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Determination of Ionic Liquids Solvent Properties Using an Unusual Probe: The Electron Donor−Acceptor Complex between 4,4′-bis(Dimethylamino)-benzophenone and Tetracyanoethene

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Michler's ketone (MK) and tetracyanoethene (TCNE) may be used as a UV−vis probe to investigate the solvent properties of ionic liquids (ILs). In molecular solvents, MK and TCNE give an electron donor−acceptor (EDA) complex, a zwitterionic species or a radical ion pair, depending on the aprotic or protic nature of the solvent and on its ionizing power. In agreement with the behavior observed in aprotic solvents, only the EDA complex was detected in ILs bearing low donor anions ($\beta < 0.7$). The formation constant determined in [bmim][Tf$_2$N] ($K_c = 5.6$ (0.5) M^{-1}) is similar to that measured in 1,2-dichloroethane at 25 °C. The visible absorption maximum ($\nu_{\max,CTC}$) of the EDA complex is quantitatively described by a multiple correlation using the Kamlet−Taft π^*, β, and α parameters of the solvents. The H-bond donating capacity of ILs is not sufficient to determine the transformation of the EDA complex into the zwitterionic species, but the Kamlet−Taft α parameter seems to affect the position of the absorption band. The high ionization power of ILs, moreover, favors the slow dissociation of the EDA complex into its corresponding radical ion pair; this behavior generally characterizes highly polar and highly ionizing protic solvents, such as TFE and HFI. Finally, since the formation of the EDA complex is strongly affected by the presence of impurities, traces of nucleophiles (chloride or amines) or water may be easily detected through the change of the solution color.

Introduction

Ionic liquids (ILs) have recently received a significant amount of attention as solvents for homogeneous (molecular), heterogeneous (supported), and enzymatic reactions.[1] Nowadays, primarily due to their negligible vapor pressure, high solvent power, high thermal and chemical stability, and the possibility to recycle, ILs are considered highly promising, ecofriendly reaction media. ILs possess many other important solvent properties, such as a large electrochemical window, a high ionic conductivity, and physical properties (density, viscosity, hydrophobicity, melting points), which can be finely tuned through variation of anion or cation.

Chemical reactivity in solution is determined by the ability of the solvent to interact with substrates, intermediates, and transition states, that is, by the solvent polarity.[2] Solvatochromic dyes and partition methods are aimed at quantifying the polarity of ILs.[3] By means of multiparameter equations, able to assess independently the variety of solvent−solute interactions, it has been evidenced that (1) the dipolarity/polarizability (π^*) of these salts is higher than that of alkyl chain alcohols and very similar for all investigated ILs; (2) the H-bond basicity covers instead a large range, from acetonitrile to lower β values, being dominated by the anion; (3) the H-bond acidity (α) is determined by the cation, although a strong anion−cation interaction reduces the ability of the cation to hydrogen bond the substrate. More recently, ILs polarity has also been investigated using other approaches, that is, through kinetic[4] and equilibria[5] investigations. In particular, the study of the solute−solvent interactions on the keto−enol tautomerism of 2-nitrocyclohexanone[5b] has evidenced that ionic liquids also own other important properties, which can affect reactivity: they are characterized by relatively low dielectric constants (ϵ), associated with high cohesive pressure values (δ^2). Moderate dielectric constants have been determined also by microwave dielectric spectroscopy,[6] whereas Hildebrand solubility parameters (δ) have been obtained both by the intrinsic viscosity measurements[7] and from the solvent dependence of the bimolecular rate constant for the Diels−Alder reaction between the first singlet excited state of molecular oxygen and 1,4-dimethylnaphthalene.[8] Since in the case of ionic liquids it is not possible to apply conventional techniques for measuring these latter specific properties (dielectric constant, Hildebrand solubility parameter, and cohesive pressure), the agreement among values obtained by applying different indirect approaches is fundamental to evaluate the confidence of each value and the limits of each method.

