Supramolecular ionic liquids based on host–guest cucurbituril imidazolium complexes

Pedro Montes-Navajas, Avelino Corma *, Hermenegildo Garcia

Instituto de Tecnologia Quimica, Universidad Politecnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain

Available online 11 August 2007

Abstract

Cucurbiturils (CB) with seven and eight glycoluril units form inclusion complexes with 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$). These complexes have been characterized by the chemical shift changes in the ^{1}H NMR and by the ESI-MS peaks. Due to complex formation, solubility of CB[7] and CB[8] in bmimBF$_4$ is remarkably high (up to one order of magnitude higher than in water). In contrast, no evidence for complex formation was obtained in the case of CB[5] and CB[6]. Molecular modelling has provided a justification of these facts based on the relative molecular size of bmim$^+$ and the corresponding dimensions of the CB capsule. Addition of minor quantities of CB[7] and CB[8] to bmimBF4 (in the order of 1–1000 molar ratio) is able to produce a remarkable influence on the viscosity of the ionic liquid. Also, the presence of low amounts of CB plays a strong influence on the performance of bmimBF$_4$ as reaction medium for the Knoevenagel condensation of benzaldehyde and diethyl malonate catalyzed by NaOH. The results exemplify the potential of applying supramolecular chemistry to derive a generation of advanced ionic liquids specially tuned for a catalytic reaction.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Supramolecular ionic liquid; Host–guest ionic liquid; Organic capsules

1. Introduction

Ionic liquids have become an alternative to conventional volatile organic solvents as medium to perform catalytic organic reactions [1,2]. Compared to volatile solvents, ionic liquids have essentially zero vapour pressure and, for this reason, they are considered as "green" solvents since no adverse vapours are evolved during the reactions [3].

One of the main limitations of ionic liquids, arising from their high viscosity, is that diffusion is slow and, in some cases, this is reflected in low reaction rates. In order to decrease the viscosity of ionic liquids as a media, one general strategy has been to use mixtures of ionic liquids and volatile organic solvents, but this methodology represents a step down with regard to the greenness of the process. Other alternative to reduce viscosity has been to use bis-triflimidate ($(CF_3SO_3)_2N^-$) and other species as counteranion. Herein, we present an original supramolecular approach to vary the viscosity and other properties of imidazolium ionic liquids. We will show that the resulting ionic liquid can also be used as solvent to perform catalytic organic reactions with higher rates than the pure bmimBF$_4$.

Cucurbiturils (CBs) are organic capsules formed by the cyclooligomerisation of several (from 5 to 10) glycoluril units [4–6]. The geometry of this cyclic molecule defines an interior cavity that is accessible to guest molecules through portals defined by carbonyl groups. The size and volume of this cavity depends on the number of glycoluril units. Table 1 summarizes the most important dimensions of the CBs employed in this work.

Recent work has demonstrated that CBs are suitable hosts to incorporate heterocyclic cations such as viologens, rhodamine, etc. [7–10]. Based on these previous reports, we anticipate that the dialkylimidalozium ionic liquids can also be suitable guests that can be incorporated inside some CBs. Since at molecular level, viscosity is governed by interaction forces between the species present in the liquid, our hope was that, by addition of small quantities of CBs and through complexation with some imidazolium cations, remarkable effects on the viscosity could be achieved.
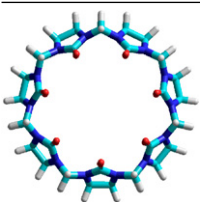
2. Results and discussion

Initially, we performed a study to show the formation of host–guest complexes between CBs and 1-butyl-3-methylimidazolium (bmim) tetrafluoroborate. For this purpose,

* Corresponding author.
  E-mail address: acorma@itq.upv.es (A. Corma).

