

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7482134>

# Ionic Liquids as an Attractive Alternative Solvent for Thermal Lens Measurements

ARTICLE *in* ANALYTICAL CHEMISTRY · DECEMBER 2005

Impact Factor: 5.64 · DOI: 10.1021/ac0512913 · Source: PubMed

---

CITATIONS

22

---

READS

24

3 AUTHORS, INCLUDING:



**Chieu D. Tran**

Marquette University

**145** PUBLICATIONS **2,861** CITATIONS

SEE PROFILE



**Mladen Franko**

University of Nova Gorica

**160** PUBLICATIONS **1,508** CITATIONS

SEE PROFILE

# Ionic Liquids as an Attractive Alternative Solvent for Thermal Lens Measurements

Chieu D. Tran,\* Santhosh Challa, and Mladen Franko†

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201-1881

The use of ionic liquids (ILs) as a solvent for thermal lens measurements has been investigated. It was found that ILs provide a better medium for thermal lens measurements than water. Specifically, not only the ILs offer at least 20 times higher sensitivity than water but that the enhancement can be appropriately adjusted by changing either the cation or the anion of the ILs. For example, the sensitivity in  $[\text{BMIm}]^+[\text{TF}_2\text{N}]^-$  is  $\sim 26$  times higher than in water. It can be increased up to 31 times by changing the anion to  $[\text{PF}_6]^-$  (i.e.,  $[\text{BMIm}]^+[\text{PF}_6]^-$ ) or to 35 times by changing the cation to  $[\text{OMIm}]^+$  (i.e.,  $[\text{OMIm}]^+[\text{TF}_2\text{N}]^-$ ). In fact, the sensitivity of thermal lens measurements in ILs is comparable to those in volatile organic solvents such as benzene, carbon tetrachloride, and hexane. However, the ILs are more desirable as they have virtually no vapor pressure. Furthermore, additional sensitivity enhancement (up to 42 times higher than that in water) can be achieved by simply adding surfactants into the ILs. Based on the thermal conductivity ( $k$ ) and  $dn/dT$  values, calculated from the measured thermal time constant  $t_c$  and thermal lens strength  $\theta$ , it is evident that the observed sensitivity enhancement by the ILs is due to their relatively better thermo-optical properties. More specifically, the enhancement is due not to the relatively modest lowering of the thermal conductivity but rather to the substantial increase in their  $dn/dT$  values. Because of the relationship between  $dn/dT$  and  $d\rho/dT$ , it is expected that ILs can serve as an attractive and superior solvent not only for thermal lens measurements but also for other photo-thermal and photoacoustic techniques as well. Also equally important is the fact that the thermal lens technique in particular and photothermal techniques, in general, can offer a unique means to determine thermo-optical and thermal physical properties of the ILs (e.g., thermal conductivity, thermal diffusivity, and phase transition temperatures). This type of data is currently lacking but is of extreme importance for implementing ILs as a solvent in various industrial applications.

Thermal lens techniques have been demonstrated to be a sensitive method for low-absorbance measurements.<sup>1,2</sup> Absorptivities as low as  $10^{-7}$  have been measured using these tech-

niques.<sup>1,2</sup> The utility of the techniques has increased substantially because it has been demonstrated recently that, in addition to the ultrasensitivity, the techniques are particularly suited for small volume samples.<sup>3</sup> In fact, the combined ultrasensitivity and small-volume capability make it possible to successfully use the techniques as a detector for microfluidic devices. The technique is based on the nonuniform temperature rise that is produced in an illuminated sample by nonradiative relaxation of the energy absorbed from a TEM<sub>00</sub> laser beam. For weak absorbing species, the thermal lens signal, which is measured as the relative changes in the laser beam center intensity in the far field,  $\Delta I_{bc}/I_{bc}$ , is related to the excitation laser power  $P$  and sample absorbance  $A$  by

$$\frac{\Delta I_{bc}}{I_{bc}} = - \frac{1.21P(dn/dT)A}{\lambda k} \quad (1)$$

where  $\lambda$  is the wavelength and  $dn/dT$  and  $k$  are the temperature coefficient of the refractive index and thermal conductivity of the solvent, respectively.<sup>1,2</sup> It is thus clear that, in addition to the sample absorbance and excitation laser power, the thermal lens signal is directly proportional to  $dn/dT$  and inversely proportional to the  $k$  value of the solvent.<sup>1,2</sup> Nonpolar, volatile organic solvents such as benzene, carbon tetrachloride, and hexane should provide good media for thermal lens measurements owing to their high  $dn/dT$  and low  $k$  values. Conversely, water, which is the most powerful and widely used solvent in spectrochemical analysis, is considered to be the worst medium for thermo-optical techniques because it has very low  $dn/dT$  and high  $k$  values.<sup>1,2</sup> In fact, we have successfully demonstrated that, for the same sample concentration and excitation laser power, the sensitivity of thermal lens measurements in volatile solvent such as carbon tetrachloride and benzene are about 40 and 26 times higher than that in water, respectively.<sup>4–8</sup> This is very unfortunate because it severely limits the scope of these techniques. As a consequence, considerable efforts have been made either to ameliorate the thermo-optical properties of water or to develop novel solvents that have better

\* To whom correspondence should be addressed. E-mail: chieu.tran@marquette.edu.

