irrespective of the concentration of our model IL in solution, a certain fraction of IL cations always enter the DNA minor groove. The finding was further strengthened by simulating two different sequences of the DNA dodecamer (5'-d(GCAAACGTTTGC)2-3' and 5'-I/CTCCCCCCATC\ 1/\:...oo__+o/[Damal[Cl]_-L....







a

) 16

⊕

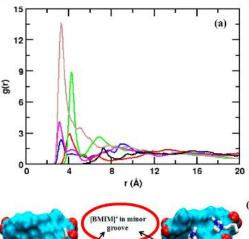


Synced 6 minutes ago

Synced

6 minutes ago

Journal of the American Chemical Society



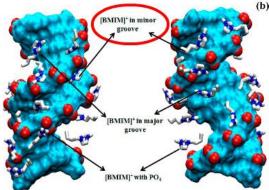
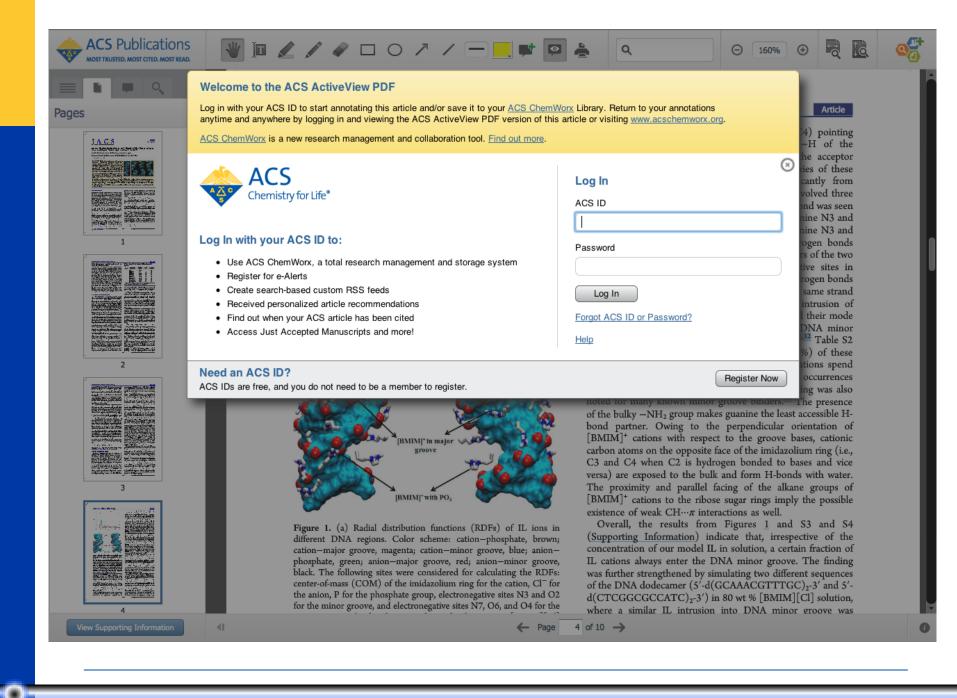


Figure 1. (a) Radial distribution functions (RDFs) of IL ions in different DNA regions. Color scheme: cation-phosphate, brown; cation-major groove, magenta; cation-minor groove, blue; anion-phosphate, green; anion-major groove, red; anion-minor groove, black. The following sites were considered for calculating the RDFs: center-of-mass (COM) of the imidazolium ring for the cation, Cl⁻ for the anion. P for the phosphate group, electronecative sites N3 and O2.

