Acceptor Number of Room Temperature Ionic Liquid Determined by the Raman Spectrum of Diphenylcyclopropenone

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Raman spectrum of diphenylcyclopropenone has been measured in various liquids including room temperature ionic liquids. We found a good linear correlation between the solvent acceptor number and the vibrational frequency of the C=C and C=O stretching mode. From the correlation, we have successfully determined acceptor number of several room temperature ionic liquids.

Room temperature ionic liquids (RTILs) attract much attention of a lot of chemists as new media, e.g., for electrochemical materials and solvents of green chemistry.[1] In accordance with expansion of the fields of applications, it becomes more important to characterize RTILs by physicochemical terms such as the polarity, the acidity, the basicity, and so on. The acidity of RTILs has been explored by the solvatochromic shift of Reichardt's dye (the $E_T(30)$ parameter),[2] which is known to have a linear correlation with the solvent acceptor number (AN).[3,4] The solvent AN is determined by the chemical shift of ^{31}P NMR of triethylphosphane oxide induced by the electrophilic actions of acceptor solvent.[3] Since $E_T(30)$ parameters of typical RTILs containing alkylimidazolium cations are around 52 kcal mol^{-1} (near those of alcohols such as methanol),[5] it has been suggested that alkylimidazolium cations have a substantial proton-donating ability.

In this letter, we will report the AN values of RTILs which have been determined by Raman spectra of diphenylcyclopropenone (DPCP). The vibrational modes of DPCP related to the cyclopropenone ring are known to show large solvent dependence.[6] The band around 1630 cm^{-1}, whose mode is assigned to the C=C and C=O stretching mode of cyclopropenone ring, shifted from 1645 cm^{-1} in *n*-hexane to 1608 cm^{-1} in methanol.[6] The authors suggested that the hydrogen bonding is an important factor which affects the vibrational frequency. It has been also reported that the Raman shifts of a C=O stretching mode of several molecules show a linear correlation with the solvent AN.[7] It is reasonable that the electrophilic property of the solvent acting on the oxygen atom of P=O bond (the indicator of AN) induces a similar effect on the oxygen atom of C=O bond; i.e., with an increase of the electrophilicity (or Lewis acidity) of the solvent, the electron is withdrawn to the oxygen atom from the double bond which reduces the bond strength. Here we will report a much better linear correlation of the Raman shift of DPCP with the solvent AN than that between $E_T(30)$ and AN. From the relation we have determined the AN values of several RTILs.

Raman spectra of DPCP were measured at the 90 degree scattering geometry, using an Ar-ion laser (Coherent, Enterprise, 514.5 nm) and a 64-cm monochromator (Jobin Yvon, T6400) equipped with a CCD detector (Princeton Instrument, Spec-10:400BXTE). The resolution of the spectrum was about 3 cm^{-1}. The wavelength dependence of the sensitivity of the system was corrected by the fluorescence intensity of the standard material.[8]

DPCP was purchased from Nacalai Tesque and used as received. Conventional organic solvents (cyclohexane (CHX), ethylacetate (EtOAc), chloroform (CF), benzene (BZ), dimethylsulfoxide (DMSO), ethanol (EtOH), methanol (MeOH), 2-propanol (2-PrOH): spectroscopic grade; acetonitrile (ACN), 2-butanol (2-BuOH), ethylene glycol (EG): guarantee grade) were purchased from Nacalai Tesque, and used as received. We have measured following four different RTILs. Three of those consisted of the same cation, 1-butyl-3-methylimidazolium ([BMIM]), and of different anions, hexafluorophosphate ($[PF_6]$), tetrafluoroborate ($[BF_4]$), and bis(trifluoromethanesulfonyl)imide ([TFSI]). The rest one was *N*,*N*,*N*-trimethyl-*N*-propylammonium ([TMPA]) [TFSI]. $[BMIM][PF_6]$ and $[BMIM][BF_4]$ were synthesized and purified as reported.[9] They were dried by evacuation before use. [BMIM][TFSI] and [TMPA][TFSI] were purchased from Kanto Kagaku, and used as received. The concentrations of DPCP in each solution were typically 25 mmol dm^{-3}. All experiments were performed at room temperature (25 °C).

