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Strong and weak interactions between ionic liquids and dyes: Test to Methylene blue removal from wastewater using1-butyl-1- pyrrolidinium hexafluorophosphate

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ABSTRACT/RESUME

Abstract: *Strong and weak interactions between ionic liquids and dyes have been studied. The study has been tested with the removal of methylene blue from wastewater by1-butyl-1-pyrrolidinium hexafluorophosphate. The attractive interaction between Ionic Liquid (IL) 1-butyl-1-methyl pyrrolidinium hexafluorophosphate [bmpyr] and Methylene Blue (MB) has been investigated using electric conductivity measurements. The formation of associates between the IL anion (PF_6^-) and cationic MB has been made in evidence by means of spectroscopic analyses namely Ultra-Violet Visible (UV-Vis), Fourier Transform Infra-Red (FTIR) and Nuclera Magnetic Resonance (NMR). The results have been compared to previous data of 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]. Having the same carbon chain, this latter gives associate constants which are higher than those of the former IL[bmpyr], suggesting the induced strong interaction between both species. In effect, the envelope of electron density of IL_{bmim}, caused by nitrogen N1 inside the cycle, increases greatly the interaction. Really, this phenomenon might be attributed to complex formation readily affected by the conjugated diene system and the presence of a low pair of electrons provided by the tertiary at N1 of [bmim] compound. Besides, the symmetrical singly charged Cl^- and PF_6- anions being structure breaker and borderline structure breaker respectively, determined the type of interaction that may occur between the IL and MB. The results suggest also the strongest interaction between the inorganic anion PF_6^- of IL and organic cation of MB leading to its reduction. At last, it has been proved through this fundamental study that IL [bmpyr] is not efficient enough to remove MB compared to other suitable ILs. It may nevertheless be good enough to detect traces of dyes in very dilute solutions.*

I. Introduction

Ionic Liquids (ILs) are salts that are liquids at room temperature. They are non-volatile, non-flammable, less toxic, chemically and thermally stable and good solvents for both organic and inorganic materials. They have good electrical conductivity and are applicable to chemical separations, extraction and electrochemistry at the IL/Water interfaces [1-3] . In addition to scientific literature, Ionic Liquids (ILs) have been described in the patent literature [4]. ILs can also be applied potentially in separation techniques [5-6] and successfully utilized in selective electrodes [7]. Known as non-chloroaluminate IL, 1-butyl-1-methyl pyrrolidinium hexafluorophosphate consists of organic cation $[bmpyr]^+$ and inorganic anion $[PF_6]^-$. Upon the addition of an IL to an electrolyte solution, the ionic conductivity rises, because of the increase of the number of ions in the solution. On the other hand, the presence of the IL increased the viscosity of the resulting electrolyte solution, due to the increase of ion-solvent interactions and Coulomb interactions between ionic species [8]. In view of these interesting physico-chemical properties, the IL can be regarded as being a good candidate for chemical separation and extraction processes.

Methylene Blue (MB) is a chemical compound also known as methylthioninium chloride. It is either a medication or a dye. It is widely used in different industrial applications. Besides, processes for preparing MB, are very known and well described in the patent literature [9]. However, it is often present in wastewater and gives rise to potential pollutants due to their inherent toxicity. Many treatment processes can be applied for its removal from wastewater, such as cation exchange membranes, electrochemical degradation, adsorption/precipitation processes. Acute exposure to methylene blue has been found to cause in humans some diseaces, such as increased heart rate, vomiting, jaundice, etc… For all these reansons, the current research on this toxic compound, is still in progress nowadays. A recent study on removal of MB dye by photocatalysis coupled with nanofiltration, has been undertake [10]. Also, the elimination of MB by new ionic liquids/salts from aqueous solution, has been recently investigated [11-14]. Pei *et al* have successfully used $[PF_6]^-$ based ILs to remove MB where they rapidly obtained precipitates [15]. Ionic liquid based nanoporous organo-silica supported propylamine was used as a highly efficient adsorbent for removal of congo red from aqueous solution [16]. Moreover, in order to preserve the environment, adsorption and biodegradation reduction of MB using natural adsorbents, has been carried out [17]. Adsorption kinetics of MB solution by activated carbon has been modelled using Peleg's equation [18]. Kinetics of MB adsorption on treated bentonite, has been currently studied. [19]. Extraction and determination of Rose Bengal in water samples by dispersive liquid—liquid microextraction coupled to UV–Vis spectrophotometry, were studied by [20].