Here, the solvent properties of some ionic liquids have been explored through the investigation of the electron donor−acceptor (EDA) complex between 4,4-bis(dimethylamino)-benzophenone (Michler's ketone) and tetracyanoethene (MK−TCNE). We decided to use this probe since (1) to the best of our knowledge in the literature[9] only few data are reported about donor−acceptor complexes in ILs. Despite this, the peculiar structure of ILs may affect the stability and physical properties of neutral EDA complexes, whose noncovalent interactions are generally markedly influenced by entropic contributes; (2) recent studies in molecular solvents have shown[10] that the transition energy of the charge-transfer UV−vis band and the structure of the Michler's ketone−tetracyanoethene complex are remarkably solvent dependent. The solvent affects not only the shift of the absorption band of this solvatochromic probe but it also determines the nature of the products. In particular, in nonprotic solvents, the Michler's ketone and tetracyanoethene give a "true"

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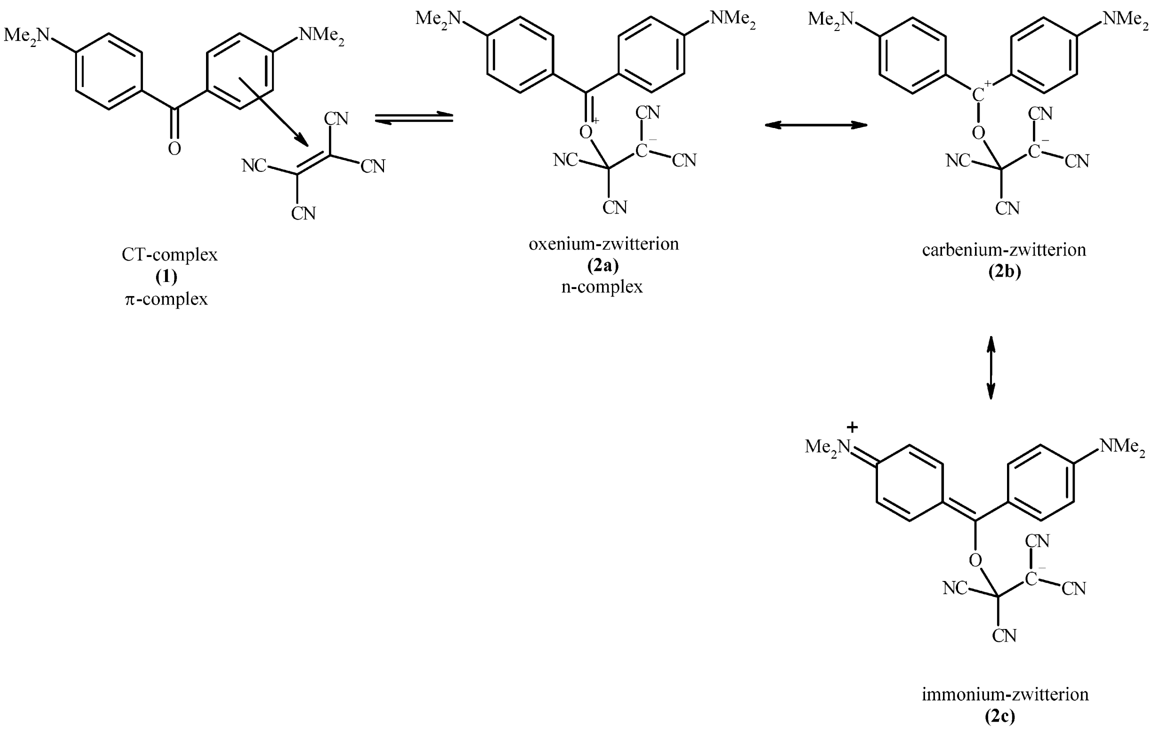
SCHEME 1. MK−TCNE Complexes in Non-protic and Protic Solvents



EDA complex (**1**), whose absorption maximum is described quantitatively by a multiparameter linear solvation energy (LSE) relationship.[10] In protic solvents, MK reacts with TCNE via the nonbonding electron pair of the carbonyl oxygen atom to give a zwitterionic species (**2**), previously defined as the "*n*-complex" (Scheme 1). Therefore, the solvent is able to switch the charge-transfer complex into the "*n*-complex", and this feature is a peculiarity of the MK−TCNE system. The EDA complex and the "*n*-complex", two species which can coexist in solution, have distinct and easily identifiable absorption bands.

