Proceeding Paper

Solvatocromic Behavior of Polarity Indicators in Pils and Their Mixtures with Molecular Solvents. Autoprotolysis and Its Relation to Acidity [†]

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Abstract: It is interesting to know the behavior of Protic Ionic Liquids (PILs) within the binary mixture of molecular solvents since it is usual to carry out processes such as organic and inorganic synthesis, or liquid-liquid extractions in the presence of another solvent. Moreover, on certain occasions the absence of water is strictly required. In this sense, it is important to note that the addition of small amounts of IL to the molecular solvent allows a fine adjustment in its microscopic properties; obtaining "new solvent systems" with particular properties. Taking into account that solvatochromic indicators are traditionally used as microscopic descriptors to determine the molecular microscopic properties of solvents. In this sense, we look for re-evaluate the behavior of solvatochromic probes and reconsider the validity of traditional polarity scales such as ET(30), in alkylammonium-based PILs and in their mixtures with molecular solvents, taking into account now that the real composition of these PILs depends on the equilibrium of autoprotolysis. In addition to the spectroscopic analysis developed, the characterization of the PILs and their binary mixtures was completed in terms of a change in the ΔpKa of the precursor species of a PIL. Thermal analysis was also employed to determine the acid strength's role in ions complete formation in pure PILs.

Keywords: Protic Ionic Liquids; solvatochromic indicators; equilibrium of autoprotolysis

1. Introduction

Ionic liquids (ILs) have a great advantage over other types of solvents due to the wide versatility they present with different applications, especially for electrochemical applications due to their physicochemical properties such as high ionic conductivity [1–5]. for this reason, they gain the 'new materials' name. In general, ILs can be classified into Protic ILs (PILs) and Aprotic ILs (AILs). PILs are a kind of ILs formed by the proton transfer from a Brønsted acid (AH) to a Brønsted base (B) [6]. One of the structural features of PILs is the formation of strong H bonds between cations and anions that define their unique physicochemical properties [7]. We have determined by cyclic voltammetry that neutral acidic and basic precursor species can coexist in PILs due to the equilibrium of autoprotolysis [8]. This equilibrium also can affect its properties such as viscosity, density, and conductivity.

Additionally, it is interesting to know the behavior of PILs within the binary mixture of molecular solvents since it is usual to carry out organic and inorganic synthesis processes, or liquid-liquid extractions in the presence of another solvent. Moreover, on certain occasions the absence of water is strictly required. In this sense, it is important to note that the addition of small amounts of IL to the molecular solvent allows a fine adjustment in its microscopic properties; obtaining "new solvent systems" with particular

properties [9,10]. Taking into account that solvatochromic indicators are traditionally used as microscopic descriptors to determine the molecular microscopic properties of solvents [11]. In this sense, we look for re-evaluate the behavior of solvatochromic probes and reconsider the validity of traditional polarity scales such as $E_T(30)$ [12,13], in alkylammonium-based PILs and in their mixtures with molecular solvents, taking into account now that the real composition of these PILs it depends on the equilibrium of autoprotolysis.

We have detected certain drawbacks in the last years of research in the group when working with IL. We are detecting the effects of different acid-base equilibria between the free precursor species of the PILs and these indicators. Thus, the parameters obtained by these scales would be contaminated and would not represent reliable results within the normalized values that constitute the scales. This is also a problem, since the solvents used to construct these scales are molecular and do not involve ionic species. Complementary, some authors [1], establish that it is possible to discuss the physicochemical properties in terms of a change in the ΔpKa of the precursor species of a PIL, in order to analyze the degree of proton transfer and thermal stability as a function of the change in ΔpKa. In addition, thermal analyses are employed to determine the acid strength's role in ions complete formation in pure PILs.

2. Materials and Methods

For the analysis we have selected Reichard's dye (I) and the PILs: ethylammonium, diethylammonium and tributylammonium with nitrate as counterion (NO_3), and the molecular solvents methanol (MeOH) with hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) properties and dimethylsulfoxide (DMSO) with HBA properties. The response of the indicators was analyzed for different ranges of concentrations of the PILs in the binary mixtures (molar concentrations (C(M)) and molar fractions (x)) in order to evaluate the solvation effect of molecular solvents.

