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What the anion tells us about the structure of tetrabutylammonium salt/phenol-based deep eutectic solvents? A combined infrared spectroscopic and DFT study

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Abstract

In this study, a series of new Deep eutectic solvents (DESs) composed of phenol as the HBD (Hydrogen Bond Donor) and tetrabutyl ammonium (TBA) salts with different molecular anions as HBA (Hydrogen Bond Acceptor) were prepared and investigated using ATR-IR spectroscopy and DFT calculations in order to understand the solvation mechanism at work in these DESs. In particular, the OH stretching mode of phenol is significantly shifted to lower frequencies in the DESs in comparison with that reported for pure phenol. Similarly, characteristic vibrational modes of the anions in the investigated DESs display significant shifts in frequency in comparison with that measure for the pure TBA salt. As a representative example, the frequency shifts observed for the azide anion as a function of the HBA:HBD molar ratio were fully interpreted by the DFT calculations putting in evidence strong hydrogen bonding interactions that occurs between the anion and the phenol molecules. Interestingly, a minimum of the calculated free energy interaction of -25.9 kcal/mol was found at a 1:3 HBA:HBD molar ratio that is consistent with thermodynamic results reported for the Choline-chloride/Phenol DES for which the lowest freezing temperature was reported at this ratio.

Keywords: Deep eutectic solvents, hydrogen bonds, Tetrabutyl ammonium salts, Phenol, Infrared, DFT

1- Introduction

Deep eutectic solvents or DESs are a new class of solvents with promising properties for a large number of applications such as gas separation and sequestration, electrochemistry, catalysis and the extraction of natural compounds for cosmetic or pharmaceutical applications.[1-4] These solvents are usually prepared by mixing two cheap and safe components, a hydrogen bond

donor (HBD) with a hydrogen bond acceptor (HBA) and characterized by a significant depression in melting points compared to those of the pure constituents. The first example was provided by Abbott et al. [5] as they discovered that mixing choline chloride (ChCl) and urea could produce a mixture with a significantly lower melting point.

Since then, a large number of DESs have been proposed combining different HBD and HBA at various molar ratios where HBD typically involve molecules with OH or NH group such as amide, amine, alcohols, organic acids, whereas HBA usually involves inorganic salts such as choline chloride and quaternary ammonium salts. As reported in many recent publications on DESs, hydrogen bonding is believed to be the key intermolecular force leading to the melting point depression observed during the DESs formation.[6] Nevertheless, anion-cation interactions as well as steric effects could play also a significant role. Therefore, efforts are still needed to identify the solvation mechanism at work at a molecular level that govern the structure–property relationships in this class of solvents.

In this context, Infrared spectroscopy is one of the most powerful tool to investigate hydrogen bond interactions and, although it might be also useful to detect impurities that may be present in a sample, a number of recent research works have primarily used it to identify the key molecular interactions that occurs in DESs in comparison with the pure constituents trying to elucidate the DESs structure.[7-12] It is interesting to notice that most of the infrared studies reported so far are devoted to the study of the hydrogen bonded structure of the HBD in the DESs and little to no information is obtained on the HBA structure from IR spectroscopy. Indeed, we remember that the majority of DESs that have been prepared and studied so far are traditionally constituted of an HBA consisting of a quaternary ammonium salt comprising Cl^- as the anion (although Br^- and I^- are proposed to a lesser extent). Therefore, it is not possible to get information about the solvation of the anion through the infrared spectroscopy. Thus, we propose to use quaternary ammonium salts comprising molecular anions in order to detect by infrared spectroscopy characteristic vibrational modes of the anion. Thus, we will get information on the structure of DESs from the view point of the anion and how the anion is solvated in the DESs in comparison with the pure ammonium salt. To the best of our knowledge, there are no studies on DESs that propose quaternary ammonium salts with molecular anions. We are only aware about Choline and Geranate (CAGE) Deep Eutectic Solvent that can be used as an antiseptic agent for preventive and therapeutic applications.[13] It might be due to the fact that atomic anions are necessary to form a DES while ammonium salts including molecular anion do not form DESs with typical HBD. Nevertheless, using molecular anions would allow

to detect them by IR spectroscopy and therefore obtain crucial information on the solvation of the anion in the DESs.

On the other hand, Choline Chloride/phenol-based deep eutectic solvents that have been reported about ten years ago by Guo et al.[14] are known to show low viscosity that is of prime importance for industrial applications. For example, it is possible to separate phenols from model oils with quaternary ammonium salts via forming deep eutectic solvents.[15] In particular, it was found that a deep eutectic was formed at about 75 % of phenolic compounds (DES 1:3). Compared with an ideal mixture of the two components, the freezing temperature of the phenol–ChCl (1:3) system depresses greatly from 127 °C to reach a freezing point of -20.1°C [15] and the phenol-TBACl (1:2) displays a freezing point of -1.1°C. [16] In a recent paper by Fan et al. [17], it was found that ammonium salt/phenol based deep eutectic solvents were less viscous than ammonium salt/glycolic acid-based DES as the interaction network stability of the latter is more robust than that of the phenolics-based one due to the strong covalency of hydrogen bond. This is the main reason that ammonium salt/phenol-based DESs show low viscosity. Therefore, phenol appears to be an interesting HBD model molecule in order to investigate the possibility to form new ammonium salt/phenol-based DESs considering various molecular anions.

