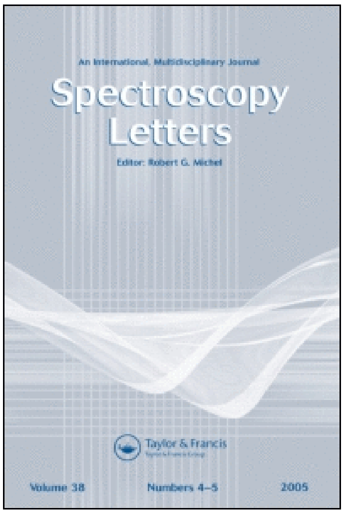
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

NMR EVIDENCE OF HYDROGEN BOND IN 1-ETHYL-3-METHYLIMIDAZOLIUM-TETRAFLUOROBORATE ROOM TEMPERATURE IONIC LIQUID

Jing-Fang Huang[a]; Po-Yu Chen[a]; I-Wen Sun[a]; S. P. Wang[a]
[a] Department of Chemistry, National Cheng Kung University, Taiwan, R.O.C.

Online publication date: 31 October 2001

To cite this Article Huang, Jing-Fang , Chen, Po-Yu , Sun, I-Wen and Wang, S. P.(2001) 'NMR EVIDENCE OF HYDROGEN BOND IN 1-ETHYL-3-METHYLIMIDAZOLIUM-TETRAFLUOROBORATE ROOM TEMPERATURE IONIC LIQUID', Spectroscopy Letters, 34: 5, 591 — 603

To link to this Article: DOI: 10.1081/SL-100106873

URL: http://dx.doi.org/10.1081/SL-100106873

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 34(5), 591–603 (2001)

NMR EVIDENCE OF HYDROGEN BOND IN 1-ETHYL-3-METHYLIMIDAZOLIUM-TETRAFLUOROBORATE ROOM TEMPERATURE IONIC LIQUID

Jing-Fang Huang, Po-Yu Chen, I-Wen Sun,*
and S. P. Wang*

Department of Chemistry, National Cheng Kung
University, Tainan, Taiwan 70101, R.O.C.

Downloaded At: 03:10 30 January 2011

ABSTRACT

The 1-ethyl-3-methylimidazolium-tetrafluoroborate (EMI-BF_4) room-temperature molten salt was investigated with NMR techniques. Diffusion coefficients measured at temperatures ranging from 300 to 360 K indicate phase-change occurred in the vicinity of 333 K, which is supported by ^{11}B quadrupolar relaxation rates. Combined with the sizes of diffusion particles obtained form the Stokes-Einstein equation, this phase change is ascribed to that the diffusion particle is transformed from "discrete ion-pair" to "individual ion" at temperatures above 335 K due to decomposition of the EMI-BF_4 ion pair. Analysis of the ^{13}C dipole-dipole relaxation rates identifies the formation of hydrogen bond(C2H...F) between the counter ions, EMI^+ and BF_4^-. That the values of viscosity in EMI-BF_4 are higher than those in EMI-$AlCl_4$ at

---

*Corresponding authors.

Copyright © 2001 by Marcel Dekker, Inc. www.dekker.com

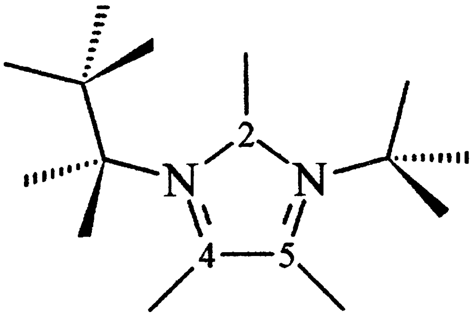
corresponding temperatures is therefore understood according to the viscosity approach employed to investigate the H-bonding in molten salts

Key Words: Room temperature ionic liquid; Hydrogen bond; Diffusion coefficients; Phase transition; NMR relaxation rates

INTRODUCTION

The room temperature molten salts composed of certain imidazolium cations such as 1-ethyl-3methylimidazolium (EMI^+) and 1-butyl-3-methylimidazolium (BMI^+) and various anions such as chloride, tetrachloroaluminate ($AlCl_4^-$), tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) have attracted abundant research interests due to their applications in electrochemistry[1]. More recently, these ionic liquids have been employed as solvents for two-phase catalysis[2] and NMR relaxation studies[3–5] as well. On the other hand, hydrogen bonding between counter ions in molten salts, which was considerably questionable, turns out to be a subject under extensive investigation[6–10]. This subject is quite important since it is closely related to some physical properties of the ionic liquids including viscosity, conductivity, and density as well as the packing in crystalline[11] structures.