Figure 1 shows typical Raman spectra of DPCP around 1600 cm^{-1} in conventional solvents and RTILs. The solvent bands are subtracted from the spectrum for the solution. As is shown in the figure, the band which appears around 1642 cm^{-1} in cyclohexane shifts to the lower wavenumber with increasing the polarity or the hydrogen-bonding ability of the solvent. Raman spectra in RTILs are very similar to the spectra in CF and DMSO. To obtain the peak position in each solvent, we have fitted Raman spectra as a summation of Gaussian functions (typically three functions), because the band under consideration becomes overlapping with other bands around 1600 cm^{-1} owing to the shift by changing the solvent. The numbers in Figure 1 indicate the peak positions obtained from the fit. Our results in conventional organic solvents are almost consistent with those reported except for methanol in which the assignment of the peak position was different from ours.[6]

Figure 2 shows the correlation between the band center and AN. The values of AN are taken from Ref. 2. In the figure we omit the result in EG since we could not find the AN value. There is a good linear correlation between the band center and AN as

$$AN = 1.565 \times (1642 - \nu/\mathrm{cm}^{-1}) \qquad (1)$$

where ν is the wavenumber of the band center. With increasing the electrophilicity or the Lewis acidity of the solvent, the electron is withdrawn to probably oxygen atom of DPCP molecule and the bond strengths of C=C and C=O were reduced. Although we tried to correlate the shift with other solvent parameters such as $E_T(30)$, β and π^*, the correlation was worse than the

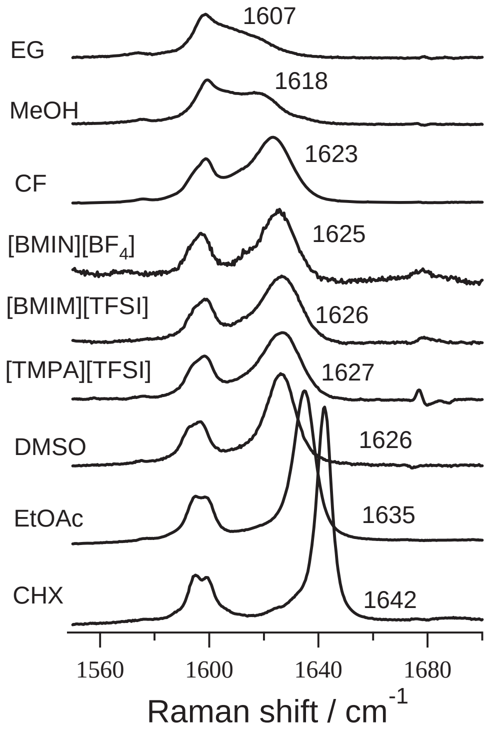

Figure 1. Raman spectra of DPCP in various solvents. The numbers are the peak positions of C=C and C=O stretching mode estimated from the fitting to Gaussian functions.

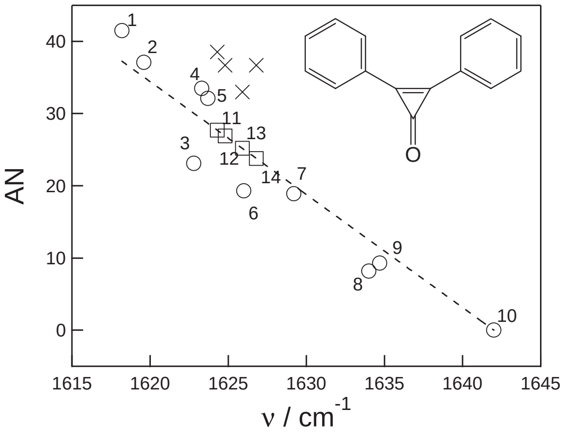

Figure 2. The correlation between AN and the band center of the C=C and C=O stretching mode of DPCP in various solvents. 1: MeOH, 2: EtOH, 3: CF, 4: 2-PrOH, 5: 2-BuOH, 6: DMSO, 7: ACN, 8: BZ, 9: EtOAc, 10: CHX, 11: [BMIM][PF_6] (28.2), 12: [BMIM][BF_4](26.6), 13: [BMIM][TFSI] (25.0), 14: [TMPA][TFSI] (23.5). The dashed line represents Eq 1. The AN values of RTILs (values in the parentheses) are calculated from Eq 1. The symbol (×) indicates the AN values for RTILs calculated by $E_T(30)$.

case of AN.