Thus, the aim of this work is to investigate a series of phenol/TBA salts mixture with various anions (Cl^- (Chloride), N_3^- (Azide), NCO^- (Cyanate), SCN^- (Thiocyanate), MDA^- (Malondialdehyde), OAc^- , (Acetate) H_2PO_4^- (Phosphate monobasic) that could form deep eutectic solvents at room temperature. Through ATR-IR experimental studies and DFT calculations, we demonstrate a peculiar solvation effect of phenol on the anion in these DESs that could be responsible for the eutectic behavior with a significant depression in the melting point of the DES compared to those of the pure components.

2- Experimental

2.1. Preparation of deep eutectic solvents

All chemicals purchased from the “Aldrich” company with analytical grade (97-99%) were used as received without any purification (see table S1 in ESI1). As the eutectic mole fraction was found to be 1:3 for the ChCl/Phenol and AmmoniumCl/Phenol DESs as previously reported [14, 17], we have prepared all the DESs at this molar ratio. Few DES have been also

prepared at other molar ratios (1:1, 1:2 and 1:4). The solid mixture was heated up to 80°C and constantly stirred for 2 hours until the formation of homogeneous transparent liquid. Upon cooling, we have checked that the mixture was still liquid at room temperature (see ESI 2).

2.2. ATR-IR spectroscopy

All DESs and their components were investigated by ATR-FTIR spectroscopy using a home-made Si ATR accessory suitable for high temperature (up to 100°C) coupled with a ThermoOptek interferometer (type 6700) equipped with a global source, a KBr/Ge beam splitter and a DTGS (Deuterated TriGlycine Sulphate) detector. The spectra were recorded in the spectral range 4000–400 cm^{-1} using a resolution of 4 cm^{-1} and averaging 50 scans to improve the signal to noise ratio. The stainless steel cell with a volume of about 3 mL screwed above the Si crystal provides one port for the inlet of mixture. A magnetic stirrer was placed into the cell to ensure good homogenization of the mixture. The ATR cell was heated using cartridge heaters disposed in the periphery of its body. A thermocouple was used and located close to a cartridge heater for the temperature regulation with an accuracy of about ± 1 °C. The mixture composed of the DESs was disposed in the cell at ambient temperature. Then, the cell was heated up to the desired temperature.

2.3. Computational details

The approach used in this study involved first simulated annealing for each of the different scenarios (TBAN3/phenol DESs at various molar ratios: 1:1, 1:2, 1:3, and 1:4) using the AMPAC program [20] at the AM1-D3H4 level of calculation. [18, 19] Then, DFT calculations of geometries, energies, and vibrational frequencies reported in this paper were carried out with the M06-2X functional[22] using the 6-311G(d,p) basis set implemented in the Gaussian 16 package.[21]. In order to determine the Boltzmann-weighted average IR spectra, the most stable conformations (within 15 kcal.mol^{-1}) were examined using DFT (see ESI 4 and 5). To compare the experimental vibrational frequencies with the calculated ones, a scaling factor of 0.946 [23] has been used.

3- Results and discussion

3-1 Preparation and ATR-IR spectra of the phenol/TBA salts

The melting properties of the pure constituents used in this study that are all solids at room temperature are displayed in Table S2 (See ESI 2). Upon preparing the TBA /phenol salts mixture at different molar ratios with the various molecular anions (N_3^- (Azide), NCO^- (Cyanate), SCN^- (Thiocyanate), MDA^- (Malondialdehyde), OAc^- , (Acetate) H_2PO_4^- (Phosphate monobasic), we observe that all the investigated mixtures are liquids at room temperature (see table S2). The ATR-IR spectra of the new TBA salt/phenol DESs obtained at a molar ratio 1:3 are reported in figure 1. The spectrum of pure phenol and the TBACl/phenol DES at a molar ratio 1:3 is also reported for comparison.