Besides the above-stated physical properties, the most widely used methods to probe H-bonding are IR and NMR spectroscopic techniques, in which the C2-H stretching frequencies (see the Scheme for numbering of atomic positions) and chemical shifts of this hydrogen bonding are ex-



Scheme. Structure and numbering of atomic positions of 1-ethyl-3-methylimidazolium cation (EMI^+).

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

amined. Adopting these approaches, Suarez et al. reported that hydrogen bonding was found in the BMI-X, X=BF_4 and PF_6, and the latter was a better H-bonding acceptor[11]. As pointed out by these authors, their results were contrary to those in earlier studies conducted on EMI-X[12,13], (X=BF_4 and PF_6). More significantly, they have found that the BMI-BF_4 molten salt possesses dual (ionic polymer-ionic pair) behavior[11].

In order to clarify the controversy concerning H-bonding in EMI-BF_4 molten salt, we have employed NMR techniques to measure diffusion coefficients (using proton resonance signals), ^{13}C spin-lattice relaxation times, and nuclear Overhauser enhancements. From the latter two experiments, one can extract the ^{13}C dipole-dipole relaxation rate[14], which in turn affords the value of correlation time (τ_c)[15] representing the time required for the C-H vector to reorient for one radian. The ^{11}B quadrupolar relaxation times have also been measured yielding supplementary or comparative information. All these NMR experiments were performed at temperatures ranging from 300 to 360 K with 5 degree increments.

EXPERIMENTAL

The EMI-BF_4 molten salt was prepared according to the procedure reported previously by this laboratory[1d]. The sample was placed in a 5 mm NMR tube, degassed by three freeze-pump-thaw cycles and sealed under vacuum. DMSO-d_6 was used as external lock solvent contained in a capillary. To avoid the contamination from water and oxygen, the manipulation of the ionic liquids was performed inside a nitrogen-filled Vacuum Atmosphere glove box.

Relaxation time (T_1), of carbon-13 and boron-11, were determined on a Bruker AMX-400 FT-NMR spectrometer recorded at 100.5 and 128.3 MHz, respectively, using the inversion recovery pulse sequence, ($-\tau-/2-$Acq-$t_D)_n$[16]. There were 10 τ values, raging from 0.1 to 1.5 times the estimated magnitudes of T_1, used and the delay times (t_D) were at least 5 times of T_1. The numbers of acquisitions, n, were 8 and 32 respectively for T_1 (^{13}C) and T_{1q} (^{11}B). Temperature calibrations were carried out using the ethylene glycol NMR thermometer. Nuclear Overhauser enhancements were measured employing the gated decoupling procedures[14]; sixteen transients were employed for determining both enhanced and non-enhanced intensities.

Measurements of diffusion coefficients were performed on a Bruker DRX-500 NMR spectrometer by means of pulsed field gradient NRM (^1H resonance signals) techniques with the longitudinal eddy current delay (LED)[17] pulse sequence. Extraction of diffusion coefficients from the LED intensities was carried out using the program SPLMOD[18].

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

RESULTS AND DISCUSSION

The temperature dependence of experimental diffusion coefficients, D, ranging from 300 to 360 K, is presented in Table 1. The most widely used theory treating diffusion in liquids is the Stokes-Einstein equation, in which one assumes the diffusion particle or molecule is spherical with radius r obeying the Stokes' law, expressed by[19]

$$D = \frac{kT}{6\pi\eta r} \tag{1}$$

Where k is the Boltzman constant, T is the temperature in Kelvin, and η represents the bulk viscosity of the liquid. The number, 6, in the above equation may vary depending on the relative sizes of the diffusing solute and the solvent molecule[19]. The values of η at various temperatures were obtained by interpolation of experimental results reported in literature[20].