Ionic association in simple systems of two constituents (cation and anion) has been dealt with widely in previous studies. Initial theories of ionic association by Bjerrum in 1926 and later on by Fuoss in 1958 are described on a recent review [21-22]. Both theories are based on long-range Coulomb interactions. However, in recent treatments non-Coulomb short-range interactions between ions, have been also taken into account, assessing the structure-making and structure breaking effects in on electrolyte solution [23]. Different types of ion association may be identified by using infrared and Raman spectroscopies [24-25].

In the present study we extend the ionic association to more complex system mixture of IL and cationic MB involving polyatomic ions, by means of conductivity measurements. We, therefore, assess the interaction between the IL and MB in terms of structure breaker effect of both anion Cl^- and polyanion PF_6^-. As reported previously by Okan *et al.* these anions are particular in that their ionic conductivities versus the reciprocal of their radii yield a single curve, despite the differences of their solvation in aqueous solutions [26]. The results suggest the strongest interaction between the inorganic anion PF_6^- of IL and organic cation of MB leading to its reduction.

II. Experimental

II.1. Materials

Ionic liquid 1-buty-l-methyl pyrrolidinium hexafluorophosphate $[bmpyr][PF_6]$ of molecular formula $C_9H_{20}F_6NP$, molecular weight 287.23 g/mol and 99% pure, was purchased from SOLVIONIC. Methylene blue of molecular formula $C_{16}H_{18}ClN_3S$, molecular weight 319.85 g/mol, density 1.0 g/mL, solubility 40 $g \cdot L^{-1}$ at 20 °C and 99% pure, was purchased from MERCK and was used without further purification. Doubly distilled water was utilized to prepare aqueous solutions.

II.2. Preparation of samples and analysis

The associates were prepared from the cationic dye (methylene blue) solution (10^{-2} mol. l^{-1}). Variable concentrations of $[bmpyr][PF_6]$ were added to obtain various ratios (C_{IL}: C_{MB}). The mixture samples were then poured into several flasks and associates were, therefore, obtained after mixing the solutions with a magnetic stirrer for 30 min. Then the solutions decanted naturally under a fixed temperature inside a cryostat. Two distinct phases appeared clearly and a sample of upper supernatant was taken and analysed. The absorbance of each solution was monitored using the SPECORD 210 Plus UV–Vis spectrophotometer to determine the concentration of dye. Besides, the presence of associated components within the complex was made in evidence by Nuclear Magnetic Resonance (NMR) analysis of the supernatant using BrukerAC 300 P (300 MHz) spectrometer. The Fourier Transform Infra Red (FTIR) spectra for associates were recorded by PerkinElmer spectrometer (Spectrum two), in the region 400 - 4000 cm^{-1} with 0.5 cm^{-1} resolution at room temperature, to confirm the formation of the associates by showing the different functional groups.

II.3. Association constants of associates

The determination of association constants of associates was achieved by conductometric method. In effect, stock solutions of methylene blue and [bmpyr][PF_6] were prepared using high quality distilled water (1µS/cm). Conductance measurements of IL and mixtures were carried out using AD 3000 conductivity meter (ADWA instruments). This latter was an electronic device-based conductivity and temperature meter. The auto-ranging feature of the electrical conductivity range set automatically the instrument to the scale with the highest resolution (i.e. 0.01 µS/cm and 0.1 °C). Measurements were compensated for temperature effect manually using the conductivity probe with the built-in temperature sensor. The temperature coefficient was then selected suitably and the electrical conductivity was finally measured. The instrument was equipped with a stability indicator, to indicate when the measurement was to be recorded. In the beginning, the apparatus was calibrated using the standard solutions of KCl 84 µS/cm (0.001 M), 1413 µS/cm (0.01 M), and 12 880 µS/cm (0.1 M) at 25 °C. Measurements were performed inside a thermostated water bath with temperatures of solutions being maintained within ± 0.5°C.