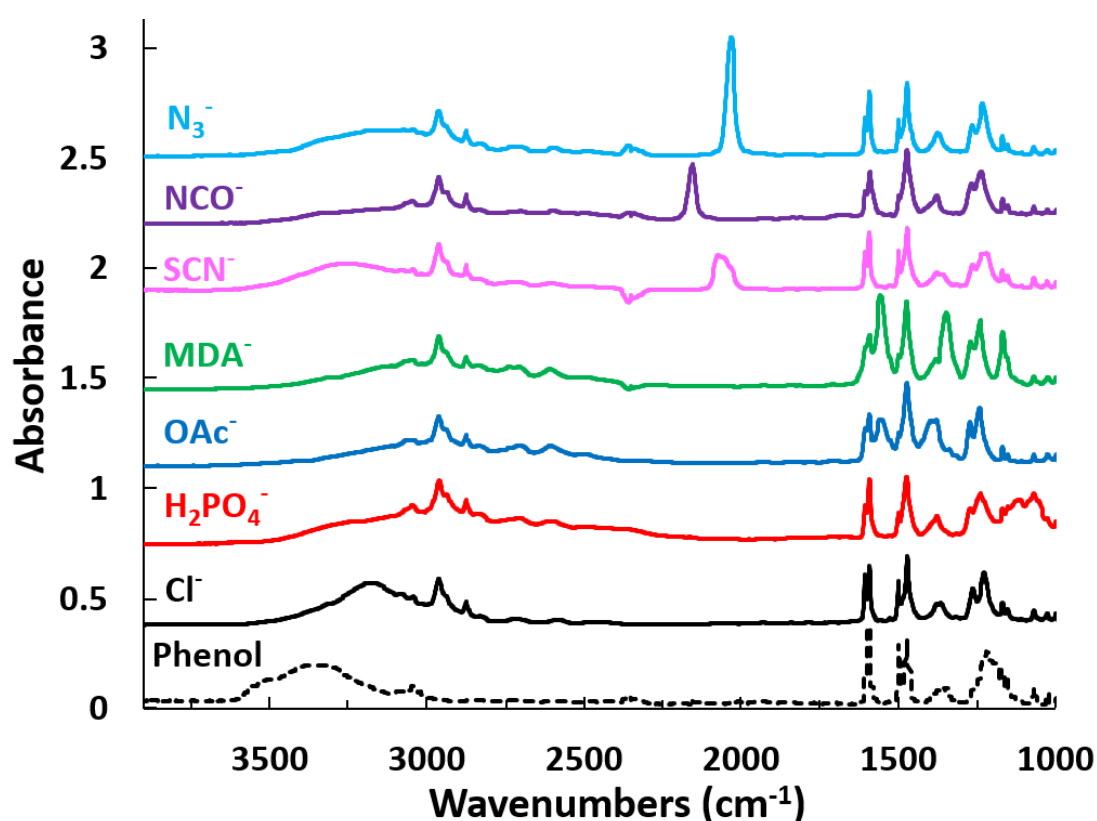


Figure 1: ATR-IR spectra of the TBA salt/phenol DESs at a HBA-HBD ratio of 1:3 investigated in this study. The spectrum of pure phenol (liquid at 50°C) is reported for comparison.

As a general rule, all the spectra of the new DESs investigated in this study display a similar shape than that reported for the TBACl/phenol DES with characteristic peaks that belong to the phenol and the TBA cation (see figure 1). Nevertheless, depending on the DES, we observe some variation of the broad band at about 3300 cm^{-1} in pure phenol that is associated with its OH stretching mode and characteristic of the hydrogen bond network of phenol. Thus, this profile is always detected at lower wavenumber in the DESs comparing to that of pure phenol.

Therefore, the hydrogen bonding network that phenol molecules adopts in the DESs seems to be stronger than in pure phenol whatever the nature of the TBA salt. In addition, we can observe for the new DESs the characteristic peaks that are associated with the anion. Although the characteristic peaks of the anions MDA^- , OAc^- and H_2PO_4^- are difficult to analyze as they are superimposed over the phenol spectrum below 1700 cm^{-1} , the characteristic bands of the asymmetric stretching mode of the anions of TBAN_3 , TBASCN , and TBANCO in the DESs spectra can be clearly observed at about 2030 , 2050 and 2150 cm^{-1} , respectively. Thus, the observation by infrared spectroscopy of the asymmetric stretching mode of these anions should allow to obtain information on how the anion is solvated in the DESs in comparison with the pure ammonium salt.

In order to evaluate the sensitivity of the asymmetric stretching mode of the anion to the structure of the DES, TBA salt/phenol mixtures with the NCO^- and N_3^- anion have been prepared at a molar ratio 1:1, 1:2 and 1:4 that do also display a stable liquid phase at room temperature. The ATR-IR spectra of the TBAN_3 /Phenol DESs at a molar ratio 1:1, 1:2, 1:3 and 1:4 are reported in figure 2.