The plot in Fig. 1 indicates that there are two distinguished linear regions, corresponding to two phases, at temperature ranges 300–330 K and 335–360 K. The mean radii of the diffusing spheres in the two phases evaluated from the slopes, according to Eq. 1, are respectively 2.79 Å (300–330 K) and 1.90Å (335–360 K).

The dipole-dipole NMR relaxation rate ($R_{1DD} = 1/T_{1DD}$) of proton-attached carbons can be extracted from the experimental spin-lattice relaxation rate, $R_{1exp} = 1/T_{1exp}$, by the expression[14,16]

Table 1. Diffusion Coefficients, D ($10^6\,cm^2/s$), for EMI$^+$ Calculated with Different Proton at Different Positions

Temp(°C)	DC2	DNCH2	DNCH2	D(106 CM2/S)
300	0.264	0.315	0.340	0.302
305	0.406	0.349	0.359	0.375
310	0.501	0.543	0.485	0.496
315	0.610	0.619	0.629	0.608
320	0.703	0.710	0.735	0.718
325	0.923	0.953	0.966	0.956
330	1.06	1.08	1.12	1.09
335	1.42	1.39	1.44	1.42
340	1.67	1.63	1.72	1.69
345	2.02	1.98	2.05	2.04
350	2.48	2.40	2.52	2.47
360	3.60	3.25	3.61	3.58

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

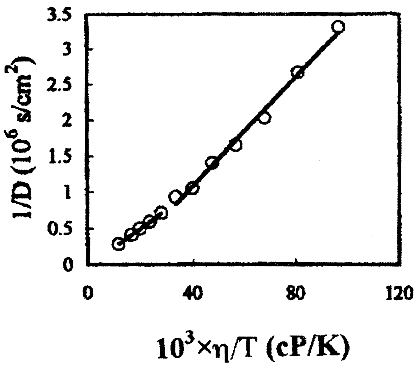


Figure 1. Plot of 1/diffusion coefficient vs viscosity/T for EMI^+ in a EMI-BF_4 melt.

Downloaded At: 03:10 30 January 2011

$$R_{1DD} = R_{1exp}\left(\frac{\eta}{1.99}\right) \tag{2}$$

where η is the measured nuclear Overhauser enhancement (nOe). The rotational correlation time, τ_c, can therefore be obtained directly from experimental relaxation rate (R_{1exp}) and magnitude of nOe (η) via the expression[14]

$$R_{1DD} = R_{1exp}\left(\frac{\eta}{1.99}\right) = N_H(h\gamma_C\gamma_H)^2 r_{CH}{}^{-6}\tau_c \tag{3}$$

where N_H is the number of hydrogens bonded to the carbon atom, γ_C and γ_H are magnetogyric ratios, and $r_{CH} = 1.09\text{Å}^3$. The correlation time, τ_c, can be related to the radius (r), temperature (T) and the Boltzmann constant (k) as[21]

$$\tau_c = \frac{4\pi r^3\eta}{3kT} = \frac{V\eta}{kT} \tag{4}$$

The combination of Eqs. 1 and 4 by eliminating η gives the expression[3]

$$\tau_c = \frac{r^2}{4.5D} + \tau_0 \tag{5}$$

Demonstrated in Fig. 2 is the plot of correlation times vs. 1/D at the high temperature region (*i.e.*, 335 to 360 K), where the values of τ_c were calculated from R_{1DD} of ring carbons (C2, C4 and C5) according to Eq. 3,

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

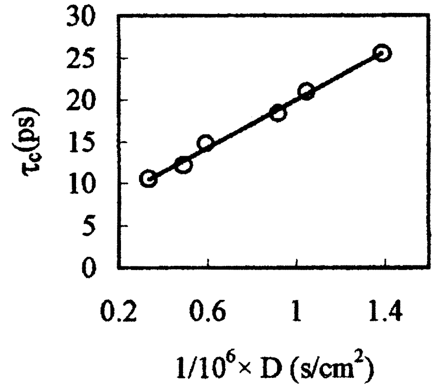


Figure 2. EMI$^+$ ^{13}C (C2+C4+C5)/3 correlation times vs 1/10^6 × diffusion coefficients for EMI-BF$_4$ melt from 335 to 360 K.