III. Results and discussion

III.1. Composition of IL–dye associates

Qualitatively, the formation of IL-Dye associates was investigated by using FTIR and NMR analyses.

III.1.1.FTIR spectroscopy analysis

***MB**

As shown in Figure 1, the spectrum of pure MB has two bands at 1595 and 1489 cm^{-1} corresponding to the stretching vibration mode C-C [27]. The absorption bands positioned at 1391, 1335 and 1217 cm^{-1} are attributed to the vibration mode of the C-N group. The adsorption bands located at 1335 cm^{-1} and 1217 cm^{-1} correspond to the C-N bond in the benzyl ring and the C-N aliphatic bond respectively. At 1141 cm^{-1}, the band is associated with the C-H bond while that at 817 cm^{-1} is attributed to the vibration deformation mode of the C = S bond.

***IL**

In the IR spectrum of the pure IL, the band at 2968 cm^{-1} corresponds to the vibration mode elongation of the group CH_3. The CH_2 group of the butyl chain attached to the pyrrolidinium ring has a band at 1469 cm^{-1} corresponding to the formation vibration mode. The weak band at 930 cm^{-1} is attributed to the deformation vibration mode of the NC (H) N bond. Whilst, the wide band at 840 cm^{-1} and the short at 554 cm^{-1} are attributed to the vibration elongation of the PF_6^- anion. These observations are in qualitative agreement with those reported elsewhere [28-31].

***Associate (IL+MB)**

The IR spectrum of the (IL+MB) mixture shows a displacement of the stretching band of the CN group of the benzyl ring. The band of the CH group of the benzyl ring of the MB exhibits a displacement of 1141 to 1131 cm^{-1} showing the existence of strong interaction between the benzyl ring and the IL. Moreover, in order to know more precision concerning IL, it is necessary to make further NMR analysis.