† Permanent address: Laboratory of Environmental Research, Nova Gorica Polytechnic, P.O.B. 301, SI-5001, Nova Gorica, Slovenia.

- (1) See: Dovichi, N. J. *CRC Crit. Rev. Anal. Chem.* **1987**, 17, 357–375. Bialkowski, S. *Photothermal Spectroscopy Methods for Chemical Analysis*; Wiley: New York, 1996.
- (2) Franko, M.; Tran, C. D. *Rev. Sci. Instrum.* **1996**, 67, 1–18.
- (3) Kitamori, T.; Takeshi, M.; Hibara, A.; Sato, K. *Anal. Chem.* **2004**, 76, 52A–60A.
- (4) Tran, C. D.; van Fleet, T. A. *Anal. Chem.* **1988**, 60, 2478–2482.
- (5) Tran, C. D. *Anal. Chem.* **1988**, 60, 182–185.
- (6) Franko, M.; Tran, C. D. *Anal. Chem.* **1989**, 61, 1660–1666.
- (7) Franko, M.; Tran, C. D. *J. Phys. Chem.* **1991**, 95, 6688–6696.
- (8) Baptista, M.; Tran, C. D. *J. Phys. Chem.* **1995**, 99, 12952–12961.

thermo-optical properties than water but do not produce pollution like traditional volatile organic solvents. Our group has successfully demonstrated that the sensitivity of thermal lens measurements in water can be substantially enhanced by use of either normal or reversed micelles.<sup>4,5,7,8</sup> We have also successfully exploited unique properties of water, namely, its unique dependency of  $dn/dT$  on the temperature, to enhance the sensitivity of thermal lens measurements in pure water without any surfactants.<sup>6</sup> While these methods have produced substantial sensitivity enhancement, they involve either adding surfactants into the sample solution or performing the measurements at different temperatures.<sup>4–8</sup> These procedures are time-consuming, cumbersome, and sometimes may produce unwanted effects. It is, thus particularly important that a new type of solvents, which has relatively better thermo-optical properties and low volatility, be developed for thermal lens measurements in particular, and photothermal techniques, in general. Room-temperature ionic liquids with their unique properties may provide the answer for this problem.

Room-temperature ionic liquids (RTILs) are a group of organic salts that are liquid at room temperature. They have unique chemical and physical properties, including being air and moisture stable, a high solubility power, and virtually no vapor pressure.<sup>9–12</sup> Because of these properties, they can serve as a “green” recyclable alternative to the volatile organic compounds that are traditionally used as industrial solvents.<sup>9–12</sup> The RTILs have, in fact, been successfully used in many applications, including replacing traditional organic solvents in (1) organic and inorganic syntheses, (2) solvent extractions, (3) liquid–liquid extractions, and (4) electrochemical reactions and (5) as a medium for enzymatic reactions.<sup>9–12</sup> Unfortunately, the success of RTILs in industrial and chemical applications has not extended to the spectroscopic field; namely, RTILs have not been exploited as solvent for spectroscopic measurements. In fact, to date, data on thermo-optical properties of RTILs are not available. This is rather unfortunate considering the fact that, in addition to their unique properties, RTILs not only have high solubility power but that their solubility can be finely tuned by changing either the cation or anion.

The information presented is indeed provocative and clearly demonstrates that the unique properties of RTILs including their nonvolatility and highly solubility power make them particularly attractive as a Green recyclable alternative to the volatile organic solvents for spectroscopic measurements. Such considerations prompted us to initiate this study that aims to explore the use of RTILs as solvents for thermal lens measurements. Different RTILs including those with different anions or cations will be used to elucidate the effect of the ions on the thermo-optical properties of the RTILs. Results obtained on the RTILs will be compared to those in water and in volatile organic solvents.