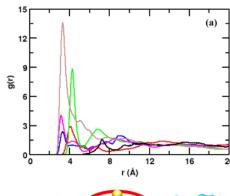
cationic carbon atoms (either C2 or C3 and C4) pointing toward the bases. In this orientation, the C-H of the imidazolium ring forms hydrogen bonds with the acceptor groups in the nucleotides. However, the geometries of these hydrogen bonds were found to depart significantly from linearity since, in most cases, these interactions involved three sites. For example, a three-centered bifurcated H-bond was seen to be prevalent between C-H and the pair of adenine N3 and thymine O2 or between C-H and the pair of adenine N3 and cytosine O2. Some of these three-centered hydrogen bonds formed a bridge between the bases and ribose sugars of the two opposite DNA strands through the electronegative sites in bases and O4' atom in riboses. Three-centered hydrogen bonds were also observed for the bases and riboses of the same strand (Figure S4c, Supporting Information). Such an intrusion of [BMIM]+ cations into the DNA minor groove and their mode of interactions resemble the binding of known DNA minor groove binders DAPI, netropsin, distamycin, etc. Table S2 (Supporting Information) lists the occurrences (%) of these hydrogen bonds. As the table indicates, the IL cations spend more time with adenine and cytosine with average occurrences of H-bonds of >60%. Such a preferential H-bonding was also noted for many known minor groove binders.31 The presence of the bulky -NH2 group makes guanine the least accessible Hbond partner. Owing to the perpendicular orientation of [BMIM]+ cations with respect to the groove bases, cationic carbon atoms on the opposite face of the imidazolium ring (i.e., C3 and C4 when C2 is hydrogen bonded to bases and vice versa) are exposed to the bulk and form H-bonds with water. The proximity and parallel facing of the alkane groups of [BMIM]+ cations to the ribose sugar rings imply the possible existence of weak $CH \cdot \cdot \cdot \pi$ interactions as well.





Journal of the American Chemical Society

Article



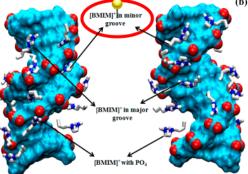
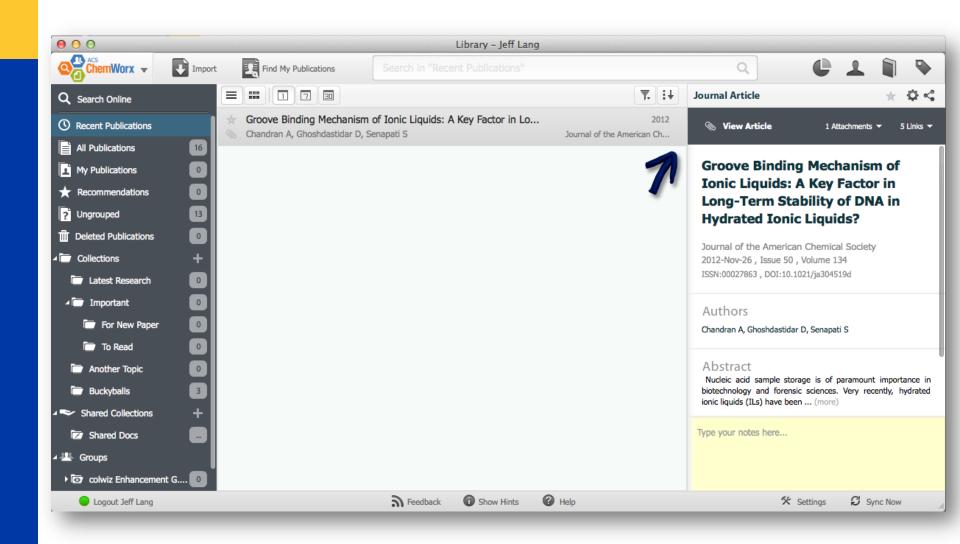


Figure 1. (a) Radial distribution functions (RDFs) of IL ions in different DNA regions. Color scheme: cation—phosphate, brown;

