The microheterogeneous structure of ionic liquid mixtures with organic solvent determined by a cyanine-dye fluorescent probe.

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Abstract

The photophysics of 3,3'-diethylthiacarbocyanine iodide (DTCI), as a fluorescence probe, in liquid mixtures of dimethyl sulfoxide (DMSO) with either trimethyl(butyl)ammonium bis((trifluoromethyl)sulfonyl)imide ([N(4)111] [Tf2N]) or 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([bmim] [Tf2N]) was studied by means of steady-state and time-resolved fluorescence spectroscopy. Steady-state properties as functions of the mixture composition, i.e. DTCI absorption and fluorescence spectra, and fluorescence depolarization, were found to be fairly similar to both mixtures. On the contrary, the DTCI fluorescence decay was observed to be double-exponential in mixtures with [N(4)111] [Tf2N] for DMSO volume fractions less than ca. 0.5 while that is single exponential in mixtures with [bmim] [Tf2N] under the same conditions. These findings are explained in terms of the Hildebrand solubility model by assuming the existence of coarsely-grained spatial micro-heterogeneities, clusters of DMSO molecules, in ammonium-based ionic liquid/DMSO mixtures.

Introduction

Room temperature ionic liquids (ILs) have unusual solvent properties and in particular a negligible low vapor pressure. Although a large viscosity inherent to ILs might be a limitation of their applications, they remain a very active field of theoretical and experimental studies as novel reaction media (see a recent review [1]).

In order to tune a reaction environment, binary solvent mixtures have long been in use. An important feature of such media, which is often ignored, is that such mixtures have microdomains, whose properties are different from that of the bulk. Organic solvent mixtures that comprise components of significantly different polarity, i.e. toluene and DMSO, provide micro-heterogeneous media for a charged solute, for example cationic cyanine dye [2].

Components of binary mixtures are not necessarily to be conventional solvents. Hapiot and coworkers [3] found a significant increase in diffusion coefficients of O₂ and superoxide that increase exponentially with increasing the dimethylformamide volume fraction in the mixture

with triethyl(butyl)ammonium bis((trifluoromethyl)sulfonyl) imide. Although such a IL singularity is not still completely understandable, one can suggest that the observed effect is mainly caused by structural heterogeneities.

It is worth noting that neat IL by itself tends to produce structural heterogeneities. For example, Wakasa and coworkers [4] observed an unusually large influence of external magnetic field on the photoinduced hydrogen-abstraction reaction between benzophenone and thiophenol in ionic liquid, N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl) imide. Such magnetic field effects require a large cage effect in reaction media that is associated with micellar solutions rather than with homogeneous liquids. The comparison of experimental results with a reasonable cage model showed that in the ionic liquid there exist domains of 20-40 Å size and 1-2 cP viscosity.

Although there are voluminous publications on the IL topic, relatively few studies of IL mixtures with organic solvents are available. So that the purpose of this work is to study the microstructure of binary solvent mixtures, one component of which is IL, by means of fluorescence spectroscopy. As a representative example, we have chosen ionic liquids, [N(4)111][NTf₂] and [bmim][Tf₂N], for studying the effect of the addition of organic solvent dimethylsulfoxide (DMSO) into these ILs on the microheterogeneous structure of mixtures. Thiocarbocyanine dye, employed earlier in studying binary mixtures of conventional solvents [2, 5], was used as a fluorescent probe.

Experimental

The dye, 3,3'-diethylthiocarbocyanine iodide (DTCI), was purchased from Fluka and used without further purification. Ammonium-based ionic liquid, trimethyl(butyl)ammonium bis((trifluoromethyl)sulfonyl)imide $[N(4)111][Tf_2N]$ and imidazolium-based ionic liquid, 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [bmim][Tf₂N], were purchased from Solvionic, France. Their water content was checked to be less than 100 ppm. The structural

formulas of cyanine dye and ionic liquids are shown in Scheme 1. Dimethylsulfoxide (DMSO) was of spectrograde (Uvasol, Merck).

Scheme 1. The structural formulas of cyanine dye (DTCl) and ions of which the used ionic liquids consist.