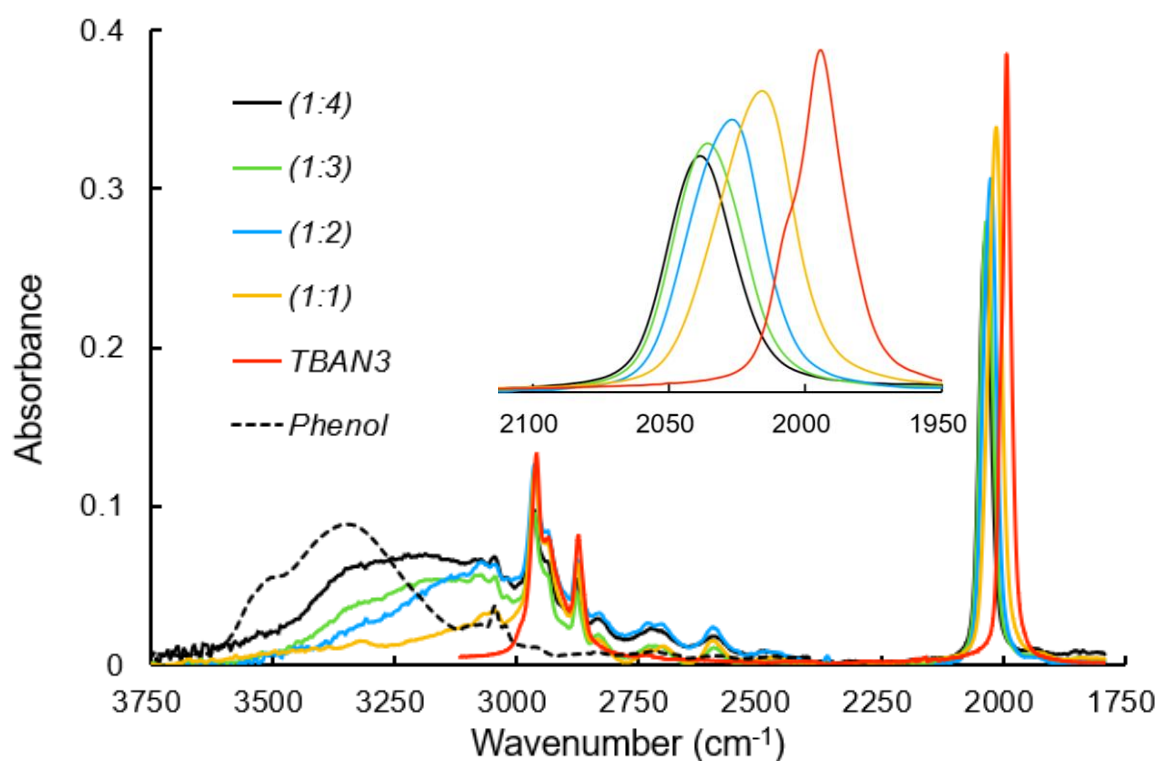


Figure 2: ATR-IR spectra of the TBAN_3 /Phenol DES with various HBA-HBD ratios 1:1, 1:2, 1:3 and 1:4. The spectrum of pure phenol (liquid at 50°C) and the pure TBAN_3 salt (solid at room temperature)

are also reported and have been scaled in intensity for a qualitative comparison with the spectra of the DESs.

For comparison, the ATR-IR spectra of pure phenol (liquid state at 50°C) and the pure TBAN₃ salt (solid at room temperature) have been also reported. The corresponding TBANCO-Phenol DESs at the same molar ratios are reported in the supplementary information (ESI 3, Figure S1). Thus, upon an increase of the molar ratio from 1:1 to 1:4, the peak associated with the ν_3 mode of the N₃⁻ anion is progressively shifted to higher wavenumbers as found at about 2040 cm⁻¹ in the DES 1:4 and only at about 1995 cm⁻¹ in the pure TBA salt. The OH band of phenol is more difficult to analyze as it displays a broad profile that is characteristic of the hydrogen bond network of phenol. However, we qualitatively observe that this profile that is barely detected in the 1:1 mixture shifts to higher wavenumbers towards that of pure phenol upon an increase of the molar ratio from 1:2 to 1:4. These observations seem to indicate that the hydrogen bond network of phenol molecules in the presence of the anion in the DESs is stronger than that observed in pure phenol. All these observations could be related to the formation of specific hydrogen bonding interactions between the anion and phenol molecules in these DESs.

In order to evaluate the sensitivity of such hydrogen bonding interactions to temperature effects, we have investigated the DES TBAN₃/Phenol at a molar ratio 1:3 at different temperatures from 25°C up to 90°C (see figure 3). As a general trend, we do not observe any

