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TTA solvation kinetics in the ionic liquid BumimTf$_2$N

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Abstract

TTA, a classical complexing agent of metallic cations, has been studied by UV−vis in the ionic liquid (IL) 1-methyl-3-butyl-imidazolium bistriflimide (BumimTf$_2$N), in the presence of variable amounts of water. Depending on the water content, the keto-hydrate/enol equilibrium kinetics can last up to tens of hours. Modelling by use of classical homogeneous kinetic equations appears unsatisfactory, which pledges for the existence of non-homogeneous phenomena in such solutions, most probably related to the state of water in ILs. ***To cite this article: I. Billard et al., C. R. Chimie 10 (2007).***
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Résumé

Le comportement de la TTA, complexant généraliste des cations métalliques, a été étudié par spectroscopie UV−vis dans le liquide ionique (LI) 1-méthyl-3-butyl-imidazolium bistriflimide (BumimTf$_2$N). Selon la teneur en eau du LI, la TTA, introduite sous forme de céto-hydrate, présente une cinétique d'équilibre hydrate/énol s'étalant sur plus d'une dizaine d'heures. La modélisation par une cinétique homogène classique s'avère insatisfaisante et laisse supposer l'existence de phénomènes non homogènes dans ces solutions, probablement liés à l'état de l'eau dans ce milieu. ***Pour citer cet article : I. Billard et al., C. R. Chimie 10 (2007).***
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1. Introduction

Ionic liquids (ILs), although known for a long time, have appeared only recently as potential "green" solvents in all fields of chemistry, in replacement of those traditional organic phases for which generation of volatile organic compounds is nowadays considered as a critical issue [1]. They display tunable properties, as a consequence of their variable chemical structure, and some ILs properties can be very different from those of usual organic solvents. In particular, ILs possess the

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almost unique advantage to dissolve both neutral and charged entities, allowing rather uncommon chemistry to occur. So far, the understanding of solvation mechanism in ILs is still in its infancy, which in turn limits their use. In the field of radiochemistry, ILs have already demonstrated their potential as An/Ln organic extracting phases [2−5] and as practical electrodeposition media [6−8]. Many papers have highlighted some of the very specific properties of ILs, which may open new routes for separation/partitioning of An/Ln, but very few works have focussed yet on the problems that can arise from the relatively high viscosity most of them display. Actually, large viscosity is usually associated with slow kinetics, which would hamper the development of ILs as solvents. In the present work, we take advantage of the keto-hydrate/enol equilibrium kinetics of thenoyltrifluoroacetone (TTA) dissolved in 1-butyl-3-methyl-imidazolium bistriflimide (BumimTf$_2$N) to demonstrate that although viscous, BumimTf$_2$N displays kinetics that is faster than can be observed in cyclohexane, a more common solvent. These experiments give some insights into the state of water in such media.

2. Experimental

1-Methyl-3-butyl-imidazolium bistriflimide (thereafter denoted as BumimTf$_2$N, Tf$_2$N$^-$ standing for (CF$_3$SO$_2$)$_2$N$^-$) is purchased from Solvionic (Verniolle, France). BumimTf$_2$N was not fully dry and the amount of water in this solvent was measured both by IR and Karl−Fischer titration, leading to a value of 2.44×10^{-2} M (310 ppm). For all the solutions of this work, the water amount was adjusted by a rigorous degassing procedure, according to a previously published protocol [9], followed by addition of the required amount of ultra pure water, which was dissolved in the IL. The water amount in the BumimTf$_2$N solutions of this work was measured taking advantage of the work of Tran and co-workers [10], extending the range up to 1 M of added H$_2$O. We have established and used all throughout this work a linear calibration curve relating the water amount in BumimTf$_2$N as determined by Karl−Fischer titration to the surface area in the range 5085−5385 cm^{-1} of the IR spectrum. A regression coefficient above 0.996 was obtained.