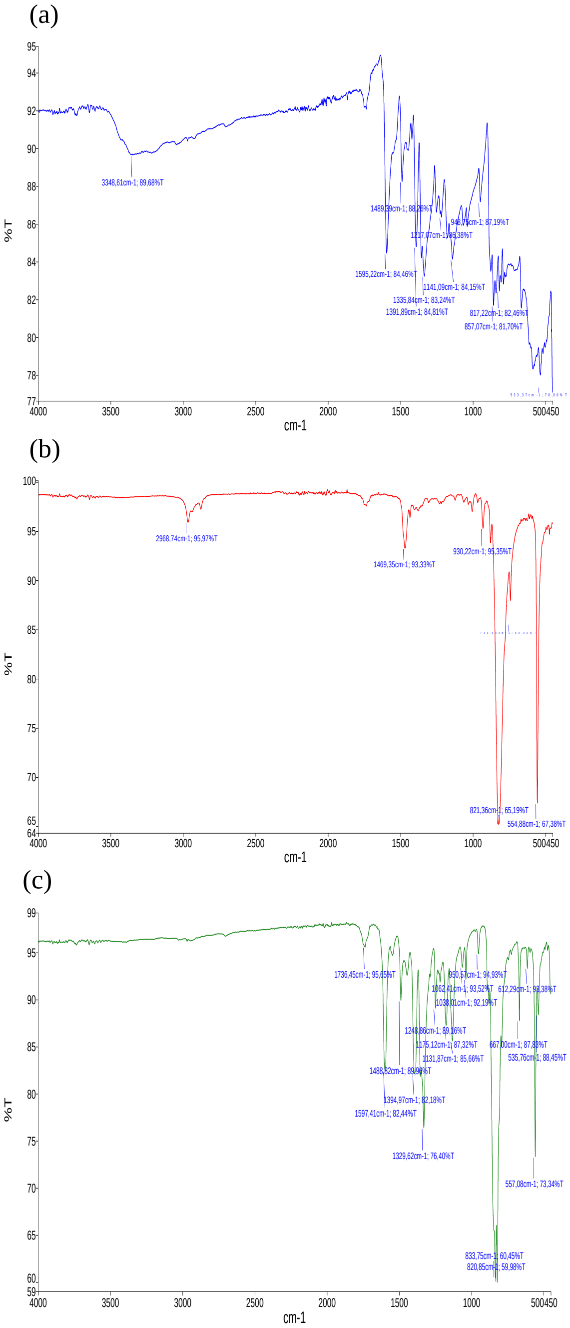


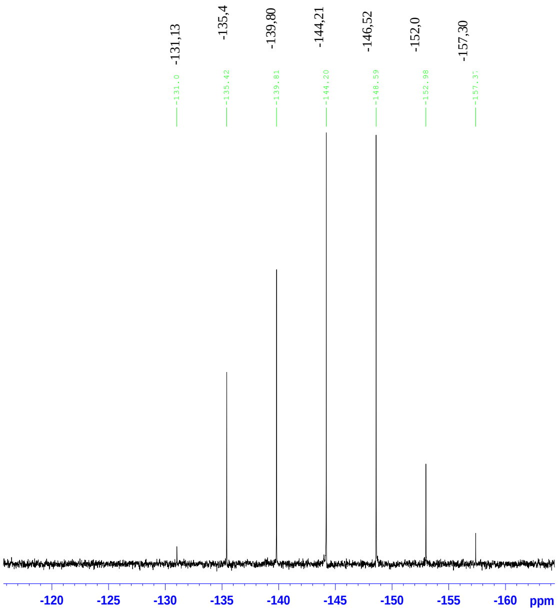
***Figure 1.** FTIR spectra of (a) MB, (b) IL and (c) MB + IL associate.*

III.1.2. NMR spectroscopy analysis

After the phase of separation of the MB solution at 7 mg /L by the [bmpyr][PF$_6$]at 1.7% by weight, the organic phase obtained was removed and dried at 60 ° C for 24 hrs. Then 0.3 ml of IL rich phase was removed and introduced into a 5 mm NMR tube. A capillary loaded with deuterated acetone was introduced into the tube. The deuterium and acetone atoms were used to fix the magnetic field of the RM, while the residual protons served as an external reference for the proton signal at 2.050 ppm. The use of the capillary made it possible to maintain the chemical displacement of the acetone constant because it was not affected by the composition of the sample. The ^{31}P NMR spectra were recorded with an NMR spectrometer with a resonance frequency of 300 MHz.

In order to obtain information on the interactions between IL and MB, ^{31}P NMR was used. Chemical shifts of pure and mixed [bmpyr][PF$_6$] occurred in the region of -125.2 to -163.2 ppm, as shown in Figure 2. A strong variation of the chemical shift was observed with respect to the pure IL. Besides, the disappearance of two peaks at -131.13 and -152.30 were noticed, showing the presence of strong interactions between the anion of the IL and the cation of MB, in good agreement with the results obtained by [32-33].

(a)



(b)