2.1. Synthesis of Ionic Liquids

The investigated PILs were synthesized as detailed in the literature.[8]

2.2. Microsensors and Spectroscopic Behavior–UV-Vis Spectroscopy

General Procedure: The spectroscopic data were obtained with a SHIMADZU UV-1800 spectrophotometer, equipped with a thermostatic cell holder. The pure solvents were mixed in appropriate proportions by weight to give binary solvent mixtures at various compositions. The temperature was maintained at 25 ± 0.1 °C. The concentrations of the indicators solutions were: 0.1 and 0.25 mM for the Reichardt's dye (I).
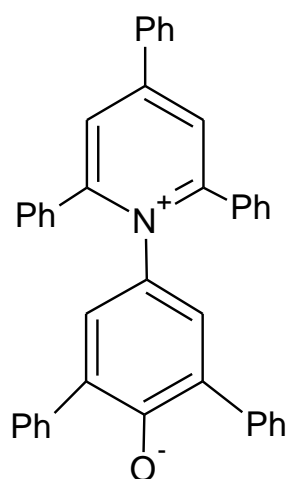
Scheme 1. Structure of the Reichardt's dye (I).

The parameter $E_T(30)$ is determined from the wavelength corresponding to the maximum of the UV-Vis absorption band of betaine (**I**) 2,6-diphenyl-4- (2,4,6-triphenyl-1-pyridinium) -1-phenolate (Scheme 1) and is calculated by applying Equation (1):

$$E_T(30) \text{ [kcal mol-1]} = hc\, N = 2.859 \times 10^{-3}\, x\, (\text{cm}^{-1}). \qquad (1)$$

Where h is Planck's constant, c is the speed of light, N is Avogadro's number and is the wave number in cm^{-1}. This equation converts the electronic transition within the probe into the corresponding intramolecular charge transfer energy, indicated in kcal/mol.

2.3. Thermogravimetric Analysis (TGA)

The decomposition temperatures of the PILs were determined by using thermogravimetric analyzer (TGA) in the thermal stability analysis [1]. An approximate 10 mg of sample was weighted in a crucible pan and the analysis was performed in the temperature range of 30–650 °C under 20 mL/min nitrogen flow with a heating rate of 10 °C/min.

3. Results and Discussion

3.1. Solvatochromic Behavior of the Reichardt´s Dye (I)

3.1.1. Range of Mole Fractions (X)

The Figure 1 showed that there are no significant changes in the spectrum from $x_{PIL} \sim$ 0.2 to 1 for dye **I**, sensitive to polarity and acidity. This possibly indicates that the ionic lattice is organized, and as a consequence of this, the solvation effect of the molecular solvent is negligible.
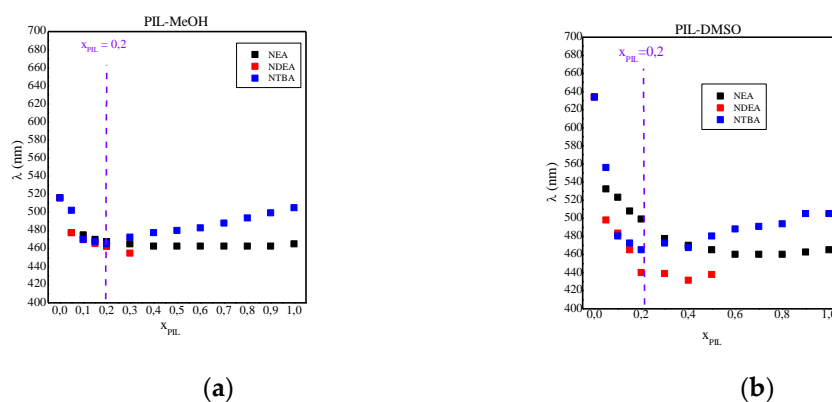

Figure 1. Variación de la λ (nm) del indicador **I** **vs.** la x_{PIL} en las mezclas: (**a**) (MeOH+PIL) y (**b**) (DMSO+PIL). (■ NEA, ■ NDEA, ■ NTBA).

Taking as a reference the observed behavior of NTBA by cyclic voltammetry,[8] where NO free molecular species were detected for this PIL in its pure state, we can associate the behavior of the probe with molar fractions close to 1 ($x_{PIL} \sim 1$) as an indicator of a microenvironment ionic polar.