Table 1
Relevant dimensions of the CB used in this work

CB	Entrance diameter (Å)	Internal diameter (Å)	Cavity volume (Å^3)
CB[5]	2.4	4.4	82
CB[6]	3.9	5.8	164
CB[7]	5.4	7.3	279
CB[8]	6.9	8.8	479

Fig. 1. Aromatic and aliphatic regions of the ^{1}H NMR spectra in CB saturated D$_2$O of bmimBF$_4$.

Table 2
ESI-MS peaks observed for the mixtures of CBs and bmimBF$_4$

Sample	ESI-MS species (mass, Da)
bmim–CB[6]	bmim$^+$ (139), (bmim)$_2$BF$_4$$^+$ (365), K$^+$-CB[6] (1037)
bmim@CB[7]	bmim$^+$ (139), (bmim)$_2$BF$_4$$^+$ (365), (K-bmim)$^{2+}$@CB[7] (1342/2), bmim$^+$@CB[7] (1301)
bmim@CB[8]	bmim$^+$ (139), (bmim)$_2$BF$_4$$^+$ (365), (bmim)$_2$$^{2+}$@CB[8] (1607/2), bmim$^+$@CB[8] (1468)

we performed an ^{1}H NMR study in D$_2$O using saturated solutions of CBs to which bmimBF$_4$ was added. Fig. 1 shows the relevant regions of the ^{1}H NMR spectra recorded for these samples. As it can be seen there, the signals corresponding to the three heterocyclic protons and the *N*-alkyl substituents do not undergo any shift in the presence of CB[5]. In sharp contrast, in the presence of CB[7] (Fig. 1, spectrum D) remarkable changes in the chemical shifts of the protons were observed.

These shifts are taken as spectroscopic evidence for the formation of the bmim$^+$@CB[7] complex. In the case of CB[6] the situation is less clear since a remarkable broadening of the signals was observed (Fig. 1, spectrum C). This remarkable broadening of the lines is accompanied with the presence of new peaks (also broad) and indicates an interaction between bmim$^+$ and CB[6]. The most reasonable explanation is to assume that there is a distribution of species and during the time scale of NMR observation there is a dynamic change between them. The above study allows us to conclude that only in the case of CB[7] there is sound spectroscopic evidence for the formation of a host–guest bmim@CB[7] complex, while CB[5] on the other extreme does not interact at all with bmim$^+$.

The above results can be easily rationalized based on the diameter of the CB cavities (Table 1). Thus, the size of CB[5] is too small to allow the inclusion of bmim$^+$, while for CB[6] certain interaction between the negative carbonyl groups of the CB portal and positive bmim$^+$ is stablished. Only CB[7] is large enough to accommodate in its interior bmim$^+$ and this inclusion is responsible for the remarkable shifts in the ^{1}H NMR peaks of bmim$^+$ due to carbonyl anisotropy. Molecular modelling agrees with this interpretation, that is also in accordance with previous literature data that has shown that CB[5] and CB[6] are too small to include molecules of similar size as the bmim$^+$ [9,10]. Fig. 2 shows two views of the bmim$^+$ inclusion complex showing in the case of CB[5] the host–guest atom overlapping.