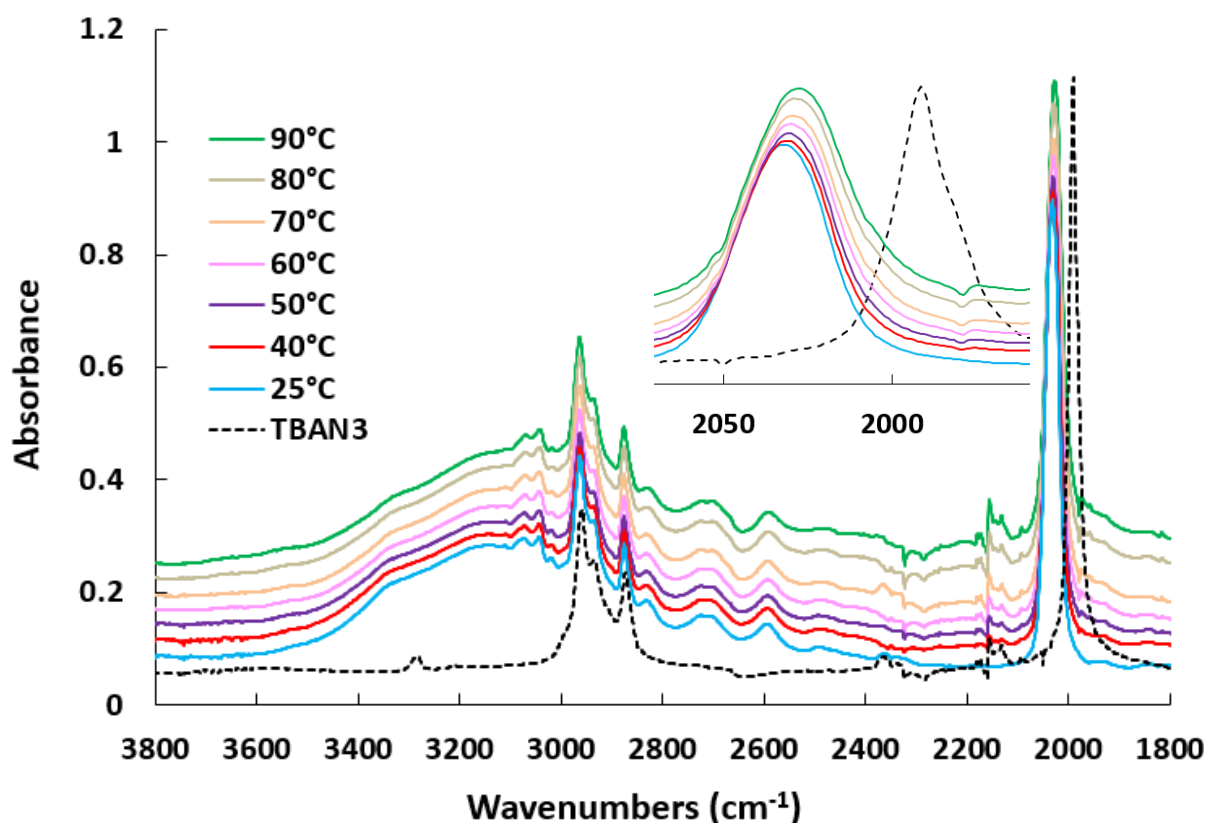


Figure 3: ATR-IR spectra of the TBAN₃/Phenol DES at a molar ratio 1:3 at different temperature from 25°C up to 90°C. The spectrum of the pure TBAN₃ salt (liquid at 90°C) is also reported and has been scaled in intensity for a qualitative comparison with the spectra of the DES at various temperature.

significant variation of the spectrum of the DES upon an increase of the temperature from 25 up to 90°C. In particular, the broad band at about 3200 cm⁻¹ associated with the OH stretching mode of phenol do not displays significant evolution. However, we observe a weak shift towards lower wavenumbers of the ν_3 mode of the N₃⁻ anion in the DES from 2032 cm⁻¹ at 25°C up to 2028 cm⁻¹ at 95°C (see insert of figure 3). This trend put in evidence that only a weak lowering of the anion-phenol hydrogen bond interactions is observed in this DES upon a temperature increase that is even barely detected in the OH stretching region. The shift to lower wavenumbers is consistent with the fact that the ν_3 mode of the N₃⁻ anion in pure TBAN₃ characteristic of the N₃⁻ anion “free” from hydrogen bonds is found at much lower wavenumber at 1992 cm⁻¹.

3-2 Analysis of the anion solvation by DFT calculations

In order to correlate the observed evolution of the asymmetric stretching mode of the N₃⁻ anion with the hydrogen bonding structure of the TBAN₃/Phenol DESs for the different molar ratios 1:1, 1:2, 1:3 and 1:4, we have performed DFT calculations on TBAN₃-phenol complexes for different molar ratios 1:1, 1:2, 1:3 and 1:4. For each ratio, several geometries (i.e. different orientations of phenol molecule(s) with respect to TBAN₃) were considered and have been used to evaluate their stabilization energies and to generate a Boltzmann-weighted average IR spectra for a given TBAN₃:Ph ratio (see ESI 4 for details).

Structural and energetic considerations

The lowest energy structure of the fully optimized geometries of the TBAN₃: Phenol species are presented in figure 4, namely, the TBAN₃ salt (a), the TBAN₃:Ph 1:1 complex (b); the TBAN₃:Ph 1:2 complex (c); the TBAN₃:Ph 1:3 complex (d) and the TBAN₃:Ph 1:4 complex (e).