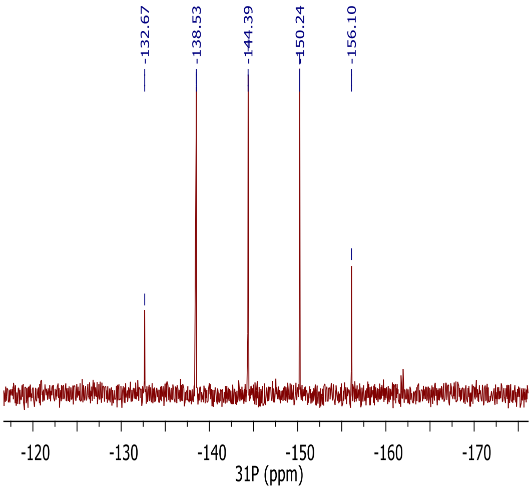


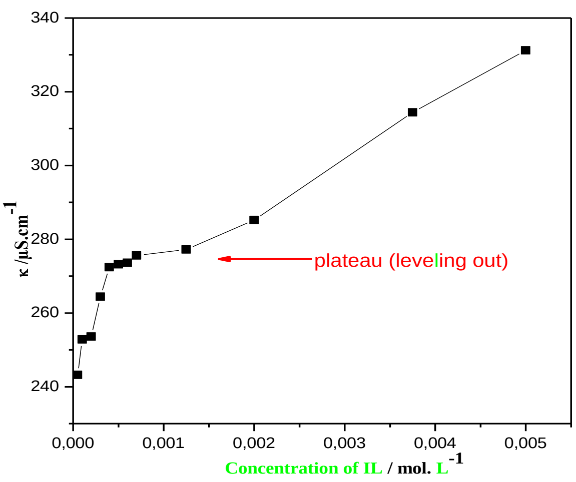
Figure 2. *^{31}P-NMR spectra of PF$_6^-$: [bmpyr][PF$_6$] pure (a); {[bmpyr][PF$_6$] + MB} (b).*

III.2. Conductivities of IL-Dye mixtures

Quantitatively, associates were investigated by the conductivity method. In effect, Figures 3-5 (a) represent conductivity versus concentration of added IL, making in evidence of the formation (MB+IL) associates. As concentration increased, the conductivity rose up sharply reaching a plateau (i.e. occurrence of non-conducting species) and then increased steadily as it has been reviewed elsewhere using gel polymer electrolytes and IL mixtures [34]. On the other hand, Figures3-5 (b) represent changes in the concentration of MB with the ratio of added IL. The concentration of MB dropped off linearly with concentration ratio IL/MB. As can be seen, the final concentration of MB in mixture remained almost constant when the ration was greater than or equal to one, in accordance and correspondence to the levelling out (plateau) found in conductivity curve.

In addition, the effect of temperature was also investigated for temperatures 5, 25 and 45°C. As the temperature increased, the conductivity increased as well. The same trends of curves were found for the other temperatures i.e. 15 and 35°C. This has a direct impact on associate formation. In effect, the minimum concentrations of IL required for the associate formations were 0.0003, 0.0005 and 0.0007 mol. l^{-1} at temperatures 5, 25 and 45°C respectively.

(a)



(b)

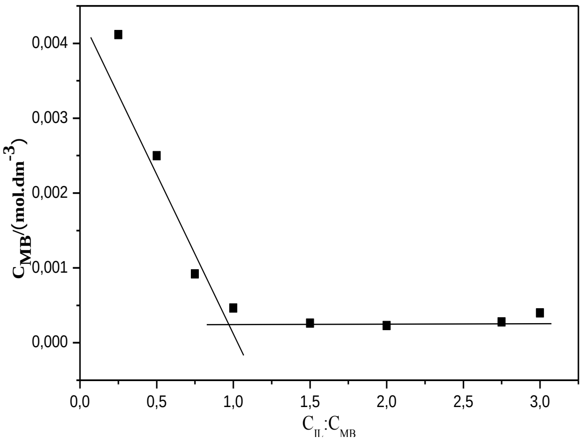


Figure 4. *Conductivity (a) and change of MB concentration with added IL (b) at 25 °C*

(b)