Results and Discussion

Initially, to verify the ability of MK to give a stable species with TCNE in ionic liquids (EDA and/or *n*-complex), equal volumes of solutions of MK (ca. (3−4) × 10^{-2} M) and TCNE ((1.5−5) × 10^{-2} M) were mixed at 25 °C in [bmim][Tf$_2$N]. Despite the fact that ILs polarity is often correlated to that of short chain alcohols, in analogy with the behavior in aprotic molecular solvents, we observed the immediate formation of a colored species, having an absorption maximum around 630 nm (Figure 1, spectrum a).

This species was sufficiently stable to be investigated by conventional spectrophotometric techniques. Spectral data were then collected at 25 °C in the 450−900 nm wavelength range working at 3 × 10^{-2} M MK and 10^{-2} M TCNE. The absorbances of the new band increased almost linearly when the ketone concentration was increased up to higher values (ca.10^{-1} M), at constant TCNE concentration, as well as when TCNE was increased at constant MK concentration, pointing to the formation of a 1:1 stoichiometry EDA complex. The formation constant and the molar extinction coefficient at the absorption maximum evaluated by means of the Scott method[11] were K_c = 5.6 (0.5) M^{-1} and ϵ_{max} = 175.9 M^{-1} cm^{-1}, respectively. A value of K_c = 7.5 (0.5) M^{-1} has been reported[10] for the same complex in the moderately polar 1,2-dichloroethane. Since the formation constants of the EDA complexes generally decrease with increasing solvent polarity,[12] as a consequence of the difference between the solvation energy of the complex and of its components, the data reported above suggest a slightly more polar character of [bmim][Tf$_2$N] with respect to 1,2-dichloroethane.

To evaluate the effect of ILs solvent properties on the absorption maximum of the EDA complex, both hydrophilic and hydrophobic ILs have been tested. The values measured in several ILs and in their 1:1 binary mixtures are reported in Table 1, where the charge-transfer absorption maxima measured[10] in molecular solvents and the solvent parameters used in the correlation analysis are also tabulated. The values of E_T^N, α, β, and π* for pure ionic liquids and their 1:1 mixtures were obtained using a single set of dyes: Reichardt's dye, 4-nitroaniline, and *N*,*N*-diethyl-4-nitroaniline. It is worth noting that, using [bmim][BF$_4$] and [emim][EtSO$_4$] as solvents, the typical absorption band of the MK−TCNE EDA complex was not detected: this behavior has been attributed to the residue water

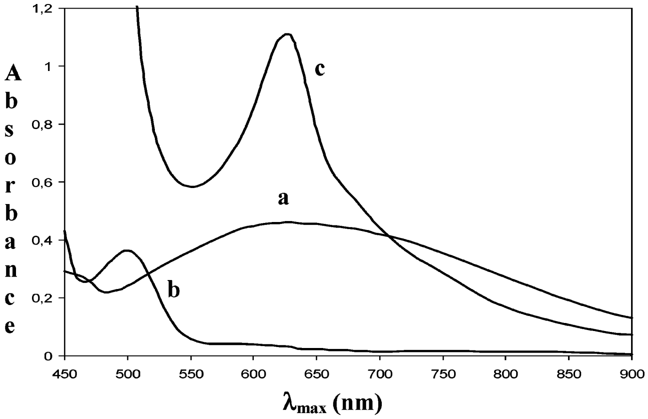


Figure 1. (a) Typical UV−vis absorption spectrum of the MK−TCNE EDA complex in aprotic solvent or ILs (in this case, [hmim][Tf$_2$N]); (b) UV−vis absorption spectrum of the MK−TCNE "*n*-complex" in water; (c) UV−vis absorption spectrum of the mixture of the MK−TCNE "*n*-complex" and MK$^{+\bullet}$TCNE$^{-\bullet}$ in trifluoroethanol.