## EXPERIMENTAL SECTION

**Instrument and Methods.** Thermal lens signals were measured using the dual-wavelength pump/probe configuration thermal lens spectrometer similar to that used in our previous

studies.<sup>4–9</sup> Essentially the sample was excited by a 514.5-nm, 20-mW excitation beam derived from an argon ion laser, and the photoinduced thermal lens was measured by a He–Ne probe laser (632.8 nm). A Uniblitz electronic shutter was used to modulate the pump beam. Typically, the thermal lens was recorded as the time-dependent change in the far-field beam center intensity (of the probe beam) after the onset of excitation laser illumination.<sup>4–8</sup>

$$I_{bc}(t) = I_{bc}(0)$$

$$\left[ 1 - \theta \arctan \left[ \frac{3\xi}{3 + \xi^2 + (9 + \xi^2)t_c/2t} \right] + \left\{ \frac{\theta}{2} \arctan \left[ \frac{2\xi}{3 + \xi^2 + (9 + \xi^2)t_c/2t} \right] \right\}^2 + \left( \frac{\theta}{4} \ln \left[ \frac{[(2 + t_c/t)(3 + \xi^2) + 6t_c/t]^2 + 16\xi^2}{(9 + \xi^2)^2 + (2 + t_c/t)^2} \right] \right)^2 \right] \quad (2)$$

where  $\xi$  is related to the distance between the sample and the beam waist  $Z_1$  and the confocal distance  $Z_c$  by

$$\xi = Z_1/Z_c \quad (3)$$

The strength of the thermal lens,  $\theta$ , is related to wavelength ( $\lambda$ ) and power of the laser ( $P$ ), the sample absorbance ( $A$ ), and  $dn/dT$  and  $k$  values of the solvent as

$$\theta = 2.303PA(-dn/dT)/\lambda k \quad (4)$$

The thermal time constant  $t_c$  is given by

$$t_c = \omega^2 \rho c_p / 4k \quad (5)$$

where  $c_p$  is the heat capacity,  $\rho$  is the density, and  $\omega$  is the beam spot size.

From the recorded time dependence of the beam center intensity,  $I_{bc}(t)$ , the thermal lens strength,  $\theta$ , and the thermal time constant,  $t_c$ , can be obtained by curve fitting of the data according to eq 2. Each sample was measured at least three times.

**Chemicals.** Chloride salts of alkylmethyl imidazolium ( $C_2$ ,  $C_4$ ,  $C_5$ ,  $C_6$ , and  $C_8$ MI $m^+$ ) were obtained from Aldrich. They were converted into the corresponding bis(trifluoromethyl)sulfonyl)-amide or  $Tf_2N^-$  salts by metathesis reaction using procedure reported in our earlier studies.<sup>10–12</sup> The ILs obtained were washed with ethyl acetate and dried under vacuum at 70 °C overnight.

## RESULTS AND DISCUSSION

Initial investigation was on the effect of the anion on the thermo-optical properties of the ILs. Butylmethyl imidazolium (BMIm $^+$ ) was used as the cation as it is one of the most widely studied and used ILs.<sup>9–12</sup> Three different anions were selected:  $Tf_2N^-$ , tetraborate ( $BF_4^-$ ), and hexafluoro phosphate ( $PF_6^-$ ) (see Table 1 for structures of ILs used in this study). Since these ILs and water do not have any measurable absorption at the excitation wavelength of 514.5 nm, a small amount of tris(1,10-phenanthroline)iron(II) sulfate or ferroin was added to induce absorption. Rather than measuring and comparing the signals of only one

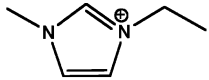
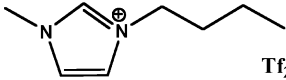
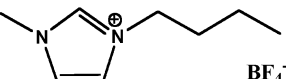
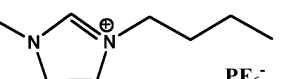
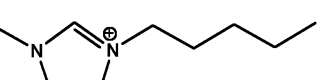
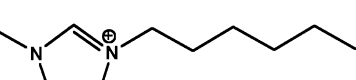
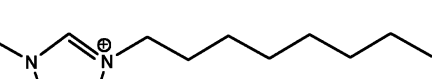
(9) Welton, T. *Chem. Rev.* **1999**, 99, 2071–2083.

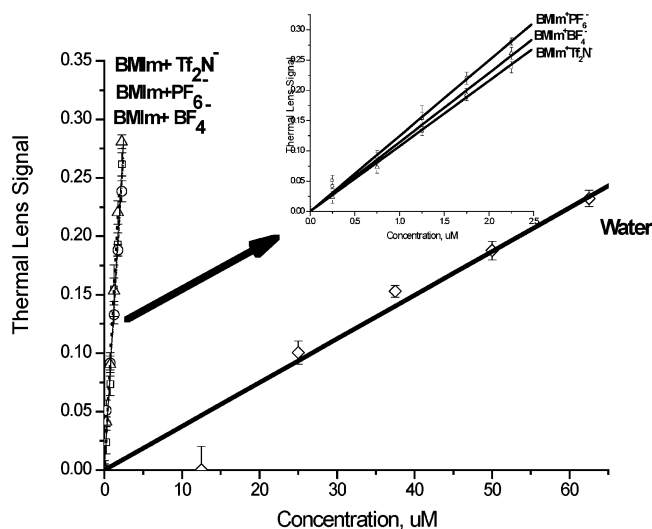
(10) Tran, C. D.; Lacerda, S. D. P. *Anal. Chem.* **2002**, 74, 5337–5341.