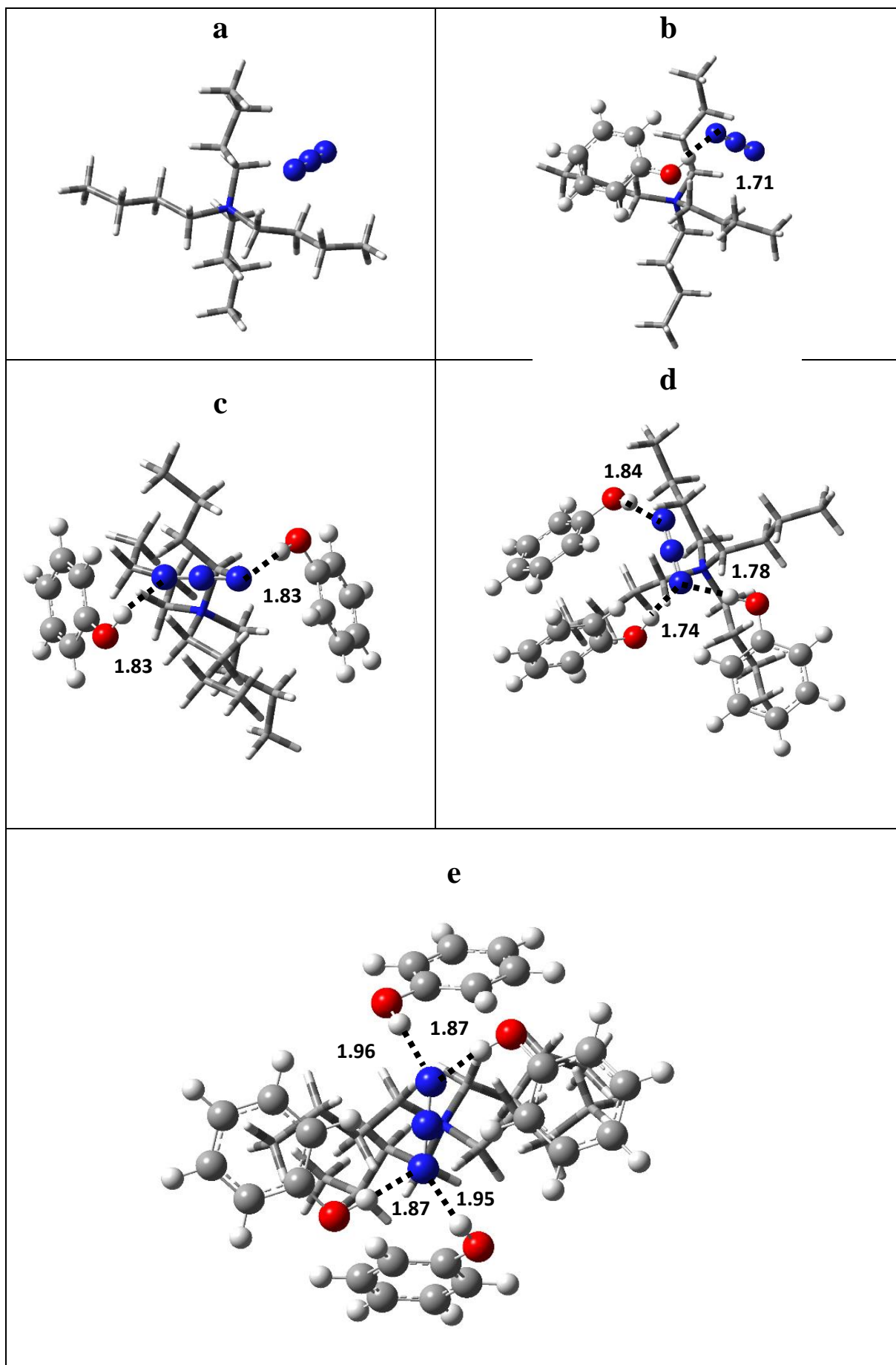


Figure 4: Optimized structures of the $TBAN_3$ /Phenol complexes at M06-2X/6-311G(d,p) level of calculation. $TBAN_3$ (a), $TBAN_3$:Ph 1:1 complex (b); $TBAN_3$:Ph 1:2 complex (c); $TBAN_3$:Ph 1:3 complex (d); $TBAN_3$:Ph 1:4 complex (e). Hydrogen bonds are displayed as dashed lines with the intermolecular distances in angstrom.

For all the complexes investigated, the donating hydroxyl group of the phenol molecule(s) points towards a nitrogen atom of the N_3^- anion that plays the role of the HBA (see figure 4). The calculated binding enthalpies/Gibbs free energies of the complexes, obtained by difference between the enthalpies/Gibbs free energies of the interacting system ($TBAN_3$:Ph) and the isolated $TBAN_3$ and phenol molecules, are reported in table 1.