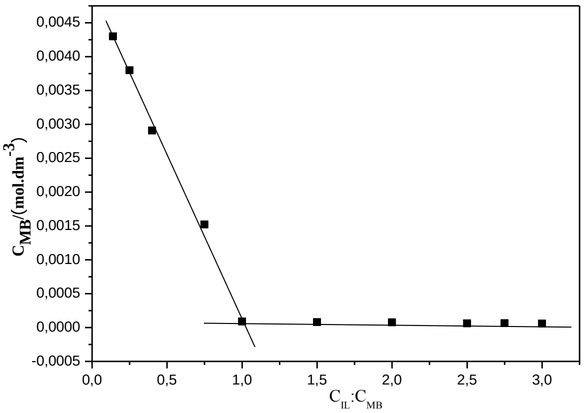
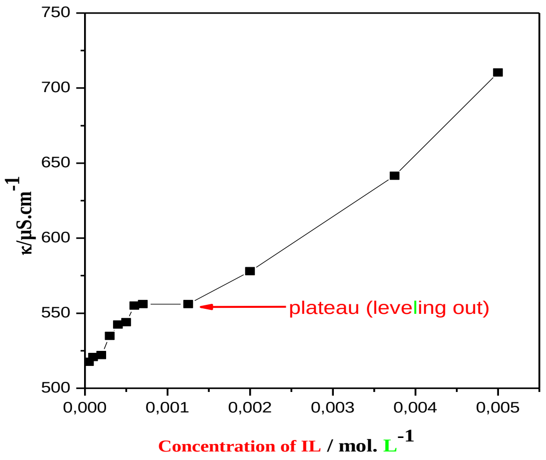
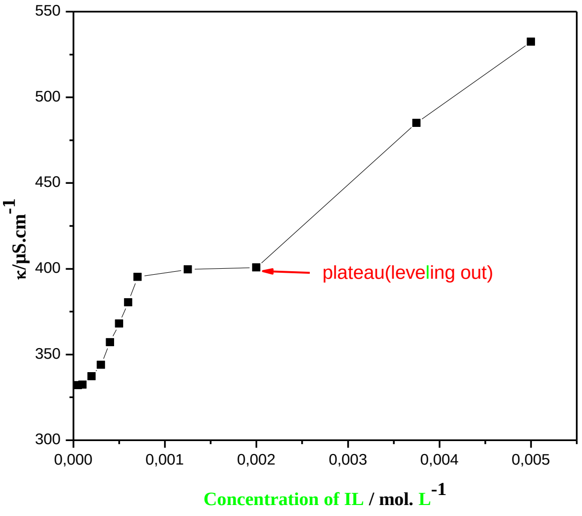


Figure 3. *Conductivity (a) and change of MB concentration with added IL (b) at 5 °C*

(a)



(a)



(b)

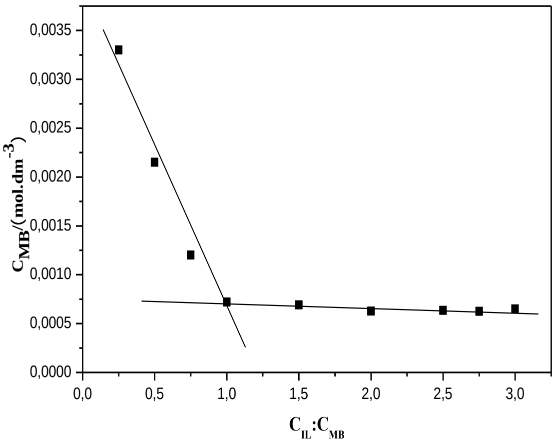


Figure 5. *Conductivity (a) and change of MB concentration with added IL (b) at 45 °C* **.**

III.3. Association constants of associates

III.3.1. Procedure of determination

Initially, the conductivities of IL ([bmpyr$^+$], [PF$_6^-$]) and dye ([MB]$^+$, Cl$^-$) may be measured individually and separately. As a matter of fact, the conductivity of the mixture of both systems was reduced making in evidence the strong interaction between the ions [PF$_6^-$] and [MB]$^+$ taking place significantly. This behaviour led to the net conductivity of the mixture which may be expressed as a function of associate concentration $C_{IL\text{-}MB}$. This latter can be approximately equal to the ratio between the conductivity of the plateau and molar conductivity at infinite dilution. Therefore, the association constant can finally be calculated using the following equation [15]:

$$K = \frac{1}{(C_{IL} - C_{IL-dye})(C_{dye} - C_{IL-dye})} \qquad (1)$$

where C_{IL} and C_{dye} are concentrations of IL and MB respectively,

The calculated values of the association constants at different temperatures are given in Table 1. The interaction between ionic species may be also supported by the acid-base properties and polarity of ILs. In effect, the acceptor number of [bmim][PF$_6$] being equal to 27.7 [1], suggests a strong association compared to [bmpyr][PF$_6$]. Moreover, the Kamlet-Taft parameter α (i.e a measurement of hydrogen bond acidity) for [bmim][PF$_6$] being equal to 0.63[1], reflects the net gain of the protons on its 2-position of the ring, as shown in Fig.6. However, both ILs are common in that they have the same anion PF$_6^-$ known as a structure breaker that tends to destabilize the ionic interaction. Compounds (a) and (b) both gave an immediate precipitate with MB, owing to their structures examined by ^{31}P NMR. Indeed, the compound (b) yielded higher association constants at all temperatures, than compound (a). This phenomenon might be explained by the complex formation readily formed with the conjugated diene system. In addition, the presence of a lower pair of electrons provided by the tertiary amine at N$_1$ (compound b).

Table 1. *Association constants of the cationic MB-[bmpyr][PF$_6$] associates*

T/°C	K_a 10^6 (L. mol^{-1})^2
5	0.13
15	0.12
25	0.09 (4.68*)
35	0.06 (2.93*)
45	0.05 (2.54*)

*Values of ref. [11]

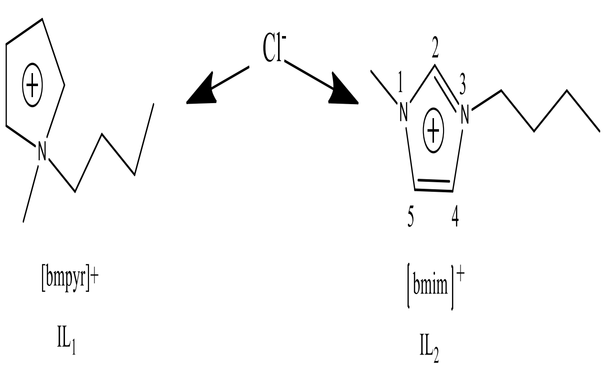


Figure 6: *Localised electron density in cation [bmpyr]$^+$ (IL$_1$) and delocalised electron density in cation [bmim]$^+$ (IL$_2$)*

III.3.2. Structure breaker effect of Cl$^-$ and PF$_6^-$ anions: Type of ionic interaction

As shown in Figure 7, the IL-MB association involves successive ionic interactions, in particular (PF$_6^-$)$_{IL}$/ (Org. cation)$_{MB}$ and (Cl$^-$)$_{MB}$ / (Org. cation)$_{IL}$. In the first one considered as the main interaction, the polyatomic anion PF$_6^-$ having an effective radius of 0.281 nm [26] and allowing more negative, interacts more strongly with the organic cation of MB and reduces its amount in the mixture. Whilst, in the second one considered as the complementary interaction, the singly charged monoatomic anion Cl$^-$ with shorter radius i.e. 0.119 nm, interacts less strongly with the organic cation of IL. Though both anions have spherical symmetries and are structure breakers [26]. Really, Okan *et al.* already studied the classification of these anions by plotting the ionic molar conductivity versus the inverse of the ionic radii of monoatomic ions and effective radii of polyatomic ions and found the anions PF_6^- and Cl^- to be laid on the same curve, along with other singly charged anions. The latter is definitely a structure breaker, while the former with greater radius is borderline structure breaker, in a quite good agreement with the classification of Marcus [35]. Indeed, we regard this classification as a relevant argument that explains the type of interaction occurring during the interaction between the IL and MB. This finding is qualitative good agreement with previous study on the addition of the salt $LiBF_4$ in mixture of 1-butyl-3-methylimidazolouim lithium tertrafluoroborate, using rotational diffusion parameter., where the structure-making and structure-breaking were well highlighted [36].