as described earlier. The hydrodynamic radius of EMI$^+$ obtained from this plot, according to Eq. 5, is 0.98 Å. The magnitudes 1.90 and 0.98 Å, acquired from Eq. 1 and Eq. 5, respectively, are in good agreement with the corresponding values, 1.77 Å and 0.95 Å, reported for EMI$^+$ by Carper et al[3]. The different radii obtained by the two various approaches may probably arise from the assumption that EMI$^+$ undergoes isotropic reorientational dynamics, as exhibited by spherical-top molecules[21]. Recent studies of reorientational motions for symmetric-top molecules are quite different even for prolate and oblate molecules[15,22]. It is therefore a very crude assumption that EMI$^+$, an asymmetric-top species, rotates as a spherical molecules. In other words, it is more physically appropriate to adopt the values calculated from the Stokes–Einstein equation, 1.90 Å (this work) or 1.77 Å[4] than those derived from the reorientation times.

Based on the "dual behavior" proposes for the BMI-BF$_4$ ionic liquid[11], there were two phases observed, "quasi-molecular" below 279 K and the "extended hydrogen-bonded network" at temperature above 279 K. The decrease of hydrodynamic radii, however, can not be reasonably ascribed to phase change between these two structural formulations. On one hand, the dual behavior has not yet been evidenced for the EMI-BF$_4$ ionic liquid prior to this study. On the other hand, the magnitudes of the hydrodynamic radii at both regions do not comply with this type of phase-transition. The reported diffusing sphere radii for EMI$^+$ where in the range 1.16–2.66 Å depending on the molten salts employed[3]. The diffusing particle at temperatures above 335 K is undoubtedly identified as EMI$^+$ based on the radius of the diffusing particle, 1.90 Å.

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

The radius of BF_4^- is in the vicinity of 1.32 Å obtained by AMI and ab initio calculation at our labs. Based on radius of diffusing sphere, 2.79 Å, at low temperature range, it is reasonable to conclude that EMI^+ diffuses with its counter ion, BF_4^-, in discrete ion-pair. The reduced sizes of diffusing spheres, due to elevation of temperature, evidently results from decomposition of the EMI-BF_4 ion-pair, *i.e.* internal Coulombic attractive force and/or H-bonding are overcome by thermal motions. The hydrogen bond cannot be excluded since there is no experimental evidence to debate the "extended H-bond network"[11] proposed for molten salts, EMI-BF_4 under this study, either.

In order to further confirm the above-mentioned argument, we have also measured ^{11}B quadrupolar relaxation rates ($R_{1q} = 1/T_{1q}$) at the same temperature ranges. The quadrupolar relaxation equation for a spin quantum number $I \geq 1$ nucleus is expressed by[14]

$$R_{1q} = \frac{3}{10}\pi^2\left(\frac{2I+3}{I^2(2I-1)}\right)\chi^2\left(1+\frac{\eta^2}{3}\right)\tau_c \tag{6}$$

In the above equation, χ is the quadrupole coupling constant, h is the asymmetric factor measuring the deviation of electron cloud from cylindrical distribution, and τ_c is the correlation time for the electric field gradient tensor. For the singly or triply bonded system, the value of the asymmetric factor (h) is less than 0.1 and neglecting this term would only introduce an error well under 5% (ca. 0.3%)[23]. Using $I = 3/2$ for ^{11}B and by eliminating the $1+\eta^2/3$ term, Eq. 6 can be simplified to

$$R_{1q} = \frac{2}{5}\pi^2\chi^2\tau_c \tag{7}$$

Combining Eqs. 4 and 7, the plot of negative natural logarithm of R_{1q} vs. 1/T gives similar information to the plot of τ_c vs. η/T, assuming the values of χ do not vary significantly. This assumption can be reasonably accepted considering the tetrahedral environment (BF_4^-) in which the boron atom resides. By definition, the quadruple coupling constant (χ) is related to the electric quadruple moment (Q), a characteristic physical property of a quadrupolar nucleus ($I \geqslant 1$), and the electric field gradient (q) in the vicinity of this nucleus as[23]