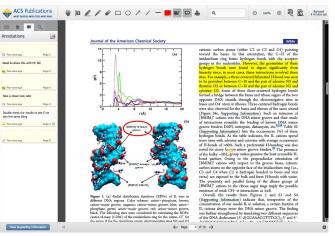
cationic carbon atoms (either C2 or C3 and C4) pointing toward the bases. In this orientation, the C-H of the imidazolium ring forms hydrogen bonds with the acceptor groups in the nucleotides. However, the geometries of these hydrogen bonds were found to depart significantly from linearity since, in most cases, these interactions involved three sites. For example, a three-centered bifurcated H-bond was seen to be prevalent between C-H and the pair of adenine N3 and thymine O2 or between C-H and the pair of adenine N3 and cytosine O2. Some of these three-centered hydrogen bonds formed a bridge between the bases and ribose sugars of the two opposite DNA strands through the electronegative sites in bases and O4' atom in riboses. Three-centered hydrogen bonds were also observed for the bases and riboses of the same strand (Figure S4c, Supporting Information). Such an intrusion of [BMIM]+ cations into the DNA minor groove and their mode of interactions resemble the binding of known DNA minor groove binders DAPI, netropsin, distamycin, etc.31,32 Table S2 (Supporting Information) lists the occurrences (%) of these hydrogen bonds. As the table indicates, the IL cations spend more time with adenine and cytosine with average occurrences of H-bonds of >60%. Such a preferential H-bonding was also noted for many kn wn minor groove binders. 31 The presence of the bulky $-\mathrm{NH}_2$ g Double check our results to see if essible Hbond partner. Owi we saw the same thing ntation of [BMIM]+ cations w 47 minute ago by me carbon atoms on the opposite face of the imidazolium ring (i.e., C3 and C4 when C2 is hydrogen bonded to bases and vice versa) are exposed to the bulk and form H-bonds with water. The proximity and parallel facing of the alkane groups of [BMIM]+ cations to the ribose sugar rings imply the possible existence of weak $CH \cdot \cdot \cdot \pi$ interactions as well.

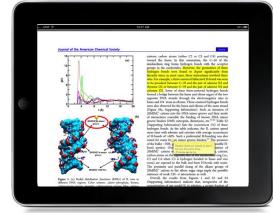
Overall, the results from Figures 1 and S4 (Supporting Information) indicate that, irres



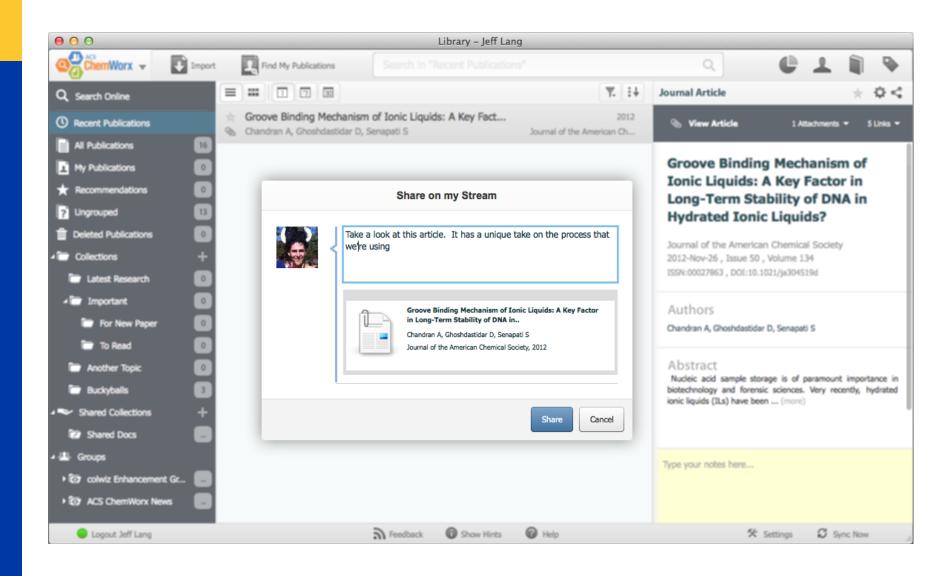












EDVIRONMENTAL Science & Technology

Special Issue on Environment and Geochemical Aspects of Carbon Sequestration Available FREE for a limited time



Time's Up!

About your speaker:

- Name: Jeff Lang
- Company: American Chemical Society
- Email: j_lang@acs.org
- Social Media:
 - Facebook facebook.com/AmericanChemicalSociety
 - Twitter twitter.com/acspublications
 - YouTube youtube.com/AmerChemSoc/