(11) Tran, C. D.; Lacerda, S. D. P.; Oliveira, S. *Appl. Spectrosc.* **2003**, 57, 152–157.

(12) Mele, A.; Tran, C. D.; Lacerda, S. H. D. *Angew. Chem., Int. Ed.* **2003**, 42, 4364–4366.

**Table 1. List of Ionic Liquids Used in This Study**

	$\text{Tf}_2\text{N}^-$	1-ethyl-3-methylimidazolium $\text{Tf}_2\text{N}^-$ or $[\text{EMIm}]^+ [\text{Tf}_2\text{N}]^-$
	$\text{Tf}_2\text{N}^-$	1-butyl-3-methylimidazolium $\text{Tf}_2\text{N}^-$ or $[\text{BMIm}]^+ [\text{Tf}_2\text{N}]^-$
	$\text{BF}_4^-$	1-butyl-3-methylimidazolium $\text{BF}_4^-$ or $[\text{BMIm}]^+ [\text{BF}_4]^-$
	$\text{PF}_6^-$	1-butyl-3-methylimidazolium $\text{PF}_6^-$ or $[\text{BMIm}]^+ [\text{PF}_6]^-$
	$\text{Tf}_2\text{N}^-$	1-pentyl-3-methylimidazolium $\text{Tf}_2\text{N}^-$ or $[\text{PMIm}]^+ [\text{Tf}_2\text{N}]^-$
	$\text{Tf}_2\text{N}^-$	1-hexyl-3-methylimidazolium $\text{Tf}_2\text{N}^-$ or $[\text{HMIm}]^+ [\text{Tf}_2\text{N}]^-$
	$\text{Tf}_2\text{N}^-$	1-octyl-3-methylimidazolium $\text{Tf}_2\text{N}^-$ or $[\text{OMIm}]^+ [\text{Tf}_2\text{N}]^-$

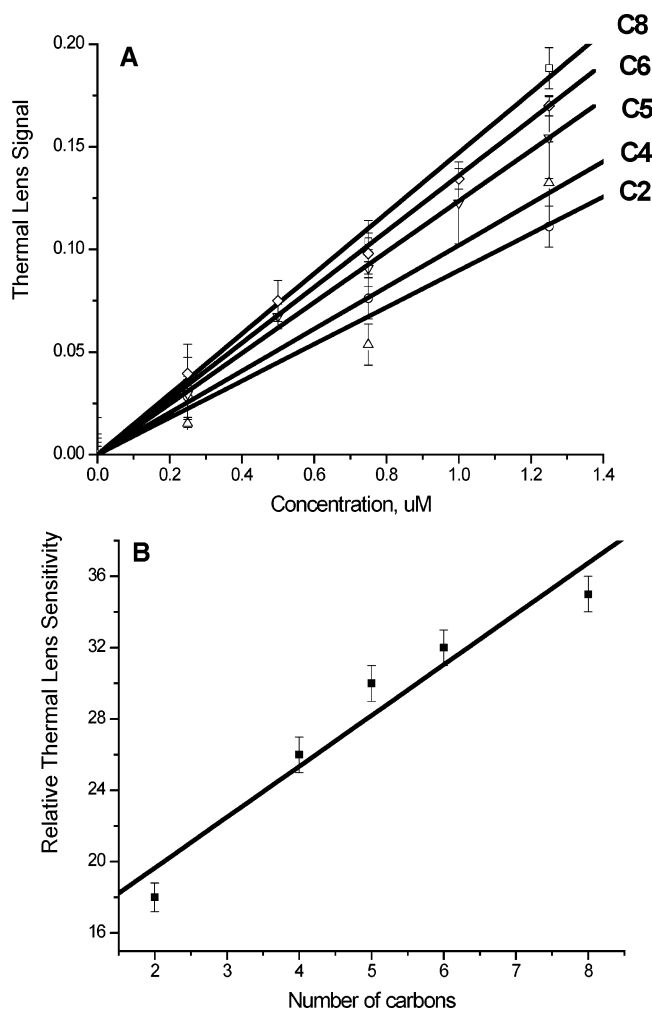
**Figure 1.** Calibration curves for thermal lens in water and in three different ionic liquids:  $[\text{BMIm}]^+ [\text{Tf}_2\text{N}]^-$ ,  $[\text{BMIm}]^+ [\text{BF}_4]^-$ , and  $[\text{BMIm}]^+ [\text{PF}_6]^-$ .