Absorption spectra were recorded by a UV-3101PC spectrophotometer (Shimadzu) and steady-state fluorescence emission spectra of solutions, by a Fluorolog-3 τ spectrofluorometer (Jobin Yvon). Steady-state fluorescence depolarization experiments were carried out by a Fluorolog-3 τ spectrofluorometer using automatically operated polarizers (the DataMax software) with excitation at the peaks of the absorption spectra, i.e., about 560 nm, and emission at the peaks of the DTCl-fluorescence spectra about 580 nm. By definition, the polarization of fluorescence is $P = (I_V - GI_H)/(I_V + GI_H)$ where I_V and I_H are the fluorescence components parallel and perpendicular to the plane of polarization of the excitation beam, respectively, and G is the correction factor that was taken into account in the course of experiment (the DataMax software). All measurements were carried out with 10 mm cells at room temperature.

Viscosity of mixtures of ILs with DMSO were measured by a cone-and plate ARES viscosimeter (Rheometric scientific) at $(25 \pm 0.1)^\circ\text{C}$ and ambient pressure.

Results and discussion

When the IL volume fraction increases in DMSO/ [N(4)111] [Tf₂N] mixtures up to 100 vol %, the absorption peak of DTCl solution slightly (about 7 nm) shifts to the shorter wavelengths from 565 nm in neat DMSO (see Figure 1).

Figure 1. DTCl absorption spectra in DMSO/ [N(4)111] [Tf₂N] mixtures for various volume fractions of DMSO.

The DTCl fluorescence shows only one peak at about 580 nm in neat DMSO that is shifted by about 7 nm to shorter wavelengths as the IL volume fraction increases; the amplitude of the fluorescence peak increases by a factor about 3 (Figure 2).

Figure 2. Fluorescence spectra of DTCl in DMSO/[N(4)111] [Tf₂N] mixtures for various volume fractions of DMSO.

The steady-state absorption and fluorescence properties of DTCl in mixtures of DMSO with [bmim] [Tf₂N] are quite similar to those in mixtures with [N(4)111] [Tf₂N].

The time-resolved fluorescence measurements have shown that upon excitation in a 560 nm spectral band, the fluorescence-decay dynamics recorded at 580 nm depends on the mixture composition (see Table 1). So that fluorescence decays were fitted to a bi-exponential function

$$I(t) = \alpha_1 \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \exp\left(-\frac{t}{\tau_2}\right), \quad (1)$$

where τ_1 and τ_2 are the lifetimes, α_1 and α_2 are their relative fractions ($\alpha_1 + \alpha_2 = 1$).

For neat DMSO and DMSO-rich mixtures (volume fraction of IL is less than 40 vol %), the decay can be fitted to a single exponent ($\alpha_2 = 0$) with the lifetime component of about 330 ps. For IL-rich mixtures, a longer component is found which increases from about 670 to 1120 ps when the volume fraction of IL becomes larger than 40 vol.%. In the case of [bmim] [Tf₂N], only a single-exponential fluorescence decay has been observed for all mixture compositions.

The appearance of a bi-exponential character of fluorescence decay seems to reflect micro-structure of binary mixtures. Such features can be regarded as spatial fluctuations of mixture's composition that are created and destroyed by random diffusional motion of solvent molecules of both components. In greatly fluctuating mixtures, the fluorophore molecule always can find the long-lived (as compared with the life time of the fluorophore fluorescence) mode of spatial fluctuation, i.e. the molecular cluster mainly consisting of similar particles either of components. The ability of the binary mixture to fluctuate can determine the observed distinction in photo-physical properties of DTCI in the mixtures that otherwise are quite similar in physical sense.

Table 1. The lifetimes and their fractions of TDCI fluorescence in mixtures of DMSO with ILs as a function of volume fraction of DMSO.