Cyclohexane was purchase from Aldrich (99.9%) and used as received. The water content was checked by means of Karl−Fischer titration (≈ 20 ppm).

TTA, purchased from ACROS Organics (99.5%), was contacted with deionized water in slight excess for about one week in the dark and at room temperature. The solid obtained, after drying, was recrystallized

from diethylether, and the white powder, characteristic of the hydrated keto form of TTA [11], was stored at 8 °C in the dark. The presence of TTA, under the predominant keto-hydrate form, was confirmed by spectrophotometric measurements (strong adsorption between 275 and 300 nm) [11−13]. A kinetic study has shown that the product is stable over several months when stored in the above conditions.

The TTA concentration in BumimTf$_2$N was in the range of 4×10^{-5} M and equal to 8×10^{-6} M in cyclohexane. All samples were protected from daylight, in order to avoid photodegradation.

The UV−vis spectra were recorded in the range 200−450 nm on a Cary 100. All measurements were performed at room temperature.

3. Results

TTA has been introduced in aliquots of BumimTf$_2$N of known water contents. The TTA concentration ranged from 3.5×10^{-5} M to 4.25×10^{-5} M, so that the water amount added with the TTA was less than 6 ppm. UV−vis spectra were recorded as a function of time. Table 1 summarises the water amount in the various BumimTf$_2$N solutions of this work, together with the values of the isobestic points observed for BumimTf$_2$N and cyclohexane. Figs. 1 and 2 display some of the UV−vis spectra recorded as a function of time for [H$_2$O] = 860 ppm and [H$_2$O] = 8650 ppm as typical examples of the observed kinetics. Fig. 3 represents the absorbance variation obtained as a function of time at the two absorption maxima $\lambda = 265$ nm and 327 nm, for the same water amounts, while Fig. 4 displays the corresponding variations in cyclohexane ([H$_2$O] ≈ 20 ppm), for which the maxima are located at $\lambda = 260$ nm and 317 nm.

Table 1
Values of the water amount, TTA initial concentration (in its keto-hydrate form) and position of the isobestic points detected (see text)

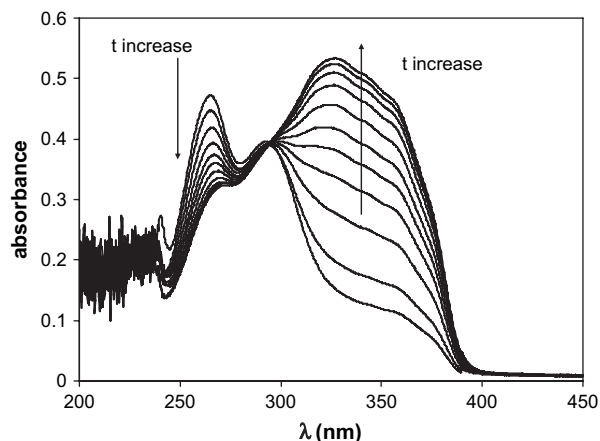| Solvent	[H$_2$O] (ppm/M)	[TTA]$_0$ (10^{-5} M)	Isobestic point (nm)
BumimTf$_2$N	$50/3.9 \times 10^{-3}$	3.5	293
	$860/6.8 \times 10^{-2}$	4.25	293
	$1600/1.3 \times 10^{-1}$	3.8	294
	$2150/1.7 \times 10^{-1}$	4.1	294
	$3000/2.4 \times 10^{-1}$	3.8	294
	$5900/4.6 \times 10^{-1}$	3.95	294
	$7100/5.6 \times 10^{-1}$	4.25	296
	$8650/6.8 \times 10^{-1}$	4.25	n.d.
	$11,900/9.4 \times 10^{-1}$	4.25	301
Cyclohexane	≈ 20	0.8	293

n.d.: not determined.

Fig. 1. Absorption of TTA in BumimTf$_2$N as a function of time in the range 15 min–1435 min; [H$_2$O] = 860 ppm (see text).