Clearly, from $x_{PIL} \sim 0.2$ to 1, the interaction with dye **I** is governed by the ion pair of the PILs, independently of the molecular solvent as shown in Figure 2 for NEA and NTBA. This would also indicate that the effect of ionic species on the probe prevails and not the mixed solvent (SM) or the LIP-SM intersolvent complex. This comparison could not be made for NDEA due to its limited solubility in the molecular solvents compared.
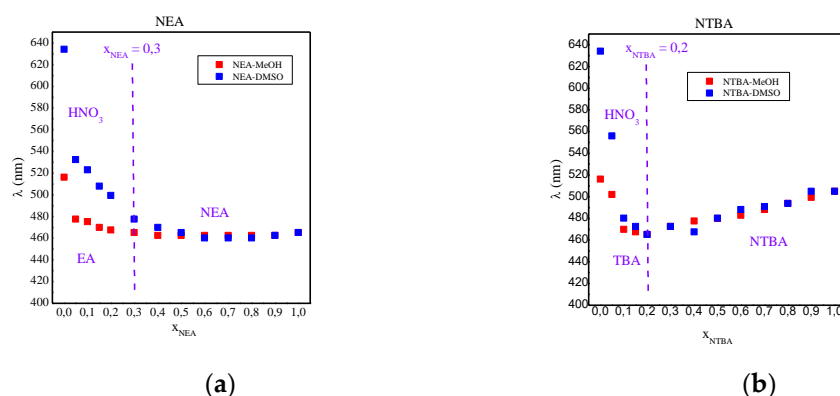
Figure 2. Variation of the λ (nm) of the indicator I vs. the x_{LI} for NEA and NTBA in: (**a**) ■ MeOH y (**b**) ■ DMSO.

On the other hand, we observe a shift to lower values of λ as the PIL concentration increases for lower molar fractions of the PIL in the range $0 < x < 0.3$. This could indicate that initially there are higher concentrations of free molecular species in the equilibrium of autoprotolysis due to a greater solvation effect by the molecular solvents that are found in a higher proportion.

3.1.2. Respuesta Solvatocrómica del Indicador I en el Rango de Fracciones Molares

Figure 3 shows the response patterns of the factor $E_T(30)$ as a function of the x_{LI} for all the solvent systems under study. The analysis was developed according to the deviation from the ideality of the curves "property vs. solvent composition".
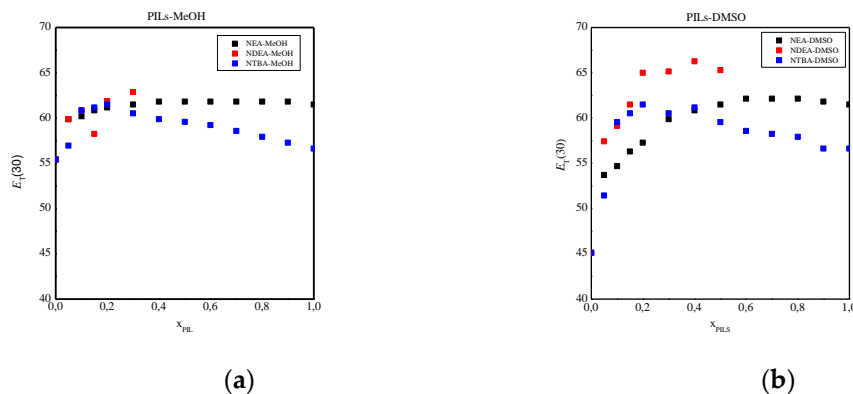

Figure 3. Variación del parámetro $E_T(30)$ vs. la x_{PIL} en las mezclas: (**a**) (MeOH+PIL) y (**b**) (DMSO+PIL). (■ NEA, ■ NDEA, ■ NTBA).

In general, the same response pattern could be observed for the $E_T(30)$ parameter (Figure 3), this observed change would be related to the possibility of forming LIP-SM complexes, which leads to ionic species with different degrees of association with respect to the Pure LIP. The highest percentage of change in the properties was observed up to a value of $x_{PIs} \sim 0.2$.