DMSO, vol. %	[N(4)111] [Tf ₂ N]		[bmim] [Tf ₂ N]
	$\tau_1 (\alpha_1)$, ps	$\tau_2 (\alpha_2)$, ps	τ , ps
100	326 (1.0)	--	326
90	328(1.0)	--	--
80	331 (1.0)	--	--
75	--	--	385
60	346 (0.93)	676 (0.07)	419
40	333 (0.2)	451 (0.8)	512
20	361 (0.1)	601 (0.9)	642
0.4	736 (0.53)	1159 (0.47)	870

Thermally generated fluctuations of the number of DMSO molecules, n , in a given nano-sized volume, i.e. $\Delta n = n - \bar{n}$ (where $\bar{n}$ is an average value), can be described as follows [6]:

$$\overline{(\Delta n)^2} = \frac{RT}{\left(\frac{\partial \mu}{\partial n}\right)_{P,T}}, \quad (2)$$

where μ is the chemical potential of DMSO, R is the universal gas constant, and T is the absolute temperature. Introducing the molar ratio of a DMSO component, x_1 , one can rewrite Eq(2)

$$\overline{(\Delta x_1)^2} \propto \frac{RT}{\left(\frac{\partial \mu}{\partial x_1}\right)_{P,T}}. \quad (3)$$

According to the Hildebrand theory [7], the chemical potential of a DMSO component is

$$\mu = \mu^0 + RT \ln x_1 + \Phi_2^2 V_1 (\delta_1 - \delta_2)^2, \quad (4)$$

where Φ_2 is the volume fraction of IL, V_1 is the molar volume of DMSO, δ_1 and δ_2 are

Hildebrand's solubility parameters for DMSO and IL respectively. Substituting Eq.(4) into Eq.(3)

and taking into account that $V_2 \gg V_1$, one can obtain for small values of x_1 :

$$\overline{(\Delta x_1)^2} \propto \frac{x_1}{1 - \frac{4V_1(\delta_1 - \delta_2)^2 x_1^2}{RT}}. \quad (5)$$

On increasing $\overline{(\Delta x_1)^2}$, the mixture becomes more fluctuating. For $\delta_1 = \delta_2$, Eq.(5) reduces to

$\overline{(\Delta x_1)^2} \propto x_1$ that corresponds to the stochastic level of the ideal mixture. Eq(5) is physically

meaningful if the denominator is positive; on being so the closer a value of

$4V_1(\delta_1 - \delta_2)^2 x_1^2 / RT$ to unity, the stronger should be concentration fluctuations of the mixture.

Thus, in this approximation the conditions for strongly fluctuating mixtures in the range of

$x_1 \leq \frac{1}{2}$ is

$$V_1(\delta_1 - \delta_2)^2 \approx RT. \quad (6)$$

Taking $V_1 = 71.3 \text{ cm}^3$ and $\delta_1 = 12.0 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ [7]; $\delta_2 = 14.33 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for [bmim] [Tf₂N], and

$\delta_2 = 15.23 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for [N(4)111] [Tf₂N] [8], one can calculate that a value of $V_1(\delta_1 - \delta_2)^2$ is

about 387.1 cal for [bmim] [Tf₂N] and 743.9 cal for [N(4)111] [Tf₂N]. For room temperature

$RT \approx 600 \text{ cal}$, so that condition (6) is pretty well fulfilled for [N(4)111] [Tf₂N] that is confirmed

by experiment. This is in fairly good agreement with the results observed, considering the

empirical nature of Hildebrand's theory and quite contradictory data on solubility parameters of ILs available in the literature. It is worth noting that similar results were obtained in the case of binary mixtures of molecular solvents [9,10].

Figure 3. The viscosity of the [N(4)111] [Tf₂N] /DMSO mixture as a function the volume fraction of DMSO.

The values of viscosity for neat [N(4)111] [Tf₂N] and [bmim] [Tf₂N] have been measured to be 119.0 cP and 70.0 cP respectively. Fig. 3 shows the viscosity of the [N(4)111] [Tf₂N] /DMSO mixture as a function of **the** DMSO volume fraction. For volume fractions larger than 20%, viscosity does not exceed 30 cP; for volume fractions of DMSO less than 20 vol.% it goes rapidly up to 119 cP in neat IL. The viscosity of the [bmim] [Tf₂N] mixture depends upon its composition in a similar fashion (is not shown).