Table 1: Interaction enthalpies (ΔH), Gibbs free energies (ΔG), calculated M06-2X/6-311G(d,p) ($\nu_3(N_3^-)$ DFT) and experimental ($\nu_3(N_3^-)$ Exp) frequencies associated with the asymmetric stretching normal mode for the $TBAN_3$:Ph complexes.

<i>DES</i>	ΔH_{M06-2X} (kcal mol ⁻¹)	ΔG_{M06-2X} (kcal mol ⁻¹)	$\nu_3(N_3^-)$ DFT ^{a)} (cm ⁻¹)	$\nu_3(N_3^-)$ Exp (cm ⁻¹)
<i>TBAN₃ monomer</i>	-	-	2037	1995
<i>TBAN₃:Ph 1:1</i>	-26.7	-13.3	2069	2015
<i>TBAN₃:Ph 1:2</i>	-46.8	-21.3	2083	2027
<i>TBAN₃:Ph 1:3</i>	-61.9	-25.9	2089	2035
<i>TBAN₃:Ph 1:4</i>	-74.5	-25.1	2092	2039

a- Scaled with a factor of 0.946 (from [23])

It appears that the calculated binding enthalpies vary from -26.7 kcal mol⁻¹ for the $TBAN_3$:Ph 1:1 complex, up to -74.5 kcal mol⁻¹ for $TBAN_3$:Ph 1:4. Such values put in evidence that strong interactions occurs in these complexes such as H-bonds between phenol and the azide anion as well as CH/ π hydrogen bonds between the aliphatic chain of TBA^+ and the aromatic core of phenol molecule(s). Moreover, increasing the number of phenol molecules around the anion lead to an increase of the stabilization energy of the complex. Such strong hydrogen bonding structures are consistent with the experimental observation of the OH stretching profile of

phenol molecules at lower frequencies in the DESs in comparison with pure phenol and is also put in evidence by calculated Gibbs free energies that vary from $-13.3 \text{ kcal mol}^{-1}$ for the TBAN₃:Ph 1:1 complex, up to $-25.1 \text{ kcal mol}^{-1}$ for TBAN₃:Ph 1:4. However, we observe that a minimum Gibbs free energy is obtained for the 1:3 complex hence putting in evidence entropic effects that compete with enthalpic effects when the number of phenol molecules increases in the TBAN₃/Phenol complex. Therefore, it appears that the most stable structure for these TBAN₃/Phenol DESs is expected to be reached for a 1:3 molar ratio. Such result is fully consistent with thermodynamic results reported for the Choline-chloride/Phenol DES for which a 1:3 HBA:HBD molar ratio has been found to display the lowest freezing temperature. [14]

Vibrational spectra

In order to correlate the DFT calculations with the experimental infrared spectra, the vibrational analysis of the TBAN₃/Phenol complexes has been performed starting from the optimized structures (see ESI 4). In figure 5, the scaled calculated frequencies associated with the asymmetric stretching normal mode of the azide anion in TBAN₃ and its complexes with Phenol are compared with the experimental values (Table 1). It appears that whatever the number of phenol molecules, we observe a systematic difference between the calculated and experimental absolute values of about 40 cm^{-1} . As far as we know that numerical values of scaling factors can vary slightly as a function of the database used to establish it, the value used in this study might not be perfectly appropriate to scale the asymmetric stretching mode of the azide anion. In addition, as DFT methods use harmonic approximations, discrepancies can arise because of anharmonic and finite temperature effects. Therefore, such uncertainties in the DFT calculations of vibrational frequencies could explain the systematic difference of about 40 cm^{-1} observed between the calculated and experimental frequencies. However, the observed shift with the number of phenol molecules to higher frequencies of the asymmetric stretching mode $\nu_3 (\text{N}_3^-)$ in the complexes is well reproduced by the calculations. Interestingly, the experimentally observed non-linear evolution of the shift as a function of the number of phenol molecules is particularly well reproduced by the calculations. Therefore, we can postulate that the calculated equilibrium geometry reported for the TBAN₃/Phenol complexes should correspond to the most probable hydrogen bonding structure that TBAN₃ and phenol molecules adopts in these DESs.