ferroin concentration in four different media (water,  $\text{BMIm}^+ \text{Tf}_2\text{N}^-$ ,  $\text{BMIm}^+ \text{BF}_4^-$ ,  $\text{BMIm}^+ \text{PF}_6^-$ ), a calibration curve with different concentrations of ferroin was constructed for each of the four solvents in order to accurately determine the sensitivity of the thermal lens in these media. Figure 1 shows the calibration curves in water as well as in three ILs (each calibration curve has a small intercept due to very small background absorption by water and ILs. Since the intercepts are rather small and do not have effect

**Table 2. Relative Thermal Lens Sensitivity in Different Media**

solvent	relative thermal lens sensitivity
water	1
benzene	$26 \pm 1$
$[\text{BMIm}]^+ [\text{Tf}_2\text{N}]^-$	$26 \pm 1$
$[\text{BMIm}]^+ [\text{BF}_4]^-$	$29 \pm 2$
$[\text{BMIm}]^+ [\text{PF}_6]^-$	$31 \pm 1$
$[\text{EMIm}]^+ [\text{Tf}_2\text{N}]^-$	$18.0 \pm 0.8$
$[\text{PMIm}]^+ [\text{Tf}_2\text{N}]^-$	$30 \pm 1$
$[\text{HMIm}]^+ [\text{Tf}_2\text{N}]^-$	$32 \pm 1$
$[\text{OMIm}]^+ [\text{Tf}_2\text{N}]^-$	$35 \pm 1$
$[\text{BMIm}]^+ [\text{Tf}_2\text{N}]^- + 0.5 \text{ M SB3-10}$	$37 \pm 1$
$[\text{BMIm}]^+ [\text{Tf}_2\text{N}]^- + 0.5 \text{ M Brij-35}$	$42 \pm 1$

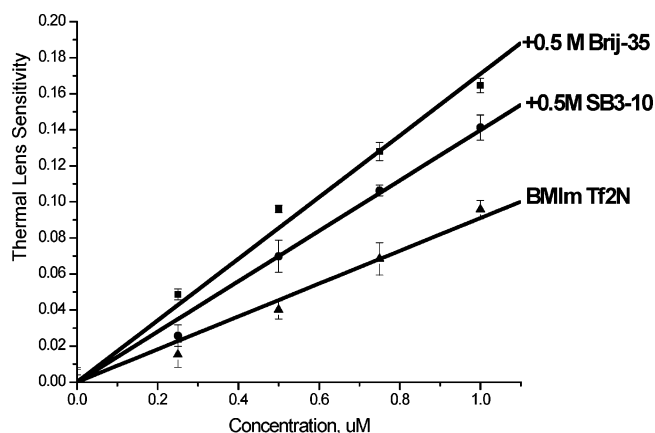
on the sensitivity of the measurements, all calibration curves were shifted to zero intercept for clarity of presentation). As illustrated, the slopes for all three ILs are much larger than that for water. Actual sensitivity values are listed in Table 2 where the sensitivity for water is normalized to be 1. It is noteworthy to add that, in this work, the sensitivities were not calculated from the thermal lens signal intensity but rather from the slope of the calibration curves (also known as calibration sensitivities). Furthermore, when relative sensitivities (to water) were calculated, the standard deviations associated with the sensitivity in the ILs and in water were taken into account to yield the standard deviation for each relative sensitivity value. As a consequence, the relative sensitivity values listed in the table represent not only the sensitivity but



**Figure 2.** (A) Calibration curves for thermal lens in ionic liquids having alkyl groups with different lengths and (B) plot of sensitivity of thermal lens against number of carbons of the alkyl group.

also, to some degree, noise associated with the ILs and water as well. It is interesting to observe that the sensitivity in all three ILs is at least 20–30 times higher than that in water. Interestingly, changing the anion of the ILs also produces significant changes in the sensitivity. Specifically, replacing  $\text{TF}_2\text{N}^-$  in  $\text{BMIm}^+\text{TF}_2\text{N}^-$  with  $\text{BF}_4^-$  increases the sensitivity from 26- to 29-fold (relative to water) or an increase of 11.5%.  $\text{PF}_6^-$  seems to produce a stronger effect as it increases the sensitivity up to 31-fold or 19% increase compared to  $\text{TF}_2\text{N}^-$ .