It could also be noted that certain solvent systems show synergism on the parameter and other mixtures show positive deviation with respect to the ideal behavior. This property depends on the cation, for example for NTBA synergism was observed with the solvents MeOH and DMSO. In this case, we can associate the lowest polarity values $E_T(30)$ corresponding to a microenvironment with high ionic character when $x_{NTBA} \sim 1$.

From the analysis of the solvatochromic scales we proposse that it makes no sense to evaluate the values of a normalized $E_T(30)$ parameter (E_T^N), since ionic organic com-

pounds are not involved in the normalization calculation. If it has a series of $E_T(30)$ values for several LIs, a new scale could be proposed.

3.1.3. Range of Molar Concentration (C) vs. X

In general, the same behavior is observed in both solvents. We observed the protonation of indicator by the acidic species precursor of the PILs in each solvent system for the C (M) range. But, surprisingly we have detected that this band return as a shoulder in all binary solvent mixture of type [PILs + Molecular Solvent] here studied when the I microsensor concentration is about 0.4 mM and the PILs concentration in the binary mixture is the order molar fraction. Figure 4 shows the behavior of Reichardt's dye (I) for the ([NDEA] + MeOH/DMSO) system binary for both ranges of working concentrations. This system was taken as a model, but similar behaviors were observed for all binary systems here studied.
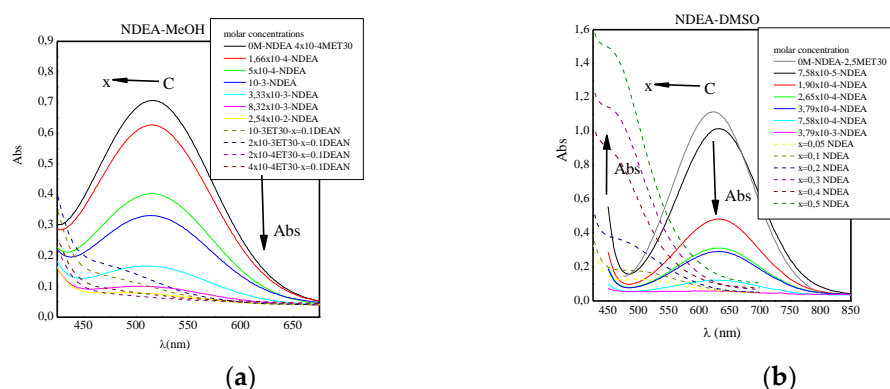

(**a**) (**b**)

Figure 4. The UV/Vis absorption spectra of Reichardt's dye dissolved for a) [I] = 4 × 10⁻⁴ M in MeOH, after addition of increasing amounts of [NDEA] in concentration (mol L-1) (—) and mole fraction (- - -). b) [I] = 2.5 × 10⁻⁴ M in DMSO, after addition of increasing amounts of [NDEA] in concentration (mol L⁻¹) and mole fraction.

The behavior of the probe in the presence of PILs in the range of molar concentrations is manifested as an indicator signal that turns off. This is clearly due to the presence of free acid in the medium and the consequent protonation of the indicator that absorbs at lower wavelengths.

When the [PILs] is the order of molar fraction, the dye signal returns to 'switching-on'. This unexpected behavior in principle, could explained based on the equilibrium of autoprotolisis at different amounts of PILs.

3.2. Δ pKa

Some authors analyze the physicochemical properties in terms of a change in ΔpKa of its precursor species ($\Delta pKa^{solvent} = pKa^{AmH+/B} - pKa^{HA/A}$) [14]. They analyze the applicability of the relationships between different parameters with the ΔpKa of the PILs to establish a generalized concept to understand the physicochemical properties. In this analysis, special emphasis is given to the degree of proton transfer and termal stability depending on the change in ΔpKa. Based on the above, we can find some relationship in molecular solvents between the parameters determined in our work and the ΔpKa of the PILs analyzed here. And in this way, we could analyze the degree of ion pair formation that these PILs present in MeOH and DMSO to be able to apply them to non-aqueous systems. This is important because most of the reported data were obtained in aqueous systems.