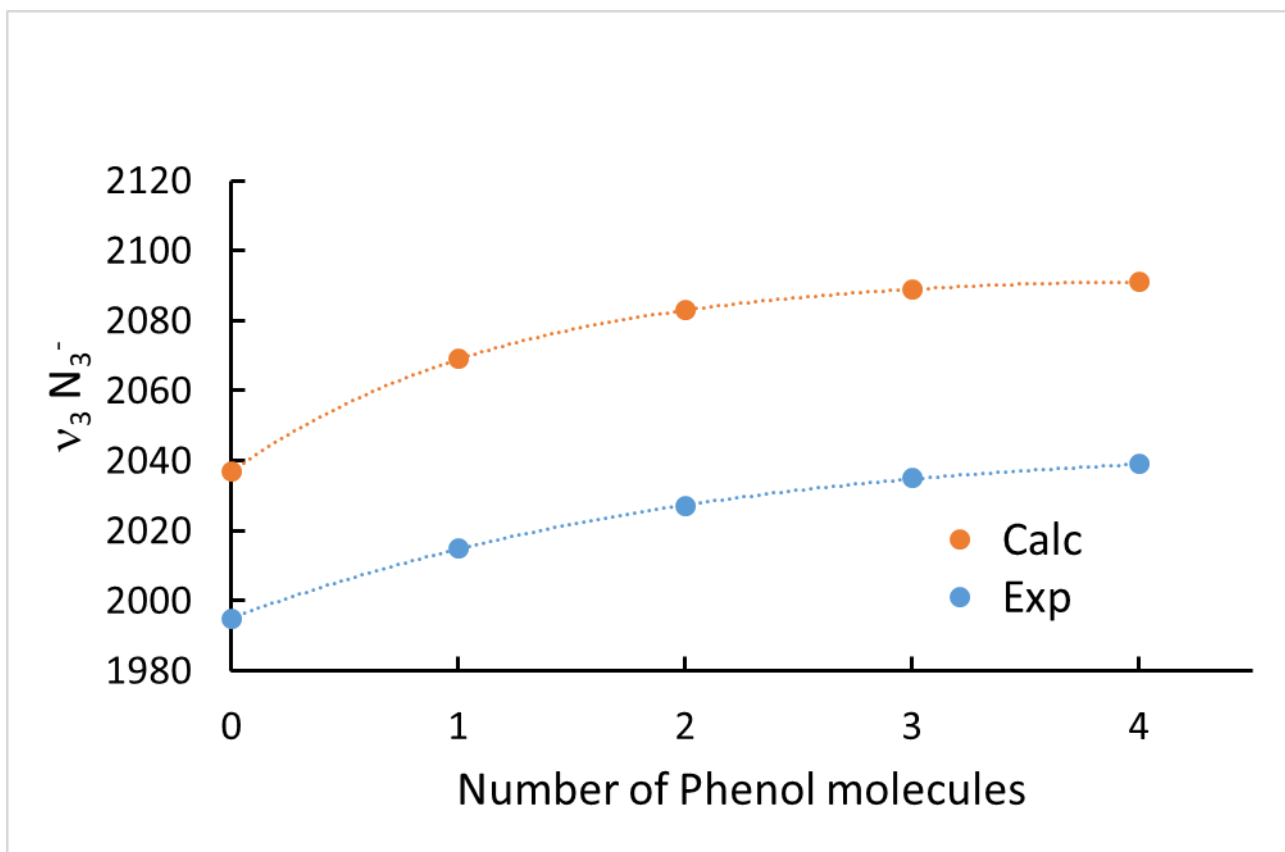


Figure 5: Comparison of the experimental and scaled calculated frequencies at the M06-2X/6-311G(d,p) computational level of the C–I stretching normal mode of “free” C₄F₉I and [C₄F₉I-LB] complexes. A scaling factor of 0.946 was used to scale the calculated frequencies.[23]

4- Conclusion

A series of new DESs were obtained by mixing Phenol with TBA salts with various anions (Cl⁻, N₃⁻, NCO⁻, SCN⁻, MDA⁻ (Malondialdehyde), OAc⁻, H₂PO₄⁻). The analysis of the ATR-IR spectra of these DESs reveals that the OH stretching mode of phenol is significantly shifted to lower frequencies in the DESs in comparison with that reported for pure phenol. The characteristic peaks that are associated with the anions were also detected. In particular, the characteristic band of the asymmetric stretching mode of the N₃⁻ anion in the TBAN₃/Phenol DES was found to display significant shifts upon a variation of the temperature and the TBAN₃/Phenol molar ratio from 1:1 to 1:4. The frequency shifts observed for the azide anion as a function of the HBA:HBD molar ratio were well reproduced by the DFT calculations putting in evidence strong hydrogen bonding interactions that occurs between the anion and the phenol molecules. A minimum of the calculated free energy interaction of -25.9 kcal/mol was obtained at a 1:3 molar ratio that is consistent with the lowest melting point depression observed

experimentally at this ratio for the Choline chloride-Phenol DES [14]. This peculiar hydrogen bonded structure where phenol molecules are strongly hydrogen bonded to the azide anion of the TBA₃ salt is expected to occur in the common TBA salts with atomic anion (Cl⁻, Br⁻, I⁻). Such structure rearrangement of phenol molecules with TBA salts is believed to be the main reason for the formation of a liquid phase at room temperature resulting from a significant depression in the freezing temperature the DES compared to those of the pure components.

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