Subsequent investigation was on the effect of the cation. Four different ILs with the same anion ( $\text{TF}_2\text{N}^-$ ) but different cations ( $\text{C}_2\text{MIm}^+$ ,  $\text{C}_4\text{MIm}^+$ ,  $\text{C}_5\text{MIm}^+$ ,  $\text{C}_6\text{MIm}^+$ ,  $\text{C}_8\text{MIm}^+$ ) were used. Figure 2A shows the calibration curves in these five ILs. As illustrated, increasing the chain length of the alkyl group on the imidazolium cation led to an increase in the sensitivity. As listed in Table 2, the sensitivity increase from 18-fold by  $\text{C}_2\text{MIm}^+$  to 26-, 30-, 32-, and 35-fold by  $\text{C}_4\text{MIm}^+$ ,  $\text{C}_5\text{MIm}^+$ ,  $\text{C}_6\text{MIm}^+$ , and  $\text{C}_8\text{MIm}^+$ , respectively. Interestingly, as shown in Figure 2B, the relative sensitivities seem to be linearly related to the number of carbons in the alkyl group of the imidazolium cation. The origin of this linear relationship is unclear at this time and may be just a coincidence. However, the results clearly indicate that increasing the chain length of the alkyl group or increasing the hydrophobic-



**Figure 3.** Calibration curves for thermal lens in  $[\text{BMIm}]^+[\text{TF}_2\text{N}]^-$  ionic liquid without surfactant and with 0.5 M SB3–10 and with 0.5 M Brij–35.

ity of the ILs leads to an increase in the sensitivity of thermal lens measurements. In fact, the results observed here are in agreement with those obtained in our previous studies; namely, we found that the sensitivity of the thermal lens is higher in a hydrocarbon with a longer carbon chain (e.g., *n*-heptane) than those of relatively shorter chain (e.g., pentane).<sup>4–8</sup>

It was found recently by our group and also by others that surfactants can aggregate to form micelles in ILs.<sup>13,14</sup> Because of the aggregations, it may be possible to enhance the sensitivity of thermal lens measurements in ILs by simply adding surfactants into them. The possibility stems from our previous studies in which we showed that enhancement in the thermal lens sensitivity can be achieved by simply adding surfactants into aqueous solution. This possibility was investigated by comparing thermal lens signals in  $\text{BMIm}^+\text{TF}_2\text{N}^-$  alone with those in  $\text{BMIm}^+\text{TF}_2\text{N}^-$  with 0.5 M zwitterionic surfactant SB3–10 and in  $\text{BMIm}^+\text{TF}_2\text{N}^-$  with 0.5 M of nonionic surfactant Brij-35. Figure 3 shows calibration curves in these three media. As illustrated, adding surfactants into the IL led to a substantial increase in the sensitivity. As listed in Table 2, adding 0.5 M zwitterionic surfactant SB3–10 led to 37-fold higher sensitivity than that in pure water and a 42% increase compared to the pure IL without surfactant. The effect of the nonionic surfactant Brij-35 is even higher: adding 0.5 M concentration of this surfactant into the IL led to a 61-fold increase in the sensitivity.

In addition to providing additional enhancement in the sensitivity of the thermal lens, surfactants also improve the solubility of the ILs. Specifically, fullerene compounds such as  $\text{C}_{60}$  and  $\text{C}_{70}$  are insoluble in the ILs. However, adding surfactants into the ILs makes it possible to dissolve the fullerenes into them. As a consequence, it is possible to confirm that the observed sensitivity enhancement is not specific for ferriin but is rather general for other analytes including  $\text{C}_{60}$  as well. This conclusion stems from the fact that enhancements observed for ferriin in  $[\text{BMIm}]^+[\text{TF}_2\text{N}]^-$  with 0.5 M SB3–10 and with 0.5 M Brij-35 are the same, within experimental error, as those observed for  $\text{C}_{60}$  in the same IL–surfactant solutions. Furthermore, by using either ferriin or  $\text{C}_{60}$  as an analyte, it is possible to compare the enhancement observed

(13) Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V.; Armstrong, D. W. *Chem. Commun.* **2003**, 2444–2446.

(14) Tran, C. D.; Yu, S. J. *Colloid Interface Sci.* **2005**, *283*, 613–618.



for pure ILs and ILs with surfactants with that in benzene (Table 2). That is ferroin was used as analyte for water, for pure ILs, and for ILs with surfactants while  $C_{60}$  was used for benzene and for ILs with surfactants (this is because ferroin is not soluble in benzene while  $C_{60}$  is insoluble in water and pure ILs).

It is evidently clear that the higher sensitivity observed in ILs is due to the fact that ILs have relatively better thermo-optical properties than those of water; that is they may have either higher  $dn/dT$  or lower thermal conductivity than water. Since ILs are relatively new compounds, data on their thermal physical and thermo-optical properties (e.g.,  $dn/dT$  and  $k$  values) are currently not available. Fortunately, it is possible to use data obtained from thermal lens measurements to estimate the  $dn/dT$  and  $k$  values. Specifically, the thermal conductivity value can be calculated from the measured thermal time constant  $t_c$  according to eq 5. However, because it is relatively difficult to measure the beam spot size  $\omega$  accurately, it is more appropriate to calculate  $k$  by comparing the  $t_c$  values in IL to that in water. Specifically, assuming that the beam spot sizes in water and in the IL are the same, eq 5 can be rearranged to give