Formation of the host–guest inclusion complexes was also acertained by ESI-MS. Table 2 lists the mass of the peaks and the corresponding species that have been detected by ESI-MS. Thus, for CB[6] only the peaks corresponding to bmim$^+$ and (bmim)$_2$BF$_4$$^+$ were observed together with a peak corresponding to CB[6]. In contrast to this, in the case
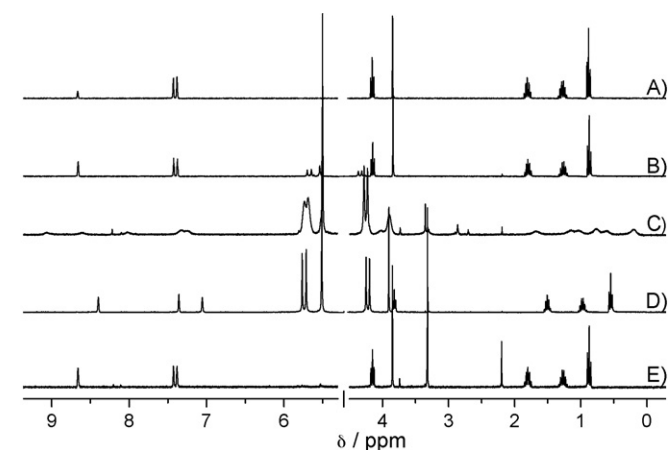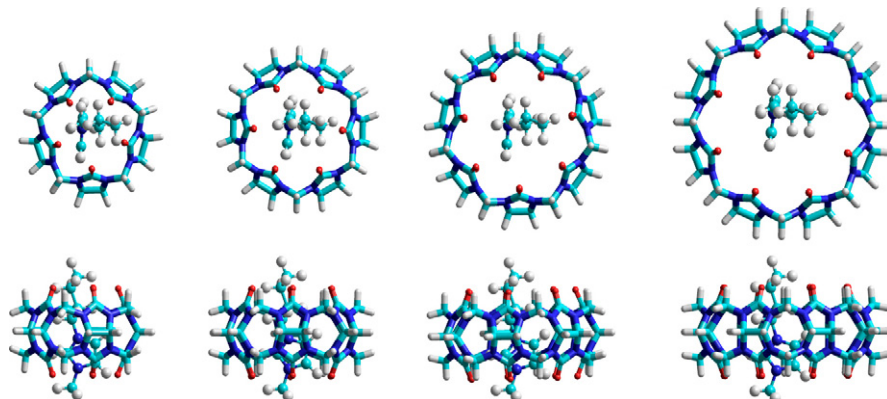

Fig. 2. Molecular models for host–guest complexes between CBs and bmim$^+$.

of CB[7] in addition to the peak corresponding to bmim+, $(bmim)_2BF_4^+$ we observed two additional peaks corresponding to bmim+@CB[7] and $(K-bmim)^{2+}$@CB[7]. Observation of the latter two peaks gives strong support to the formation of the inclusion complex. Also, precedents in the literature have reported the observation in ESI-MS of peaks corresponding to clusters of two imidazolium ions associated to one counteranion [11]. The intensity of the (imidazolium)$_2$·anion cluster has been related to the nature and charge density of the counteranion. In any case, observation of the peaks corresponding to adducts of bmim+ and CB[7] together with data of the ^{1}H NMR and molecular modeling clearly indicates that a inclusion complex between imidazolium and CB[7] was formed.

One case worth to be discussed in more detail is the interaction between bmim+ and CB[8]. Precedents in the literature have shown that CB[8] is also able to form complexes for those molecules already complexed by CB[7] [4,6]. Also molecular modelling predicts that host–guest bmim@CB[8] complex should be possible in the case of CB[8]. Moreover, very frequently it has been observed for CB[8] the formation of a two-to-one complex in which two guest molecules have been accomodated inside a single CB[8] host [12]. However, as it can be seen in Fig. 1, no evidence for the formation of such complex was inferred by ^{1}H NMR spectroscopy. However, ESI-MS clearly shows in addition to the bmim+ and $(bmim)_2BF_4^+$, two more peaks corresponding to the one-to-one bmim+@CB[8] and two-to-one $(bmim)_2^{2+}$@CB[8] (see Table 2). Thus, based on the observation of these two peaks, we propose that host–guest complexes both 1:1 and 1:2 are also formed in the case of CB[8], even though this is not reflected on the ^{1}H NMR spectrum of bmim+. One possibility to reconcile both ^{1}H NMR and ESI-MS spectra is that, due to its larger dimensions, CB[8] carbonyls are sufficiently far from the bmim+ protons to not produce variations in the chemical shifts. However, a careful inspection of ^{1}H NMR shows that for the case of bmim+ and CB[8], the protons of the CB[8] capsule (appearing at 5.81 and 4.21 ppm as two doublets and at 5.53 ppm as a singlet in D_2O) are considerably shifted when bmim+ is present. Thus, based on ESI-MS and the signals of CB[8] in ^{1}H NMR we also propose that the bmim+ is included inside CB[8] as in the case of CB[7] even though this is not apparent from ^{1}H NMR shifts of bmim+.