TABLE 1: Charge-transfer UV−vis Absorption Maxima of the MK−TCNE Complex Measured in Ionic Liquids and in Nonprotic Molecular Solvents and the Solvent Parameters Used in the Correlation Analysis

solvent	$\nu_{\max,CT} \times 10^{-3}$	E_T^N	π^*	β	α
1,1,2,2-tetrachloroethane	14.30		0.95	0.00	0.00
dichloromethane	14.87	0.309	0.82	0.10	0.13
nitrobenzene	15.05	0.324	1.01	0.30	0.00
acetonitrile	15.64	0.460	0.75	0.40	0.19
1,1,1-trichloroethane	15.72	0.170	0.49	0.00	0.00
benzene	15.80	0.111	0.59	0.10	0.00
acetophenone	15.84	0.306	0.90	0.49	0.04
toluene	16.12	0.099	0.54	0.11	0.00
1,4-dioxane	16.32	0.164	0.55	0.37	0.00
cyclohexanone	16.44	0.281	0.76	0.53	0.00
DMSO	16.69	0.444	1.00	0.76	0.00
ethyl acetate	16.80	0.228	0.55	0.45	0.00
tetrahydrofuran	16.92	0.207	0.58	0.55	0.00
[emim][Tf_2N]	15.44	0.685	0.980	0.233	0.705
[bmim][Tf_2N]	15.97	0.645	0.971	0.248	0.635
[bmim][PF_6]	15.69	0.675	1.015	0.246	0.654
[hmim][Tf_2N]	15.62	0.653	0.971	0.259	0.650
[bpy][Tf_2N]	15.45	0.613	1.009	0.214	0.539
[hmim][Tf_2N]-[BPy][Tf_2N] (1:1)	15.7	0.625	0,98	0.273	0.587
[hmim][Tf_2N]-[bmim][Tf_2N] (1:1)	15.50	0.652	0.977	0.269	0.644
[hmim][Tf_2N]-[bmim][PF_6] (1:1)	15.87	0.678	0.990	0.262	0.683
[bmim][PF_6]-[BPy][Tf_2N] (1:1)	16.04	0.653	1.025	0.214	0.604
[bmim][Tf_2N]-[BPy][Tf_2N] (1:1)	15.52	0.675	1.041	0.250	0.624
[bmim][PF_6]-[bmim][Tf_2N] (1:1)	15.90	0.669	0.994	0.247	0.662
[bmim][$N(CN)_2$]	n.d.	0.629	1.129	0.708	0.464

present in the ionic solvent even after prolonged drying procedures. Similarly, the formation of the EDA complex was suppressed in ionic liquids bearing highly donor anions, such as [bmim][$N(CN)_2$] ($\beta = 0.708$): in this latter medium, the mixing of the two reagents yielded an unidentified species, characterized by a strong absorption below 250 nm. This behavior was observed previously only in strong donor solvents (DMSO or DMF) able to give competing reactions with the acceptor component of the complex. The data reported in Table 1 clearly show that [bmim][$N(CN)_2$] has a value of H-bond basicity (β) very close to those of DMSO and DMF, thus supporting a similar reactivity. Finally, in agreement with the behavior characterizing aprotic polar molecular solvents, charge-transfer MK−TCNE EDA complex **1** was observed in all the used hydrophobic non-nucleophilic ILs and the absorption maximum depended on the medium properties. Data collected so far clearly reveal that, although the bathochromic band shift observed for the MK−TCNE complex in molecular solvents ranged from 17 260 cm^{-1} (trimethyl phosphate) to 14 300 cm^{-1} (1,1,2,2-tetrachloroethane), the shift characterizing ILs varies in a more limited interval, from 15 440 to 16 040 cm^{-1}.