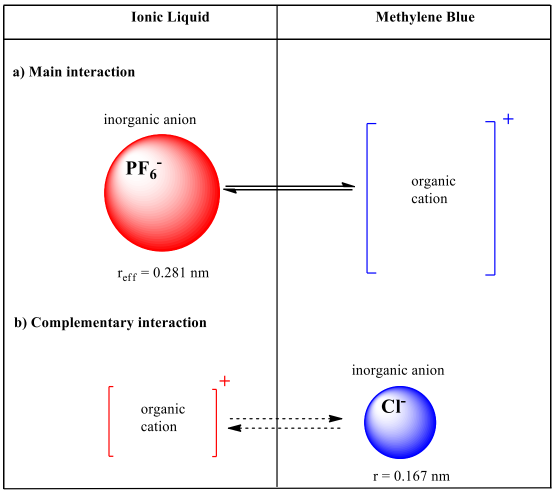


Figure 7. *Scheme of ionic interactions between IL and MB: Main interaction involving polyatomic anion* PF_6^- *(a) and Complementary interaction involving monoatomic anion* Cl^- *(b)*

III.4. Thermodynamic parameters

The thermodynamic parameters namely Gibbs free energy, enthalpy and entropy changes for the formation of the associates have been calculated by using the equations of literature [1]. Their values are given in Table 2 along with those of [15]. From the ΔG^0 values, it is apparent that the complex species $[MB^+ + PF_6^-]$ are less associative as the temperature increased. Moreover, they are negative for all the temperatures studied, reflecting thus the spontaneous and preferential association process. However, ΔH^0 remained constant and negative, indicating the exothermic nature of the association. This finding may be attributed to the attractive interaction between $[MB^+]$ and $[PF_6^-]$. In contrast, the observed positive entropies may be ascribed to the dehydration of both species before their association. Besides, in comparing the two sets of thermodynamic data, it may be noticed that our values of [bmpyr][PF_6] are relatively less than those of [bmim][PF_6] [15], for the same reasons cited above.

Table 2. *Thermodynamic parameters (kJ.mol^{-1}) for the cationic* $[MB^+ + PF_6^-]$ *associates.*

T/°C	ΔG^0	ΔH^0	$T\,\Delta S^0$
5	-27.20	-19.35(-24.2*)	8.13
15	-28.11		8.42
25	-28.24(-38.1*)		8.72 (13.9*)
35	-28.16		9.01
45	-28.60		9.30

*Ref. [11]

IV. Conclusion

Similarly to previous studies, MB can also be eliminated by IL 1-butyl-1-methyl pyrrolidimium hexafluorophosphate to form associates between inorganic anionic IL [PF_6] and organic cation MB. This achievement has been carried out by conductivity measurements and completed by spectroscopic measurements. Unfortunately, the association constants of associates obtained with $IL_{bpyr,}$ were much lower than those of IL_{bmim}, due to the strong interaction between the delocalised electron density on its 2-position of the ring. The symmetrical singly charged Cl^- and PF_6- anions being structure breaker and borderline structure breaker respectively, determined the type of interaction that may occur between the IL and MB. The results suggest the strongest interaction between the inorganic anion PF_6^- of IL and organic cation of MB leading to its reduction. Moreover, the negative ΔH^0 value (i.e. -19.35 kJ. mol^{-1} indicated the exothermic for the associate formation, due to the attractive interaction between $(PF_6^-)_{ILbpyr}$ and (Org. cation)$_{MB}$. However, the value of -24.2 kJ. mol^{-1} for the Il_{bimim} explained the strongest association obtained with this IL, due to the net gain of the protons on its 2-position of the ring and thus electron density delocalisation. At last, we proved through this fundamental study that IL [bmpyr] may not efficient enough to remove MB compared to other ILs. However, it may be good enough to detect traces of dyes in very dilute solutions.

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