$$\chi = \frac{(eQ)(eq)}{h} = \frac{e^2qQ}{h} \tag{8}$$

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

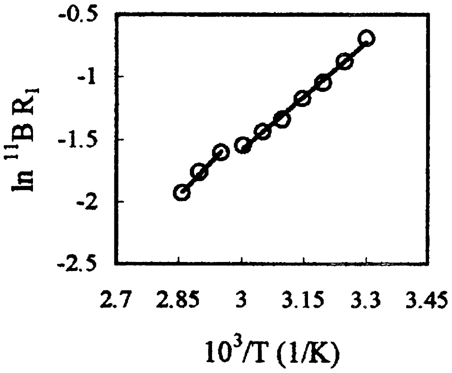


Figure 3. Plot of ln ^{11}B relaxation rate vs 1000/T (1/K) for EMI-BF_4 melt.

Downloaded At: 03:10 30 January 2011

where e is the charge of an electron and h is the universal Planck's constant. In the ion-pair, the spherical electron distribution in BF_4^- $(q = 0)$ is polarized by MEI^+ and hence increases the magnitude of χ (^{11}B) since q is greater than zero in magnitude. This effect is not significant, however, owing to the distortion of electron distribution near the boron nucleus which is not notably evident unless one of the fluorine atom is replaced by other species. This is verified experimentally by monitoring the line width of the ^{11}B resonance peaks, less than 3 ppm in the present study.

It is seen, from Fig. 3, that there was also a discontinuity near 333 K identical to the plot illustrated in Fig. 1 although the two regions are not so obviously distinguished. The latter is understood based on the conclusion made on variation of the value of χ described earlier. The two-region plot (Fig. 3) not only verifies the above-mentioned phase transition but also indicates that the BF_4^- ion is affected by the phase transition as well. The phase-change detected by ^{11}B relaxation, *i.e.* from the BF_4^- viewpoint, is informative since it is consistent with the argument that the phase transition arises from decomposition of the ionic pair. In other words, the ^{11}B NMR relaxation data provide additional evidence in support of the cleavage of the ion pair deduced from investigation of measured diffusion coefficients.

With the aim to examine whether the hydrogen bonding is involved in the interaction between EMI^+ and BF_4^-, spin-lattice relaxation rates of all carbons in EMI^+ were measured at various temperatures (see Fig. 4). It is evident that the carbon, C2, to which the attached hydrogen is involved in H-bonding, exhibits a much more pronounced phase-change appearance than other carbons, C4 and C5, far away from C2. On the other hand, the

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

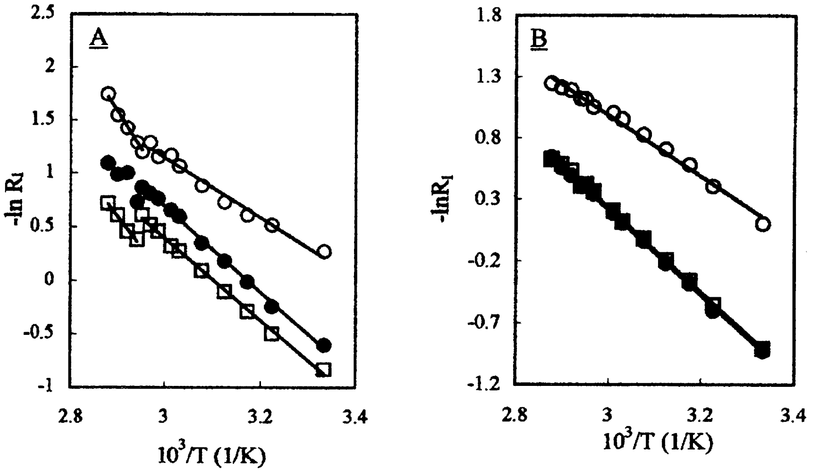


Figure 4. Plots of ln ^{13}C spin-lattice relaxation rates vs 1000/T for (A) C2(○), NCH$_3$(●), and NCH$_2$(□), (B) CH$_3$(○), C4(●), C5(□).

Downloaded At: 03:10 30 January 2011

carbons in NCH$_2$ and NCH$_3$, neighboring to C2, also offer indications of comparative susceptibilities toward the departure of BF$_4^-$. The same observation is found in the Arrhenius plot of R$_{1DD}$ as displayed in Fig. 5. Hence, we concluded that BF$_4^-$ enters into hydrogen bonding with EMI$^+$. This is in accord with the work reported by Suarez et al.[11] carried out in BMI-BF$_4$ ionic liquid. These authors also concluded that PF$_6^-$ exhibited a better H-bond accepting characteristic than BF$_4^-$[11].