Multiple correlation analyses of the charge-transfer (CT) band maxima with various empirical solvent parameters were carried out including both molecular solvents and ILs. In nonprotic molecular solvents, $\nu_{\max,CT}$ of the EDA complex has been described[10] quantitatively by a multiple LSE relationship (eq 1), using the Kamlet−Taft dipolarity/polarizability (π^*) and basicity (β) parameters of the solvents.

$$\nu_{\max} \times 10^{-3} = 16.667 + 3.028\beta - 2.426\pi^* \ (r^2 = 0.93) \quad (1)$$

The respective influences of the β and π^* terms of the solvent are opposite; an increase in dipolarity/polarizability (π^*) causes a bathochromic shift due to a stronger solvation of the larger dipolar and more polarizable excited state ($D^{+\bullet}A^{-\bullet}$) of the EDA complex, whereas the hypsochromic shift of the CT band upon increasing the Lewis basicity of the solvents, as measured by the β parameter, suggests a specific solvation of the electronic ground state of the EDA complex. However, this equation was not suitable to explain sufficiently the solvatochromism of the MK−TCNE complex when ILs have also been included; see eq 2 and Figure 2.

$$\nu_{\max} \times 10^{-3} = 16.110 + 2.561\beta - 1.260\pi^* \ (r^2 = 0.737) \quad (2)$$

All the examined ILs and their mixtures pointed out the correlation together with three molecular solvents (toluene, benzene, and 1,1,1-trichloroethane).

Improved results have been obtained using a multiple correlation according to eq 3, which also includes the Kamlet−Taft α parameter (Figure 3). All ILs are clustered about a narrow range of values of $\nu_{\max,CT}$, and the high correlation coefficient is to be attributed largely to the molecular solvents. However, it is to note that, with the sole exception of a mixture of ILs,

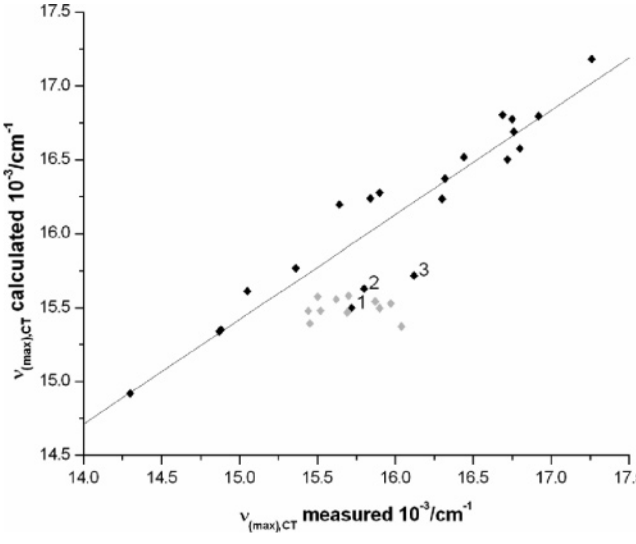


Figure 2. Comparison between the values of $\nu_{\max}$ calculated using eq 2 and the experimental values: black points, molecular solvents; gray points, ILs and their mixtures. (1 = 1,1,1-trichloroethane; 2 = benzene; 3 = toluene).