Specifically, Angell et al. demonstrated that ΔpKa > 10 is required to ensure sufficie proton transfer to produce highly ionized PILs.[3] Then, the PILs with high ΔpKa show

high ionic behavior owing to complete proton transfer and weaker interactions between the cation and the anion. However, MacFarlane et al. proposed that ΔpKa = 4 is sufficient for the completion of proton transfer [4]. ILs with lower ΔpKa values indicate incomplete proton transfer and the formation of ion-pairs or ion-aggregates between the protonated cation and the anion, similar to AILs [5]. This PILs with low ΔpKa exhibit poor ionic behavior owing to the hydrogen bonding interaction between the protonated cation and the anion through the N–H bond as a result of incomplete transfer proton [14].

Teniendo en cuenta lo anterior, podemos comparar el ΔpKa de los PILs en MeOH y DMSO (Table 1).

Table 1. Calculated ΔpKa values for PILs in MeOH and DMSO [1].

Specie	pKa^w	PKa^{MeOH}	PKa^{DMSO}	ΔPKa^W	ΔPKa^{MeOH}	ΔPKa^{DMSO}
HNO$_3$	−1.3	3.18	−1.72	Am/HNO3		
EA	10.63	11.00	10.90	11.93	7.82	12.62
DEA	10.98	11.00	10.50	12.28	7.82	12.22
TBA	10.89	10.78	8.4	12.19	7.60	10.12

We obtained an ΔpKa > 10 for the PILs in water and DMSO indicating a sufficient proton transfer to produce a PIL with high ionic character, while in MeOH the character of the IL as an ionic pair is evidently lower. This is consistent with the highest $E_T(30)$ values obtained for the MeOH solvent in the range of x$_{PILs}$ between 0 and 0.2 corresponding to a poor ionic character. This also agrees with the lower value of pKa determined by the indicator method (Table 2) in MeOH with respect to DMSO due to the greater dissociation of the PILs in MeOH generating free HNO$_3$. We can corroborate the high degree of ionization observed in DMSO by comparing the pKa values of HNO$_3$ (Table 1), being more acidic in DMSO, however, these PILs having high pKa values show a low amount of free acid in this solvent.

Table 2. Acidity constants for selected PILs in MeOH and DMSO [11].

PILs	pKaPIL	
	MeOH	**DMSO**
NEA	5.38	8.67
NDEA	5.21	7.87
NTBA	4.34	6.33
pKa^{dye}	5.10	8.90

The previously published pKa values show that in DBH solvents such as MeOH there is a shift from the equilibrium of autoprotolysis towards molecular species, while DBH solvents such as DMSO cause the opposite effect favoring the existence of PILs mainly as ionic pairs.

Some authors propose that PILs with weaker bases are poor ionic liquids [1]. If we compare the different cations EA, DEA and TBA for the same acid, we corroborate that for the strongest amine TBA as a base, the PILs with the highest ionic character are obtained in the pure state. However, the presence of molecular solvents modifies this fact due to the solvation effect, with NTBA being the most acidic PILs in both solvents.

3.3. TGA

Some authors experimentally established that, in addition to inter-ionic interactions such as Coulombic interactions and, van der Waals forces seen in aprotic ionic liquids (AILs) [4], strong hydrogen bonds between the cation and anion are present in PILs through N–H bonds. Furthermore, they demonstrated that the bond strength may be varied by changing the structure and strength of the constituent acids and bases. The

successive breaking of hydrogen bonds with temperature explains the characteristic properties of PILs such as relatively low ionic character and its decrease with temperature [5].

The study of thermal analysis of a substance is crucial as it will provide information on how PILs behave as heat flows. The thermal stability of the PIL was examined by thermogravimetric analysis (TGA) and TGA profiles are graphically presented in Figure 5. The TGA for studied PILs was performed at scanning rate of 10 °C/min. In the TGA study, the main factor of thermal stability is dependent on the strength of the heteroatom–carbon and heteroatom–hydrogen bond [6]. Figure 5 shows the results obtained in TGA for PILs. To determine the Td (decomposition temperature), the data were fitted to the Boltzman equation, it is taken as the initial temperature where weight begins to be lost in the TGA analysis, also called the initial decomposition.
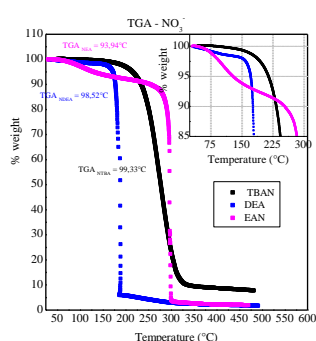

Figure 5. TG curves of PILs recorded at 10 °C/min for NEA, NDEA and NTBA.