Having demonstrated the ability of CB[7] and CB[8] to form supramolecular complexes with bmimBF$_4$ ionic liquid, we wanted to determine the influence of the presence of these complexes on the viscosity of the ionic liquid and on its performance as medium in a catalytic reaction. As commented, the common procedure to overcome the problems arising from the high viscosity of ionic liquids is to perform the reaction using cosolvents. Thus, very frequently the reactions using ionic liquids are carried out in one-to-one mixtures of bmimBF$_4$ and methanol or other miscible organic solvent. This high percentage of cosolvents is different from our methodology that consists in the addition of small amounts of non-volatile CBs. Therefore in our case, the lack of vapour emission to the atmosphere that is one of the green advantages of ionic liquids, is preserved. Thus,

addition of CBs to ionic liquid is advantageous with respect to volatile organic solvents. In this regard, it is remarkable that although CBs are extremely insoluble in most organic solvents, CB[7] and CB[8] are highly soluble in bmimBF$_4$ probably due to complexation. Even more, while CBs are commonly used in diluted acid aqueous solutions (about 1 g/L, approximately 10^{-3} M), the solubility in bmimBF$_4$ is two orders of magnitude higher. We have been able to solubilize in bmimBF$_4$ at room temperature 100 and 120 g/L of CB[7] and CB[8], respectively. Given the high cost of CBs, a supramolecular ionic liquid made exclusively of a one-to-one bmim+@CB complex is unpractical. Fortunately enough, the viscosity of a liquid is the result of shear forces between the molecules present in the medium and thus, viscosity can be significantly modified by minor amounts of some additives. Therefore, instead of considering the use of pure bmim+@CB complex, our approach was to investigate the addition of minor percentages of CB with the hope that by dynamic complexation–decomplexation processes it would influence largely the macroscopic viscosity of the bmimBF$_4$.

We were pleased to observe dramatic changes in viscosity by addition of minor amounts of CB[7] and CB[8]. Fig. 3 presents the viscosity measured for some of the ionic liquid samples prepared in this work. To put these values into context, it is worth to remind that the viscosity of the vast majority of conventional solvents is well below 1 cP. For instance, the viscosity of methanol and water is 0.544 and 0.89 cP, respectively. Thus, the addition of CB[7] or CB[8] very minor in amounts modifies the viscosity of bmimBF$_4$ by a value that is 10 times the viscosity of water. The fact that even small amounts of CB[7] and CB[8] are able to effect a strong influence on the viscosity of bmimBF4 rules out that moisture of other impurities that could be present in CB in small percentages could be responsible for the observed viscosity decrease.

The influence of minor amounts of CB[7] and CB[8] is also reflected in the performance of the bmimBF$_4$ ionic liquid as medium to carry out catalytic reactions. To illustrate this, we
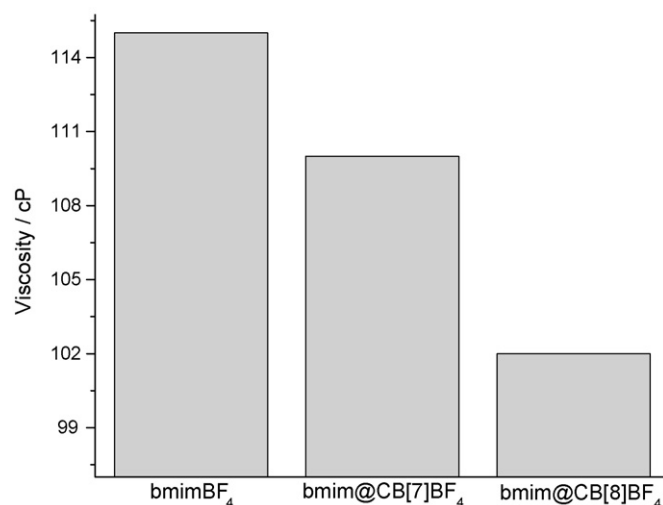