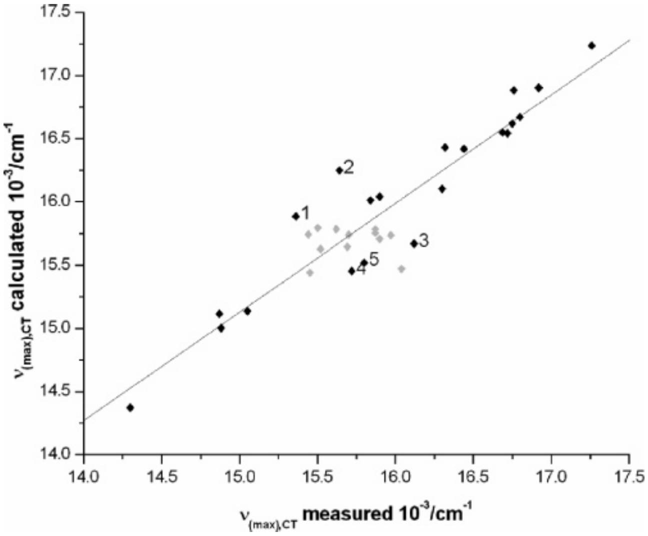


Figure 3. Comparison between the values of ν_{max} calculated from eq 3 and the experimental values: black points, molecular solvents; gray points, ILs and their mixtures. (1 = 1,2-dichloroethane; 2 = acetonitrile; 3 = toluene; 4 = 1,1,1-trichloroethane; 5 = benzene)

the scatter in the values of $\nu_{max,CT}$ characterizing the ionic solvents from the correlation straight line is lower than that found for several molecular solvents (1,2-dichloroethane, 1,1,1-trichloroethane, acetonitrile, benzene, and toluene), both using eqs 3 or 2. Moreover, it is interesting that the terms π^* and β

$$\nu_{max} \times 10^{-3} = 16.605 + 3.018\beta - 2.351\pi^* + 1.043\alpha \ (r^2 = 0.859) \quad (3)$$

(eq 3) have coefficients very similar to those obtained in the absence of ILs, using eq 2, whereas the term α is characterized by a positive coefficient indicating that the increase of this term determines an hypsochromic shift of the charge-transfer band. This behavior can be attributed at the specific solvation of the electronic ground state of the EDA complex. Although the H-bond acidity of ionic liquids is not sufficient to determine the transformation of the EDA complex into the corresponding "*n*-complex", **2**, evidencing significant differences between these new solvents and alcohols, the hydrogen bond donating ability, as expressed by the Kamlet−Taft α parameter, seems to be able to affect the spectral position of the charge-transfer absorption band of the EDA complex, **1**.

Finally, it is worthy to note that, although it was possible to observe the EDA complex **1** using a conventional UV−vis spectrophotometer, the stability of this species in ILs is limited in time. The absorption spectra of **1** in ionic media decayed slowly on the hours time scale. The first-order decay of the charge-transfer band of the EDA complex occurs simultaneously with the first-order growth of another narrow absorption band centered at 630 nm, which has been assigned to the radical ion-pair salt ($MK^{+\bullet}TCNE^{\bullet-}$), by comparison with literature data.[10]

The immediate and exclusive formation of this radical ion pair salt was previously observed in 1,1,1,3,3,3-hexafluoropropanol (HFI), that is, in an extremely polar solvent having a high ionizing power. These properties were considered responsible for the formation and stabilization of the radical cation. In the less polar and ionizing trifluoroethanol (TFE), MK and TCNE yield a mixture of both "*n*-complex" and $MK^{+\bullet}TCNE^{-\bullet}$ (Figure 1c), whereas formation of the sole MK−TCNE "*n*-complex" can be detected in protic solvents or in water (Figure 1b). Considering the different species which may be present in solution on changing molecular solvents properties, it is evident that ILs differ both from aprotic and from protic molecular solvents. In analogy with aprotic molecular solvents, at least the investigated ILs give a sufficiently stable MK−TCNE EDA complex; the moderate H-bond acidity is not sufficient to determine the transformation of EDA complex **1** into *n*-complex **2**. On the other hand, the higher ionizing power of ILs with respect aprotic molecular solvents favors the slow but progressive transformation of this complex into the radical ion pair salt, $MK^{+\bullet}TCNE^{-\bullet}$.