Analysis of atomic charges, obtained from AMI calculations, reveals that the fluorine atoms in the PF$_6^-$ are more negatively charged (−0.650) than those in BF$_4^-$ (−0.325), which might account for the relative capability in forming the H-bond. Moreover, it is instructive to rationalize the rather incomparable charges acquired for PF$_6^-$ and BF$_4^-$ (BF$_3$+F$^-$). Both electronegativity and number of valence electrons cannot satisfactorily explain the very different charges on fluorines in the two anions. From the viewpoint of PF$_5$+F$^-$ and BF$_3$+F$^-$, one would even predict an inverse result considering the number of F-atoms available to accommodate the negative charge from the fluoride and neglecting the effects of hybrid-type.

The negative hyperconjugation (NHC) phenomenon[24], originally employed to account for the strengthening of C−F bond(s) in fluorinated methanes, stresses on that the interaction of the lone-pair p-orbital(s) on F-atom with the antibonding C−F orbital, σ^*(C−F)[25], would stabilize these molecules. Consequently, the H-bond of accepting tendency of fluorine

Copyright © Marcel Dekker, Inc. All rights reserved.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

ORDER REPRINTS

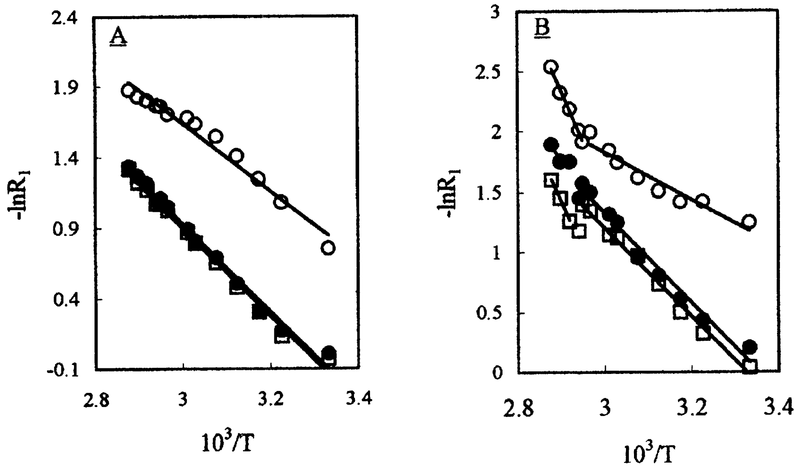


Figure 5. Plots of ln ^{13}C dipole-dipole relaxation rates vs 1000/T for (A) C2(○), NCH$_3$(●), and NCH$_2$(□), (B) CH$_3$(○), C4(●), C5(□).

would be reduced. The NHC effect is rather weak or not existent for the second-row elements, *e.g.* sulfur and phosphorus[20]. We can employ negative hyperconjugation to explain the much smaller charge on F-atom in BF_4^- or weaker ability to form hydrogen bond than PF_6^-. In other words, the relative capability of the two anions in forming H-bonding is consistent with the result predicted by negative hyperconjugation, which has been extensively examined by theoretical chemists[24–26].

It is noteworthy that the values of viscosity reported for EMI-BF$_4$ are higher than those measured for EMI-AlCl$_4$[20] and the correlation times obtained for C2-H bonds in EMI-BF$_4$ are also longer than those in EMI-AlCl$_4$, *i.e.* the reorientational motion is faster in the latter ionic liquids. Apparently, this cannot be correlated with the molecular sizes, which would predict reverse results for both quantities. Based on the viscosity approach employed to probe information of H-bonding, however, the above experimental results can be understood. Furthermore, H-bonding can also account for the relative C2-H correlation times obtained for the two molten salts.

The existence of H-bonding concluded from NMR spectroscopic techniques indicates, to a certain degree, that the extended hydrogen-bonded network[11] is present in the EMI-BF$_4$ ionic liquid under this study. Nonetheless, experimental data in the current work are insufficient to support the dual behavior reported for BMI-BF$_4$ molten salts. Subsequent investigation in this aspect is underway.