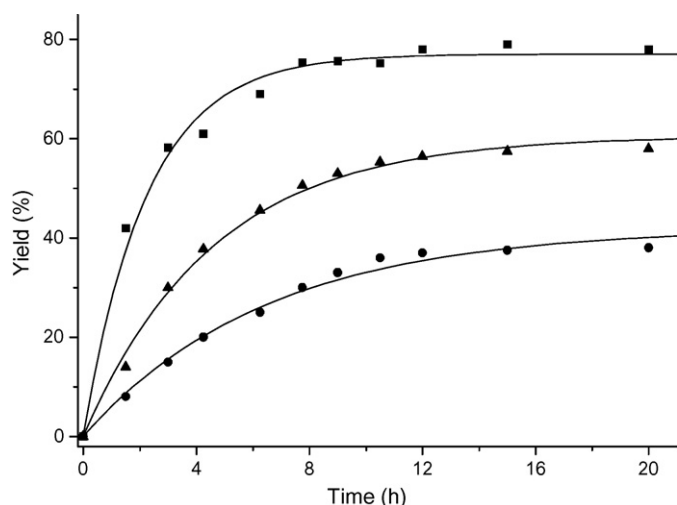Fig. 3. Viscosity values (in cP) of bmimBF$_4$ and after addition of minor concentrations of CB[7] and CB[8].

Fig. 4. Time–conversion plots for the reaction of benzaldehyde with diethyl malonate catalyzed by NaOH in bmimBF$_4$ with CB[7] (▲), bmimBF$_4$ (●) and bmimBF$_4$ in the presence of CB[8] (■). Reaction conditions: benzaldehyde (189 mg), diethyl malonate (311 mg).

have selected the Knoevenagel condensation of benzaldehyde with diethyl malonate catalyzed by NaOH, a reaction that we have already conducted in bmimBF$_4$ [13,14]. As expected, the only product observed in all cases was the corrresponding adduct (Eq. (1)). However, the formation reaction rate was remarkably different depending on the presence of CB[7] and CB[8] as bmimBF$_4$ additives.
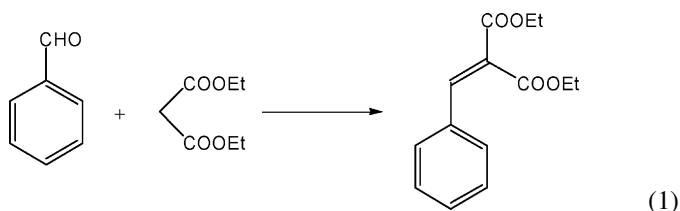

$$(1)$$

Fig. 4 shows the time–conversion plots for the formation of the condensation product. From this plot the initial reaction rates were estimated as the slope of the conversion curve at zero time. The data (see Fig. 4) shows that CB[8] is able to accelerate significantly the condensation by a factor of 5 compared to CB[7]. We interpret these results as reflecting the ability of CBs to simultaneously bind bmim$^+$ (solvent) and Na$^+$ (catalyst), thus reducing viscosity and increasing at the same time the basicity of NaOH by complexing the sodium. In support of this interpretation, we have been able to detect by ESI-MS the peaks corresponding to the K-bmim@CBs.