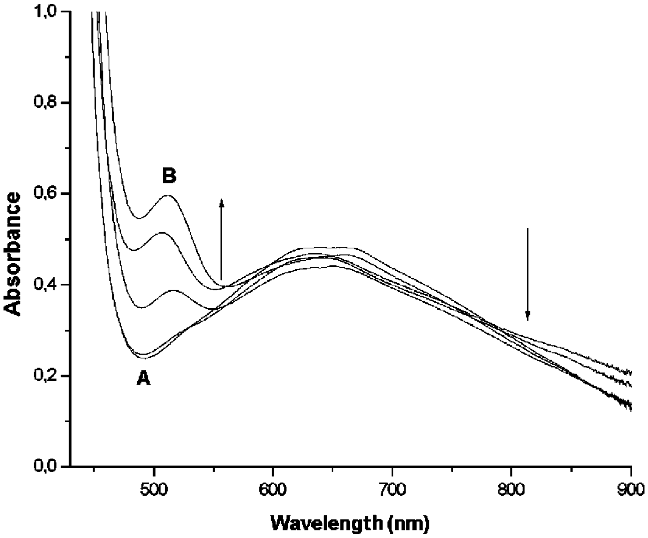


Figure 4. UV−vis absorption spectra series of the MK−TCNE complex in [bpy][Tf$_2$N] as obtained with successive additions of water: (A) before water addition and (B) in the presence of the highest water amount.

The formation and the possibility of detection of the MK−TCNE EDA complex in ionic liquids are moreover strictly related to the purity level of the medium. The presence of small amounts of water or of nucleophilic impurities (halides, amines) determines drastic changes in UV−vis absorptions of MK−TCNE solutions. Moreover, the addition of water causes the decrease of the characteristic CT band of the EDA complex and the simultaneous appearance of a new absorption band at 500 nm. The color of the solution progressively changes from bright-blue to brownish. Water is able to convert (partially or completely) the EDA MK−TCNE complex into the corresponding "*n*-complex" both in molecular solvents and in ILs (Figure 4).

Identical spectra series, characterized by an isosbetic point at 530 nm (Figure 5), can be obtained by titration of MK−TCNE complex **1** in acetonitrile with water. In this case, a simple equation has been found to correlate the absorption at 530 nm with water concentration.

$$A_{\lambda max} = 7.788\sqrt{[H_2O]} + 0.0829 \ (r = 0.9936) \quad (4)$$

Although the similarity of the behavior observed after water addition in ILs and acetonitrile (Figure 4) should suggest the possibility of using the same correlation in both media, the low solubility of water in the ionic media determines the formation of microemulsions, thus preventing the possibility to apply this procedure to quantify the residue water. Apart from that drawback, when using the MK−TCNE EDA complex as a "purity" probe, the immediate appearance of a shoulder around 500 nm is a clear sign of a nonefficient drying of the IL (a water amount greater than 0.2 mg in 2 g of solvent, >100 ppm, may be detected).

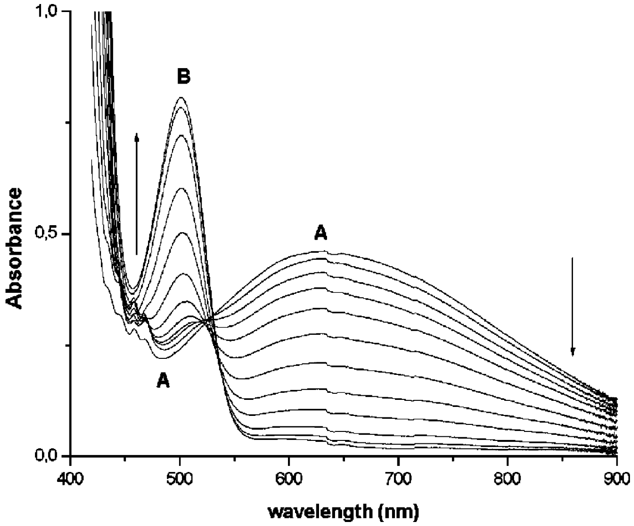


Figure 5. UV−vis absorption spectra series of the MK−TCNE complex in acetonitrile as obtained with successive additions of water: (A) before water addition and (B) in the presence of the highest water amount.