In Figure 2, we also show the AN values of RTILs calculated from Eq 1. These values are around 25, which are close to that of chloroform, and smaller than those of methanol and ethanol. As is mentioned in the introduction, AN is linearly correlated with the $E_T(30)$ parameter according to $AN = 1.850 \times E_T(30) - 59.5$, as established for 51 solvents ($r = 0.944$) by Marcus.[4] Using this relation and $E_T(30)$ values of RTILs,[1,5] the AN values of RTILs studied here are estimated around 36, which is larger than our estimation. We consider that our estimation of AN is more appropriate for the values of RTILs, because the correlation between $E_T(30)$ and AN is worse in the intermediate region of AN from 10 to 30,[4] and because the vibrational frequency including the carbonyl group is sensitive to the Lewis acidity of the solvent[7] as is mentioned in the introduction. From the study on the redox potential of O_2/O_2^-, the AN value of trimethyl-*n*-hexylammonium [TFSI] has been estimated to be near those of DMSO and ACN,[10] which is close to our estimation.

It is to be noted that [TMPA][TFSI] shows a meaningful Lewis acidity comparable to [BMIM][TFSI]. Considering that the AN value of triethylamine is only 1.4, the large AN value of [TMPA][TFSI] is due to the positive and negative charges in solution characteristic to RTILs. On the other hand, the AN values shows a slight decrease in the order of [PF_6], [BF_4], and [TFSI] for the series of the same cation [BMIM]. It is quite an interesting fact that the ratio ($\Lambda_{imp}/\Lambda_{NMR}$) of the measured conductivity (Λ_{imp}) to the calculated conductivity from the diffusion coefficient determined by NMR measurement (Λ_{NMR}) shows the same dependence on the anion.[11] The ratio is suggested to represent the extent of the ionic association between cation and anion in RTILs.[11] It is reasonable that AN is smaller in RTILs where the ratio $\Lambda_{imp}/\Lambda_{NMR}$ is smaller (the larger extent of ionic association), i.e., the solvation due to the cation is less effective because of the ionic pair formation between cation and anion. The detailed discussion on the origin of the acidity of RTILs will be presented in the near future together with the results on other probe molecules.

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References

1 See, e.g., "Ionic Liquids in Synthesis," ed. by P. Wasserschied and T. Welton, Wiley-VCH, Weinheim (2003); "Ionic Liquids: The Front and Future of Material Development," ed. by H. Ohno, CMC, Tokyo (2002).
2 See, e.g., C. Reichardt, "Solvents and Solvent Effects in Organic Chemistry," 3rd ed., Wiley-VCH, Weinheim (2003).
3 V. Gutmann, "The Donor-Acceptor Interactions," Plenum Press, New York (1978).
4 Y. Marcus, *Chem. Soc. Rev.*, **22**, 409 (1993).
5 See, e.g., S. N. V. K. Aki, J. F. Brennecke, and A. Samanta, *Chem. Commun.*, **2001**, 413; M. J. Muldoon, C. M. Gordon, and I. R. Dunkin, *J. Chem. Soc., Perkin Trans. 2*, **2001**, 433; S. V. Dzyuba and R. A. Bartsch, *Tetrahedron Lett.*, **43**, 4687 (2002).
6 L. C. Almeida and P. S. Santos, *Spectrochim. Acta, Part A*, **58**, 3139 (2002).
7 Q. Liu, X. Xu, and W. Sang, *Spectrochim. Acta, Part A*, **59**, 471 (2003); Q. Liu, D. Fang, and J. Zheng, *Spectrochim. Acta, Part A*, **60**, 1453 (2004).
8 K. Iwata, H. Hamaguchi, and M. Tasumi, *Appl. Spectrosc.*, **42**, 12 (1988).
9 J. G. Huddleston, H. D. Wilauer, R. P. Swatloski, A. E. Visser, and R. D. Rogers, *Chem. Commun.*, **1998**, 1765; J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, **1999**, 2133; L. Cammarata, S. G. Kazarian, P. A. Salter, and T. Welton, *Phys. Chem. Chem. Phys.*, **3**, 5192 (2001); J. Dupont, C. S. Consorti, P. A. Z. Suarez, and R. F. de Souza, *Org. Synth.*, **79**, 236 (2003).
10 Y. Katayama, H. Onodera, M. Yamagata, and T. Miura, *J. Electrochem. Soc.*, **A59**, 151 (2004).
11 H. Tokuda, K. Hayamizu, K. Ishii, Md. A. B. H. Susan, and M. Watanabe, *J. Phys. Chem. B*, **108**, 16593 (2004).

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