3. Conclusions

In the present work we have shown that starting from imidazolium ionic liquids, a new generation of ionic liquids can be derived by applying principles of supramolecular chemistry. Thus, we have taken advantage of the ability of CB[7] and CB[8] to form host–guest complexes with organic cations to reduce the viscosity and improve the performance of this imidazolium as solvent for catalytic reactions. The major point of our work is

that we can achieve this remarkable effects adding only very minor amounts of CBs, thus bringing our methodology close to practicality.

4. Experimental

BmimBF$_4$ was a commercial sample (Green solutions S.A.) and it was submitted to the dehydration prior its use by outgassing the liquid at 50 °C under vacuum. CBs were commercial samples (Aldrich) and used as received.

^{1}H NMR were recorded on a Bruker AV-300 spectrometer at 300 MHz in D$_2$O. The chemical shifts were measured in δ scale (ppm) with respect to TMS as standard. To record the spectra, bmimBF$_4$ (5 mg) were dissolved in 5 mL of D$_2$O. This stock solution was split into five NMR tubes, each of which was saturated with the corresponding CB except one that was taken as a blank. Spectra were recorded at room temperature.

ESI-MS of host–guest bmim-CBs complexes were measured in a 1100 Series LC/MSD Agilent instrument by injecting the sample dissolved in H$_2$O, operating at 70 eV in the positive ion mode. Pure nitrogen (>99%) was used to operate the electrospray.

Viscosity values were measured at room temperature for samples exposed to the ambient using a Thermo Haake Rotovisco 1 rheometer based on a rotating disk procedure.

Knoevenagel condensation of benzaldehyde (189 mg, 1.783 mmol) with diethyl malonate (311 mg, 1.945 mmol) was carried out by dissolving the reagents in 2 ml of bmimBF$_4$ that already contained the corresponding CB[7] (10.6 mg) or CB[8] (12.3 mg, 0.009 mmol) and NaOH (1 mol% with respect to benzaldehyde). The solution was magnetically stirred at 90 °C. Periodically aliquots (25 μL) of the reaction mixture were taken, dissolved in D$_2$O containing acetonitrile as internal standard and the product distribution determined by ^{1}H NMR based on the integrals of the peaks of benzaldehyde (H at 9.8 ppm), diethyl malonate (2H at 3.5 ppm). At the same time, formation of the product was observed in the region between 6.7 and 8.0 ppm.

References

[1] D. Bradley, P. Dyson, T. Welton, Chem. Rev. (Deddington, United Kingdom) 9 (2000) 18–21.
[2] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. (Washington, DC, United States) 102 (2002) 3667–3691.
[3] R. Sheldon, Chem. Commun. (2001) 2399–2407.
[4] K. Kim, N. Selvapalam, D.H. Oh, J. Inclus. Phenom. Macro. 50 (2004) 31–36.
[5] P. Cintas, J. Inclus. Phenom. Mol. 17 (1994) 205–220.
[6] J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, Angew. Chem. Int. Ed. 44 (2005) 4844–4870.
[7] J. Mohanty, W.M. Nau, Angew. Chem. Int. Ed. 44 (2005) 3750–3754.
[8] C. Marquez, W.M. Nau, Angew. Chem. Int. Ed. 40 (2001) 3155–3160.

[9] W. Ong, A.E. Kaifer, J. Org. Chem. 69 (2004) 1383–1385.

[10] W. Ong, A.E. Kaifer, Angew. Chem. Int. Ed. 42 (2003) 2164–2167.

[11] R. Bini, O. Bortolini, C. Chiappe, D. Pieraccini, T. Siciliano, J. Phys. Chem. B 111 (2007) 598–604.

[12] A.Y. Ziganshina, Y.H. Ko, W.S. Jeon, K. Kim, Chem. Commun. (Cambridge, United Kingdom) (2004) 806–807.

[13] P. Formentin, H. Garcia, A. Leyva, J. Mol. Catal. A 214 (2004) 137–142.

[14] S. Chowdhury, R.S. Mohan, J.L. Scott, Tetrahedron 63 (2007) 2363–2389.