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

CONCLUSIONS

The diffusion coefficients have been measured by PFG-NMR techniques, according to resonance signals of protons (attached to C2, C4 and C5 in EMI^+), at temperatures ranging from 300 to 360 K. According to the Stokes–Einstein equation, the radii of diffusing spheres reduce from 2.79 Å at 300–330 K to 1.90 Å at 335–360 K.

The latter is consistent with the size of diffusing particle, $r = 1.87$ Å, calculated from correlation time-diffusion coefficient relationships at the high-temperature range. Based on the radius of EMI^+ reported in the literature and the radius of BF_4^-(1.32 Å) obtained from AMI method, the above experimental results can be rationalized by decomposition of the $EMI\text{-}BF_4$ ion-pair at higher temperature. The departure of BF_4^- in this phase change is also supported by ^{11}B NMR relaxation results. The into-a-whole hydrodynamic behavior is that $EMI\text{-}BF_4$ exhibits discrete ion-pair diffusion at temperature below 330 K and individual ion diffusion at temperature higher than 335 K.

The existence of the hydrogen bond (C2H$\cdots$F) is verified by the temperature dependence ^{13}C dipole-dipole relaxation rates. C2 and its neighboring carbons (NCH_3 and NCH_2) reveal phase-change at the same temperature where decomposition of the ion-pair takes place, whereas the other carbon (C_4 and C_5) are virtually inert toward phase change. The higher values of viscosity reported for $EMI\text{-}BF_4$ than those in $EMI\text{-}AlCl_4$ molten salts at corresponding temperature can therefore be explained by formation of the hydrogen bond. The dual behavior in $EMI\text{-}BF_4$ is not evident in this study despite of the conclusion that BF_4^- enters into H-bonding with EMI^+. That PF_6^- exhibits higher capability in forming H-bonding with EMI^+ or BMI^+ than BF_4^- is quite significant since it provides an experimental evidence of negative hyperconjugation.

ACKNOWLEDGMENTS

The authors thank the National Science Council of the Republic of China, Taiwan for supporting of this work (Grant NSC89-2113-M006-016).

REFERENCES

1. (a) Osteryoung, R.A. In *Adv. in Molten Salt Chem.*; Mamantov, G. Mamantov, C. Eds.; Elsvier: New York, 1987; 6–329.

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

(b) Hussey, C.L. In *Chemistry of Nonaqous Solvent: Current Progress*; Mamantov, G., Popov, A.I., Eds.; VCH publishers: New York, 1994.

(c) Fuller, J.; Carlin, R.T.; Osteryoung, R.A. J. Electrochem. Soc. **1997**, *144*, 3881.

(d) Chen, P-Y.; Sun, I-W. Electrochim. Acta **1999**, *45*, 441.