In general, the studied PILs showed thermal stabilities in the range of approximately 25 to 90 °C. For the PILs, it was observed that the Td increases as the substitution of the cation increases in the N, which corresponds to a greater thermal stability for the NTBA. When speaking of greater thermal stability, it is consistent with a lower amount of free precursor species of PILs in the autoprotolysis equilibrium.

The TGA profiles of the studied PILs indicate a one-step decomposition temperature for all ammonium-based PILs, except for NEA. In this cases, there is the two stage decomposition. In the first stage, about 10% decomposed about 93.94 °C and the 90% disappeared at about 300 °C in the second stage.

3.4. Correlations

Td vs. ΔpKa and pKa

We can analyze the physicochemical properties in terms of changes in ΔpKa of PILs. The PILs with low ΔpKa undergo weight loss from the beginning as temperature is increased, which is indicative of free acids and bases present in the system. In this sense, to understand the physicochemical properties and the behavior of these PILs, we can analyze the relationship between the experimental weight loss that indicates their thermal stability and the changes in ΔpKa for the MeOH and DMSO solvents. Special emphasis is given to the degree of proton transfer and termal stability depending on the change in ΔpKa. Additionally, we can compare the previous parameters with the pka data previously determined with the indicator method.

It is interesting to see the relationship between the different parameters obtained in order to compare the information they provide us on the state of the PILs studied in the molecular solvents MeOH and DMSO. For this, these parameters are graphed and shown in Figure 6.
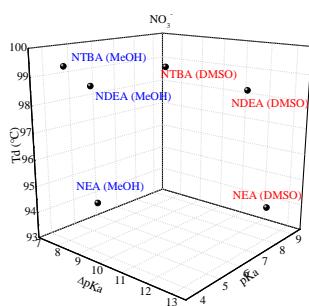
Figure 6. Variation of pKa, ΔpKa and Td values for the PILs analyzed.

In Figure 6 can be observed the NTBA with a higher Td, indicating greater thermal stability and therefore in the pure state they would present negligible amounts of free precursor species corresponding to a high ionic character. However, when PILs are found in molar concentrations in molecular solvents, their autoprotolysis equilibrium is affected by the nature of the molecular solvent and its acid-base properties by free precursor species, resulting in more basic or more acidic global systems. This can be seen in their pKa values, which are lower in MeOH relative to DMSO. For this reason, we observe a more marked solvent effect on the ionization of PILs, where the highest values of ΔpKa or higher ionic character are conditioned with high values of pKa ($\Delta pKa^{DMSO} > \Delta pKa^{MeOH}$ y $pKa^{DMSO} > pKa^{MeOH}$)).

4. Conclusions

For the range of molar fractions from $x_{PIL} \sim 0.2$ to 1, no considerable changes are observed in the spectrum of sensor I. This possibly indicates that the ionic lattice is organized, and as a consequence of this, the effect of the molecular solvent and therefore its solvation effect is negligible. For the C(M) range, we observed the protonation of the indicator I by the acidic species that was the precursor of the PILs in each solvent. On the other hand, an increase in the capacity of the molecular solvent HBD resulted in an increase in the acidity of the PILs, showing a weak cation-anion interaction, the proton being more available for solvation.

High ΔpKa values ensure a PIL with a high ion pair character in DMSO, while the opposite is observed in MeOH. This coincides with the reported values of pKa^{PILs} by the indicator method [11], where an increase in the H-bonding capacity of the molecular solvent resulted in a decrease in these values. In turn, for the pure PILs it was observed that Td increases as the substitution in the N of the cation increases, which corresponds to a greater thermal stability for NTBA, being mainly found as an ionic pair. This coincides with what was determined by cyclic voltammetry, where no neutral free species were detected for this LIP. On the other hand, in dilute solutions, the effect of molecular solvents in the solvation process for NTBA is evidenced, presenting the highest acidity values.

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement:

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