4. Discussion

The keto-hydrate TTA form (further denoted as TTA–H$_2$O) can release one H$_2$O entity to turn to the enol chemical structure, further denoted as TTA. Such a chemical equilibrium is illustrated by the presence of an isobestic point in Figs. 1 and 2. As already mentioned in the literature, one of the parameters driving the keto/enol equilibrium is the polarity of the solvent [14]. In addition, obviously, the enol/hydrate equilibrium depends on the total water amount in the solvent in which TTA is dissolved. Our data show that the higher the water amount in BumimTf$_2$N, the faster the equilibrium is reached. The keto-hydrate/enol kinetics has been studied in C$_6$H$_6$ for example [11] by UV–vis,

Fig. 3. Variation of the absorbance of TTA in BumimTf$_2$N recorded as a function of time for two H$_2$O contents and at two wavelengths. Solid lines: fits of the individual series (see text).

taking advantage of the two very distinct absorption spectra these two forms display. By comparison of the literature UV–vis spectra, the absorption spectrum obtained in the present work at short time is characteristic of the keto-hydrate observed in H$_2$O, with an absorption maximum at $\lambda = 265$ nm, while the limiting spectrum obtained for [H$_2$O] = 50 ppm and long time ($t > 1000$ min) corresponds closely to the enol form observed in benzene [11], with an absorption maximum located at $\lambda = 327$ nm and a shoulder around 360 nm. At equilibrium, the keto form is dominating the speciation for [H$_2$O] = 11,900 ppm, while the enol is the major component for [H$_2$O] = 50 ppm. It has been shown
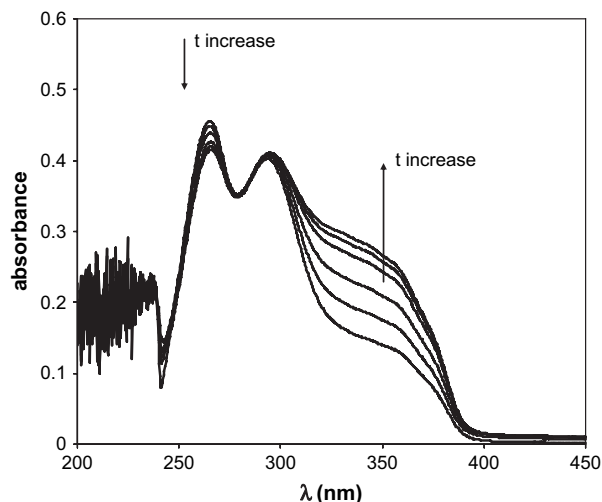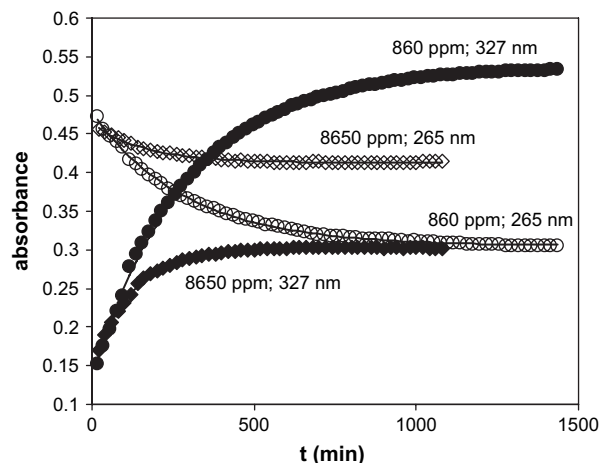