It is worth noting that such a dependence of viscosity upon the mixture composition can correspond to a heterogeneity nature of the system. One may assume that in DMSO-rich mixtures, there exist nanosized clusters of IL molecules, the structure of which is quite similar to that of neat IL. The clusters have a large local microviscosity inside it but macroviscosity is mainly determined by a DMSO component that “lubricates” the motion of IL clusters relatively

to each other. A steep increase in viscosity in the region of less than 20 DMSO vol.% is associated with the percolation threshold when small clusters form the global cluster and binary mixture begins to behave itself in terms of viscosity mainly as a neat IL. By analogy, in IL-rich mixtures there are micro-clusters of DMSO molecules.

Thus one may suggest that in the binary mixture, clusters of IL molecules are segregated from those of the second component; the mixture being in the dynamic equilibrium at a given composition and temperature. On the basis of experimental data on the depolarization of DTCI fluorescence in mixtures of DMSO with [N(4)111] [Tf₂N] (see Table 2), we can estimate the distribution of cyanine-dye molecules between these two types of clusters in the framework of the pseudo-phase model that was successively used in studying water-in-oil microemulsions [11].

By analogy with microemulsions, a binary mixture of DMSO with IL may be divided into two pseudo-phases and treated as if they are separated phases in equilibrium. The pseudo-phases introduced in this fashion are a continuous DMSO solvent and a phase of ionic liquid.

Table 2. The polarization of DTCI fluorescence, P , and the DTCI partition ratio, D , in mixtures of DMSO with [N(4)111] [Tf₂N]

DMSO, vol. %	P	D
100	0.262	-
90	0.272	1.46
80	0.287	1.16
60	0.312	1.23
40	0.355	0.77
20	0.388	0.45
0.4	0.403	-

In this approximation, one can write

$$P = \frac{N_1}{N_0} P_1 + \frac{N_2}{N_0} P_2 = P_1 + (P_2 - P_1) \frac{N_2}{N_0}, \quad (7)$$

where P_1 and P_2 are polarization in neat DMSO and neat IL respectively; N_1 and N_2 are the number of DTCl molecules which are comprised in DMSO- and IL-domains respectively; $N_0 = N_1 + N_2$, where N_0 is the total number of dye molecules in samples and that was kept the same for all experiments.

For a system of two pseudo-phases the partition ratio is defined as follows

$$D = C_1 / C_2, \quad (8)$$

where C_1 and C_2 are the concentration of the dye in DMSO and IL pseudo-phases respectively.

This definition of partition ratio, that neglects possible non-ideality effects, seems reasonable because of a very low total concentration of the dye in mixtures. It follows from Eq.(8) that

$$\frac{N_2}{N_0} = \frac{1}{1 + D \left(\frac{1}{\Phi_2} - 1 \right)}. \quad (9)$$

Substituting Eq.(9) into Eq.(7), one can easily obtain

$$D = \frac{P_2 - P}{(P - P_1) \left(\frac{1}{\Phi_2} - 1 \right)}, \quad (10)$$

where $P_1 < P \leq P_2$, and $\Phi_2 < 1$. This formula allows the estimation of the DTCl partition ratio on the basis of the measured values of polarization for various compositions of the mixture (see Table 2).

Conclusion

In summary, DMSO in the presence of ILs tends to produce clusters, instead of being completely mixed. These clusters become large and long-lived under certain conditions so that a

fluorescence probe can “see” coarse-grain structure of the binary mixture. This accounts for the observed distinction between two liquid binary mixtures, DMSO/ [N(4)111] [Tf2N] and DMSO/[bmim] [Tf2N].

The ability of DMSO and ILs to segregate at the molecular level has a dynamic character and may be considered as concentration fluctuations of the mixture. In the framework of the empirical Hildebrand's theory of solubility, the condition for the observation such micro - segregation is $V_1(\delta_1 - \delta_2)^2 \approx RT$, where V_1 is the molar volume of DMSO, R is the universal gas constant, T is the absolute temperature, δ_1 and δ_2 are solubility parameters for DMSO and IL respectively.

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