The sensitivity of the complex to the other mentioned impurities is higher. Preliminary experiments have shown that the addition of amines (1-methylimidazole or pyridine, 0.3 mg in 1 g of solvent are sufficient to destroy the complex) produces the immediate change of the color from blue to red. On the other hand, even smaller amounts of chloride ions ([bmim][Cl] around 0.005 mg in 1 g of solvent, 5 ppm) are sufficient to determine the instantaneous disappearance of the charge-transfer band of complex **1** and the solution to turn from blue to yellow. The drastic effect of chloride on complex formation fits with recent reported[13] data showing a higher nucleophilicity of this anion in imidazolium-based ionic liquids, compared with water, which has been associated with the lower solvation enthalpy of chloride in this type of solvent.

Conclusions

Michler's ketone (MK) and tetracyanoethene (TCNE) may be used as a simple UV−vis probe to investigate ionic liquids (ILs) solvents properties. MK and TCNE give in ILs, with $\beta <$ 0.7, the corresponding EDA complex, characterized by a formation constant very close to that measured in 1,2-dichloroethane, 5.6 (0.5) M^{-1} at 25 °C in [bmim][Tf_2N]. The visible absorption maxima of the charge-transfer band of the EDA complex correlate well with the Kamlet−Taft π^*, β, and α parameters of the solvents. The H-bond acidity of ILs is not sufficient to determine the transformation of the EDA complex into the zwitterionic species, **2**, although the hydrogen bond donating ability, as expressed by the Kamlet−Taft α parameter, seems to be able to affect the spectral position of the charge-transfer absorption band of the EDA complex, **1**. The study of the evolution of the EDA complex in ILs, moreover, shows that these solvents favor the slow transformation of the complex into its corresponding radical ion pair ($MK^{+\bullet}TCNE^{-\bullet}$), evidencing a behavior which generally characterizes high polar and highly ionizing protic solvents, such as TFE and HFI. Finally, since the formation of the EDA complex is strongly affected by the presence of impurities, **1** may be used as a probe to detect traces of nucleophiles (chloride or amines) or the presence of water, through the color change of the solution or by UV−vis measurements.

Experimental Section

TCNE was sublimed under reduced pressure before use. MK was recrystallized twice from ethanol and dried carefully over CaH_2. ILs [bmim][PF_6], [emim][Tf_2N], [bmim][Tf_2N], [hmim]-[Tf_2N], [omim][Tf_2N], and [BuPy][Tf_2N] were prepared, purified, and dried as previously reported.[5b] The dyes (Reichardt's dye, 4-nitroaniline, and *N*,*N*-diethyl-4-nitroaniline) were used as supplied.

UV−vis Measurements. The UV−vis absorption spectra were recorded on a Cary 2300 spectrophotometer. In a typical experiment, MK and TNCE were dissolved in pure solvent and the spectrum was immediately recorded as a function of time, after mixing of the component in the reaction vessel. The concentration of MK was around 2×10^{-2} M and that of TNCE around 1×10^{-2} M.

Determination of the Formation Constant of the EDA Complex. For the determination of the complex formation constant, solutions of MK and TCNE in the chosen IL were prepared by weighing the reagents in accurately calibrated volumetric flasks. Working-strength solutions were prepared by mixing solvent and aliquots of the reagent stock solutions withdrawn with precision microburets and weighting after each addition. The UV spectra were registered at 25 °C in 1 or 0.1 cm cells in the 450−900 nm range. The Scott equation was applied to fit the spectrophotometric data.

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