Fig. 2. Absorption of TTA in BumimTf$_2$N as a function of time in the range 15 min–1080 min; [H$_2$O] = 8650 ppm (see text).
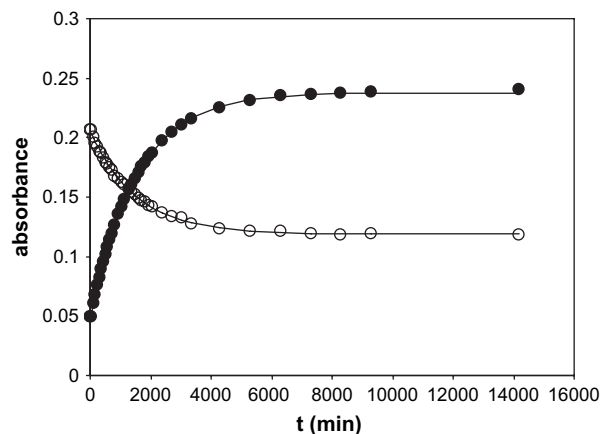

Fig. 4. Variation of the absorbance of TTA in cyclohexane recorded as a function of time for [H$_2$O] $\approx$ 20 ppm contents and at two wavelengths. Symbols: experimental values; solid lines: fits of the individual series (see text).

that the enol form predominates in water-saturated carbon tetrachloride [14], a phenomenon previously noticed for other non-polar organic solvents. In this respect, BumimTf$_2$N behaves as a classical organic solvent, with the additional feature that the ratio enol/hydrate can be tuned by monitoring the water amount. In classical liquid/liquid extraction studies with ILs, owing to its hygroscopic properties, BumimTf$_2$N is actually water-saturated, so that [H$_2$O] is fixed at its maximum value, but in the case of the less-common

above can be derived into the following differential equations:

$$\frac{d[TTA-H_2O]}{dt} = -k_1[TTA-H_2O] + k_2[H_2O][TTA]$$

$$\frac{d[TTA]}{dt} = k_1[TTA-H_2O] - k_2[H_2O][TTA]$$

The mathematical treatment (performed using the Maple facilities) leads to:

$$
\begin{aligned}
A(t) = \varepsilon_1 & \left([TTA-H_2O]_0 - \frac{k_1[TTA-H_2O]_0}{(k_1 + k_2[H_2O])} + \frac{k_1[TTA-H_2O]_0}{(k_1 + k_2[H_2O])} \exp[-(k_1 + k_2[H_2O])t] \right) \\
+ \varepsilon_2 & \left(\frac{k_1[TTA-H_2O]_0}{(k_1 + k_2[H_2O])} + \frac{k_1[TTA-H_2O]_0}{(k_1 + k_2[H_2O])} \exp[-(k_1 + k_2[H_2O])t] \right)
\end{aligned}
\tag{1}
$$

supercritical CO$_2$/LI extraction technique [15,16], such an aspect may have some interesting features. The keto-hydrate/enol equilibrium also occurs in cyclohexane, for which only one series at [H$_2$O] ≈ 20 ppm has been measured. At equilibrium, the enol form dominates, with absorption spectra at short and long times very similar to those observed in BumimTf$_2$N.

In a first attempt to fit the data, we adopted the following chemical model:

$$TTA-H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} TTA + H_2O$$
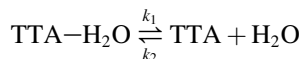
where k_1 and k_2 are the kinetic constants of the equilibrium. Such a chemical scheme can easily be derived into an analytical expression, using classical homogeneous kinetic laws, provided that [H$_2$O] is considered constant as a function of time. This assumption is valid in our case for a given series (i.e. at a given fixed water amount), but is questionable for the lowest water amount used (see Table 1). At a given wavelength, the total absorption $A(t)$ is the weighted average of the molar absorption coefficients ε_1 and ε_2 of TTA−H$_2$O and TTA, respectively:

$$A(t) = \varepsilon_1[TTA-H_2O](t) + \varepsilon_2[TTA](t)$$

The initial conditions are

$$[TTA-H_2O](0) = [TTA-H_2O]_0$$

$$[TTA](0) = 0$$

where [TTA−H$_2$O]$_0$ is the initial concentration of the ligand in its keto-hydrate form. The chemical scheme