$$k_{(IL)} = \frac{k_{(w)}\rho_{(IL)}c_{p(IL)}t_{c(w)}}{\rho_{(w)}c_{p(w)}t_{c(IL)}} \quad (6)$$

where the subscripts (w) and (IL) denote the values for water and for the IL, respectively. Since the thermal conductivity, density, and heat capacity of water are known, this equation can be used to calculate the thermal conductivity of the IL if its density and heat capacity are known. In the case where density and heat capacity of the IL are unknown, it is more useful to calculate the ratio of thermal conductivities

$$\frac{k_{(IL)}}{k_{(w)}} = \frac{\rho_{(IL)}c_{p(IL)}t_{c(w)}}{\rho_{(w)}c_{p(w)}t_{c(IL)}} \quad (7)$$

Once values of thermal conductivity are obtained,  $dn/dT$  value can be calculated by rearranging eq 4 to give

$$\frac{(dn/dT)_{(IL)}}{(dn/dT)_{(w)}} = \frac{\theta_{(IL)}A_{(w)}k_{(IL)}}{\theta_{(w)}A_{(IL)}k_{(w)}} \quad (8)$$

Accordingly, thermal conductivity and  $dn/dT$  values of the ILs such as  $BMIm^+BF_4^-$  and  $BMIm^+Tf_2N^-$  can be calculated from these two equations based on the measured  $t_c$  and  $\theta$  values in pure water and in the ILs, using  $k_w = 6.04 \text{ mW cm}^{-1} \text{ K}^{-1}$ ,  $(dn/dT)_w = 8.8 \times 10^{-5} \text{ K}^{-1}$ ,  $c_{p(w)} = 4.1819 \text{ J g}^{-1} \text{ K}^{-1}$ , and  $\rho_w = 1$ , the density  $\rho$  and the heat capacity  $c_p$  values for  $BMIm^+BF_4^-$  and  $BMIm^+Tf_2N^-$  are 1.20 and 1.438  $\text{kg/m}^3$  and 1.614 and 1.278  $\text{J g}^{-1} \text{ K}^{-1}$ , respectively.<sup>15</sup> The thermal conductivity values for  $BMIm^+BF_4^-$  and  $BMIm^+Tf_2N^-$  were found to be 1.785 and 1.062  $\text{mW cm}^{-1} \text{ K}^{-1}$  while their  $dn/dT$  values are  $-7.54 \times 10^{-4} \text{ K}^{-1}$  and  $-4.02 \times 10^{-4} \text{ K}^{-1}$ , respectively. It is of particular interest to compare these values for the ILs with those for water ( $k_w = 6.04 \text{ mW cm}^{-1} \text{ K}^{-1}$ ,  $(dn/dT)_w = 8.8 \times 10^{-5} \text{ K}^{-1}$ ). It is evident that the sensitivity of

thermal lens in the ILs is higher than in water because the ILs has relatively lower thermal conductivity and higher  $dn/dT$  values. However, the enhanced sensitivity is due not so much to the lowering of the thermal conductivity but mainly to the substantial increase in the  $dn/dT$  value. Specifically, while  $k$  values of  $BMIm^+BF_4^-$  and  $BMIm^+Tf_2N^-$  are about 70 and 82% lower than that of water (from 6.04 to 0.785 and 1.062  $\text{mW cm}^{-1} \text{ K}^{-1}$ ), their  $dn/dT$  values are about 750 and 350% higher than that of water (from  $8.8 \times 10^{-5}$  to  $8.05 \times 10^{-4}$  and  $4.02 \times 10^{-4} \text{ K}^{-1}$ ). Furthermore, simply changing the anion in the  $BMIm^+$  ILs from  $BF_4^-$  to  $Tf_2N^-$  produces a significant effect on the thermal physical properties of the ILs, not only that it lowers the thermal conductivity by 40% (from 1.785 to 1.062  $\text{J g}^{-1} \text{ K}^{-1}$ ) but also that it decreases the absolute value of  $dn/dT$  by almost the same amount (i.e., from  $-7.54 \times 10^{-4} \text{ K}^{-1}$  to  $-4.02 \times 10^{-4} \text{ K}^{-1}$  or 46%).