2. For reviews, see Chauvin, Y.; Oliver, H.; Wyrvalski, C.N.; Simon, L.; Souza, R.F. J. Catal. **1996**, *165*, 275.
3. Larive, C.K.; Lin, M.; Kinnear, B.S.; Piersma, B.J.; Keller, C.E.; Carper, W.R. J. Phys. Chem. **1998**, *102*, 1717.
4. Carper, W.R.; Mains, G.J.; Piersma, B.J.; Manfield, Larive, C.K. J. Phys. Chem. **1996**, *100*, 4724.
5. Keller, C.E.; Carper, W.R.; Piersma, B. J. Inorg. Chim. Acta **1993**, *210*, 203.
6. Fannin, A.A. Jr.; King, L.A.; Leviski, J.A.; Wilkes, J.S. J. Phys. Chem. **1984**, *88*, 2609.
7. Abdul-Sada, A.K.; Greenway, A.M.;Hitchcock, P.B.; Mohammed, T.J.; Seddon, K.R.; Zora, J.A. J. Chem. Soc. Chem. Commun. **1986**, 1753.
8. Dieter, K.M.; Dymek, C.J. Jr.; Heimer, N.E.; Rovang, J.W.; Wilkes, J.S. J. Am. Chem. Soc. **1988**, *110*, 2722.
9. Dymek, C.J. Jr.; Stewart, J.J. P. Inorg. Chem. **1989**, *28*, 1472.
10. Avent, A.G.; Chaloner, P.A.; Day, M.P.; Seddon, K.R.; Welton, T. J. Chem. Soc. Dalton Trans. **1994**, 3405.
11. Suarez, P.A.Z.; Einloft, S.; Dullius, J.E.L.; Souz, R.F.; Dupont, J. J. Chim. Phys. **1998**, *95*, 1626.
12. Wilkes, J.S.; Zaworotko, M.J. J. Chem. Soc., Chem. Commun. **1992**, 965.
13. Fuller, J.; Carlin, R.T.; DeLong, H.C.; Haworth, D. J. Chem. Soc., Chem. Commun. **1994**, 299.
14. Becker, E.D. In *High Resolution NMR: Theory and Applications*, 2nd Ed., Chap. 9, Academic Press: New York, 1980.
15. Chen, A.F.T.; Wang, S.P.; Schwartz, M. Magn. Reson. Chem. **1986**, *26*, 675.
16. Martin, M.L.; Martin, G.J.; Delpuech, J.-J. *Practical NMR Spectroscopy*; Chap. 6, Heyden: London, 1980.
17. Gibbs, S.J.; Johnson, C.S. Jr., J. Magn. Reson. **1991**, *93*, 395.
18. Vogel, R.H. In *SPLMOD Users Manual Technical Report DA06, European Molecular Biology Laboratory*; Heidelberg: Germany, 1983.
19. Levine, I.N. In *Physical Chemistry*; Chap. 16, McGraw-Hill, 1978.
20. (a) McEwen, A.B.; Ngo, H.L.; LeCompte, K.; Goldman, J.L. J. Electrochem. Soc. **1999**, *146*, 1687.

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

21. (b) Fannin, A.A. Jr.; Floreani, D.A.; King, L.A.; Landers, J.S.; Piersma, B.J.; Stech, D.J.; Vaughn, R.L.; Wilkes, J.S.; William, J.L. J. Phys. Chem. **1984**, *88*, 2614–2621.
22. Boere, R.T.; Kidd, R.G. In *Annu. Rep. NMR Spectrosc.*; Webb, G.A., Ed.; Academic Press: New York, 1982; 13, 319.
23. (a) Wang, S.P.; Schwartz, M. Spectrosc. Lett. **1988**, *21*, 919.
24. (b) Wang, S.P.; Yuan, P.; Schwartz, M. J. Raman Spectrosc. **1989**, *20*, 339.
25. (c) Wang, S.P.; Schwartz, M. J. Phys. Chem. **1990**, *94*, 2705.
26. (a) Wang, S.P.; Yuan, P.; Schwartz, M. Inorg. Chem. Soc. **1992**, *29*, 484.
27. (b) Wang, S.P.; Richmond, M.G.; Schwartz, M. J. Am. Chem. Soc. **1992**, *114*, 7595.
28. (c) Wang, K.S.; Wang, D.; Yang, K.; Richmond, M.G.; Schwartz, M. Inorg. Chem. **1995**, *34*, 3241.
29. For reviews of negative or anionic hyperconjugation, see (a) Schneider, W.F.; Nance, B.I.; Wallington, T.J. J. Am. Chem. Soc. **1995**, *117*, 478.
30. (b) Salzner, U.; Schleyer, P.v.R. Chem. Phys. Lett. **1992**, *190*, 401.
31. (c) Reed, A.E.; Schleyer, P.v.R. J. Am. Chem. Soc. **1990**, *112*, 1434.
32. (d) Schleyer, P.v.R.; Kos, A. J. Tetrahedron **1983**, *39*, 1141.
33. Wiberg, K.B.; Rablen, P.R. J. Am. Chem. Soc. **1993**, *115*, 614.
34. (a) Schleyer, P.v.R.; Jemmis, E.D.; Spitznagel, G.W. J. Am. Chem. Soc. **1985**, *107*, 6393.
35. (b) Magnusson, E. J. Am. Chem. Soc. **1986**, *108*, 11.
36. (c) Salzner, U.; Schleyer, P.v.R. J. Chem. Soc., Chem. Commun. **1990**, 190.

Received May, 5, 2000
Accepted July, 10, 2001

Downloaded At: 03:10 30 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

Downloaded At: 03:10 30 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SL100106873