In this expression, the unknown parameters are ε_1, ε_2, k_1 and k_2, the latter two being independent of the wavelength, while ε_1 and ε_2 depend on it. For each [H$_2$O] value, Eq. (1) has been fitted (least-square fit) to the experimental data with the help of a Fortran procedure, for the two wavelengths $\lambda = 265$ nm and 327 nm independently. The quality of the fit is excellent in all cases, as illustrated in Fig. 3: at any given H$_2$O content, Eq. (1) leads to a very good agreement between calculated and experimental values. This is also the case for the single series in cyclohexane (see Fig. 4). However, a close examination of the fitted parameter values for the nine experimental series in BumimTf$_2$N shows that the k_1 and k_2 values are not consistent from one series to the other, while ε_1 and ε_2 appear to be reasonably constant. The progressive shift of the isobestic point (see Table 1) as a function of the water amount may be indicative of a change in the global solvent properties, as water is added to the solution up to the solubility limit. Actually, it has been shown in the literature that ILs' properties are heavily affected by water solubilisation [17−21] and so is the viscosity η [21], displaying a rough 30% decrease from dry to water-saturated BumimTf$_2$N. In our model, this should have some impact on the k_2 value, while k_1 corresponds to a real monomolecular reaction so that, in principle, its value should not be dependent on the viscosity. In an attempt to reconcile the fitted values for all the experimental series of this work, the nine series in BumimTf$_2$N have thus been tentatively fitted together, imposing k_2 to vary as a function of $1/\eta$, keeping ε_1, ε_2 and k_1 constant from one series to another, at a given wavelength. To this aim, the

recent literature data of Widegren and co-workers on the η variation in BumimTf$_2$N as a function of [H$_2$O] have been used, for this work covers a range of variation in keeping with our experimental conditions [21]. Interpolation of the experimental η values has been made through a linear law (regression coefficient: 0.99). However, this does not improve significantly the quality of the global fit, which is poor. Furthermore, the kinetics is much longer in cyclohexane as in BumimTf$_2$N (see Fig. 4). This is unexpected, because the higher viscosity in BumimTf$_2$N as compared to cyclohexane (even for [H$_2$O] = 11,900 ppm) would pledge for a slower kinetics in the former solvent, which is not experimentally verified. Clearly, although the mathematical form of Eq. (1) appears to be in agreement with the experimental variation observed, and although the chemical model itself makes sense, as a whole, the process leading to the enol/keto-hydrate equilibrium is complex and is not only governed by macro viscosity.

At present, we cannot propose a definitive explanation for the experiments, but we can suggest various possible tracks that would deserve further work in order to quantify their contribution to the observed trend. First, it is possible that, in cyclohexane, the activation energy of k_2 is much higher than in BumimTf$_2$N (possibly in the range of ca. 1 eV). Second, in cyclohexane, the rather low viscosity (as compared to BumimTf$_2$N) most probably favors de-correlation of the H$_2$O$\cdots$TTA pairs formed through k_1 readily after the keto-hydrate has dissociated, so that although viscosity is low, the overall equilibrium needs time to be reached in cyclohexane. Finally, it has been repeatedly mentioned by various authors that water may exist as clusters or nano-domains in ILs [10,17,22]. In such a case, the effective (i.e. efficient) H$_2$O concentration would be decreased by a factor corresponding roughly to the aggregation number of such clusters. Depending on this value, homogeneous kinetics may not apply anymore in BumimTf$_2$N, but the formation of clusters would have a rather negligible effect onto the overall kinetics, which would be mostly governed by the reaction of the correlated pairs instead, leading to a faster equilibrium to be reached in BumimTf$_2$N as compared to cyclohexane.

5. Conclusion

We have investigated some of the features of TTA solvation and enolisation in BumimTf$_2$N. The slow kinetics evidenced during the course of this work is most likely a general feature of ILs, providing another topic to be studied in those liquids. Insights into the state of water in BumimTf$_2$N have been suggested, which would require additional experiments to be validated.

Acknowledgement

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