Because the density and heat capacity of other ILs and their mixtures with surfactants are currently not available, it is not possible to calculate their thermal conductivity and  $dn/dT$  values. However, insight into the effect of  $k$  and  $dn/dT$  on the thermal lens enhancement can be gained by comparing the ratio of thermal conductivities and of  $dn/dT$  for IL and for water, according to eqs 7 and 8, respectively. This can be accomplished by using the measured  $t_c$  and  $\theta$  values and assuming that the density and heat capacity of other ILs and their mixtures with surfactants are similar to those for  $BMIm^+BF_4^-$ . Interestingly, it was found that other ILs and their mixtures with surfactants behave similarly to that of  $BMIm^+BF_4^-$ . That is, in all ILs with the same cations or anions, either in pure form or with surfactants, compared to water, the  $k_{(IL)}/k_{(w)}$  ratios are much smaller than the  $(dn/dT)_{(IL)}/(dn/dT)_{(w)}$  ratios. Again, these results seem to indicate that the observed enhanced sensitivity of the thermal lens is due to not to the relatively modest lowering of the thermal conductivity but rather to the substantial increase in their  $dn/dT$  values. It is noteworthy to add that these results are in good agreement with those found in our earlier studies in which we investigated the enhanced thermal lens sensitivity induced by surfactants and electrolytes in water<sup>4,5</sup> that is, we found that the observed enhancement is due to the effect of the surfactants or electrolytes not on the thermal conductivity but rather on the  $dn/dT$  of the aqueous solution.<sup>4,5</sup>

In summary, we have successfully demonstrated that ILs can be used as an attractive and superior solvent for thermal lens measurements. The ILs are superior to water as they have relatively high solubility power, and by judicious selecting either the cation or anion, they can be made to dissolve many different types of compounds including polar as well as nonpolar compounds. More importantly, they provide a better medium for thermal lens measurements than water. Specifically, not only the ILs offer at least 20 times higher sensitivity than water, but the enhancement can be appropriately adjusted by changing either the cation or the anion of the ILs. For example, the sensitivity in  $[BMIm]^+[Tf_2N]^-$  is ~26 times higher than in water. It can be increased up to 31 times by changing the anion to  $[PF_6]^-$  (i.e.,  $[BMIm]^+[PF_6]^-$ ) or to 35 times by changing the cation to  $[OMIm]^+$  (i.e.,  $[OMIm]^+[Tf_2N]^-$ ). In fact, the sensitivity of thermal lens measurements in ILs is comparable to those in volatile organic solvents such as benzene, carbon tetrachloride, or hexane, but ILs are more desirable as they have virtually no vapor pressure. Furthermore, additional sensitivity enhancement (up to

(15) Kim, K. S.; Shin, B. K.; Lee, H. *Korean J. Chem. Eng.* **2004**, *21*, 1010–1014.

42 times higher than that in water) can be achieved by simply adding surfactants into the ILs. Results obtained for the two analytes used in this study, ferroin and  $C_{60}$ , illustrate some of potential applications of this enhancement method. Ferroin, which is insoluble in nonpolar solvent, can be dissolved in ILs instead of water to substantially enhance its thermal lens detection. Fullerenes such as  $C_{60}$  are soluble only in highly nonpolar solvent (e.g., benzene). Instead of using volatile organic compounds (VOC) such as benzene as solvent, its detection can be readily and sensitively achieved by using solutions of surfactants in ILs. As described previously in the introduction, the thermal lens technique is particularly suited as a detection method for microfluidic devices because of its ultrasensitivity and small-volume capability (conventional spectrophotometric technique cannot be used for such devices because it has much lower sensitivity and its sensitivity is proportional to the path length of the sample). The IL-induced thermal lens enhancement reported here can, therefore, be synergistically used in microfluidic devices by simply replacing either water (to enhance detection sensitivity) or VOC solvent (to prevent pollution and also to enhance the sensitivity) with ILs.

It is evident, based on the thermal conductivity ( $k$ ) and  $dn/dT$  values, calculated from the measured thermal time constant  $t_c$  and thermal lens strength  $\theta$ , that the observed sensitivity enhancement by the ILs is due to their relatively better thermooptical properties (as compared to water). More specifically,

it seems that the enhancement is due not to the relatively modest lowering of the thermal conductivity but rather to the substantial increase in their  $dn/dT$  values. Due to the relationship between  $dn/dT$  and  $d\rho/dT$ , it is expected that ILs can serve as an attractive and superior solvent not only for thermal lens measurements but also for other photothermal and photoacoustic techniques as well. Also equally important is the fact that the thermal lens technique in particular and photothermal techniques in general can offer a unique means to determine thermooptical and thermal physical properties of the ILs (e.g., thermal conductivity, thermal diffusivity as well as phase transition temperatures). This type of data is currently lacking but is of extreme importance for implementing ILs as a solvent in various industrial applications. Experiments are currently in progress in our laboratory to investigate these possibilities.

#### ACKNOWLEDGMENT

The authors are grateful to Ms. Shaofang Yu for her technical assistance. Acknowledgment is made to NATO for financial support of this work (through NATO Collaborative Linkage Grant, Grant CBP. EAP. CLG981394).

Received for review July 20, 2005. Accepted September 8, 2005.

AC0512913