JOC The Journal of Organic Chemistry

Article

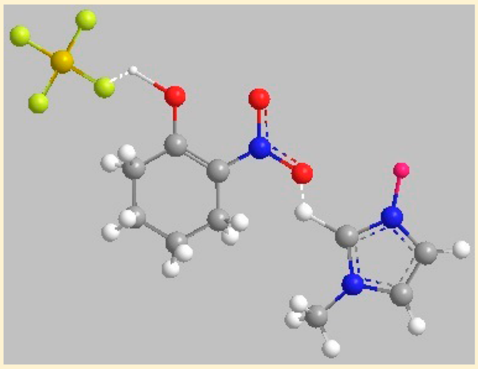
pubs.acs.org/joc

Thermodynamic Analysis of Anion and Cation Effects on the Keto–Enol Equilibrium in Ionic Liquids. A Comparative Study with Conventional Solvents

Romina Zappacosta, Antonello Di Crescenzo, Pietro Di Profio, Antonella Fontana, and Gabriella Siani*

Dipartimento di Farmacia, Università “G. d’Annunzio”, Via dei Vestini 31, Chieti, Italy

ABSTRACT: A comparative thermodynamic investigation of the keto–enol interconversion reaction has been performed in several organic solvents and room-temperature ionic liquids (RTILs) to evaluate the role of the solvent and the effect of the ionic composition of RTILs. The tautomeric constant (K_T) values at different temperatures have been analyzed in terms of the van't Hoff relationship to give the relevant thermodynamic parameters. The $\Delta G°$ values are the results of quite different combinations of the $\Delta H°$ and $\Delta S°$ values depending on the nature of the solvent. As expected, in conventional solvents, the tautomeric equilibrium is enthalpically disfavored and entropically favored by the increase in solvent polarity. In ionic liquids, the nature of the anion seems to play a primary role in the thermodynamics of the reaction that is endothermic and enthalpically driven in PF_6- and TF_2N-based RTILs and exothermic but entropically driven in BF_4-based RTILs. The cation effect on the thermodynamics of the reaction is more complex and is consistent with a prevalence of the alkyl side chain segregation in the organization of the ILs.



INTRODUCTION

Organic reactions are commonly conducted in solution so that the choice of the “best” solvent is crucial for a reaction to occur successfully. Indeed, solvents can interact with substrates, intermediates, and/or transition states, strongly influencing the thermodynamics of a reaction, changing the position of the equilibrium, and its kinetics, changing the reaction rate constant.[1] For a molecular solvent, the effect on organic reactivity is related to its “polarity”, generally expressed by the permittivity value, ε, even if this single macroscopic physical parameter is often inadequate as it does not take into account all the specific and nonspecific solute–solvent interactions at the molecular level.

In the past several decades, room-temperature ionic liquids (RTILs) have gained considerable and widespread attention because of their peculiar properties, such as good thermal stability, low volatility, and low flammability, and they have been proposed as “green” alternative reaction media to conventional organic solvents for many organic reactions.[2] By definition, RTILs are compounds constituted solely by cations and anions that melt below 25 °C. The most important feature of RTILs is their versatility arising from the fact that their physicochemical properties could be fine-tuned simply by combining different cations and/or anions so that the best RTIL for a specific application could be “designed”. To choose the best combination of cation and anion, it is important to understand how the ionic constituents of RTILs might interact with the reagents, the intermediates (or transition states), and the products of a reaction. Indeed, RTILs offer unusual solvation environments to potential solutes, in which Coulombic, van der Waals, and hydrogen bonding interactions could greatly affect solvation processes and reactivity.[3−5] For ionic liquids, the determination of polarity is very difficult, and a number of polarity scales have been developed by using solvatochromic dyes.[6] However, a single probe molecule cannot take into account all the possible, nonspecific and specific interactions between the solute and the solvent molecules. Several parameters, such as hydrogen bond acidity (α), hydrogen bond basicity (β), polarity/polarizability (π^*), and cohesive pressure (δ^2), have to be considered to correlate and predict experimental data such as rate and equilibrium constants by applying the classical Abboud–Kamlet–Taft multiparametric approach.[7]

Moreover, RTILs can organize themselves into polar domains of cations and anions, connected by hydrogen bonds, and nonpolar domains, because of the alkyl side chains that are excluded from the charged network.[8] The degree of order may also influence solvation and organic reactivity by ordering the reactants.[9,10]

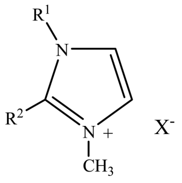
In a previous paper,[11] we have shown that the keto–enol interconversion of 2-nitrocyclohexanone (2-NCH) is a suitable probe reaction for investigating the complexity of the effects of RTILs at the molecular level.

The keto–enol interconversion of carbonyl compounds is one of the most studied reactions in terms of solvent effects.[12] In particular, α-nitroketones represent an interesting class of carbonyl compounds as they are characterized by high acidities

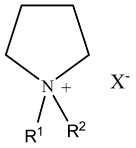
Received: December 22, 2014
Published: January 23, 2015

DOI: 10.1021/jo502898s
J. Org. Chem. 2015, 80, 2333−2338

Scheme 1. Structures of the Investigated RTILs



BMIM PF_6	$R^1 = C_4H_9$	$R^2 = H$	$X^- = PF_6^-$
EMIM TF_2N	$R^1 = C_2H_5$	$R^2 = H$	$X^- = TF_2N^-$
BMIM TF_2N	$R^1 = C_4H_9$	$R^2 = H$	$X^- = TF_2N^-$
BM_2IM TF_2N	$R^1 = C_4H_9$	$R^2 = CH_3$	$X^- = TF_2N^-$
OMIM TF_2N	$R^1 = C_8H_{17}$	$R^2 = H$	$X^- = TF_2N^-$
BMIM BF_4	$R^1 = C_4H_9$	$R^2 = H$	$X^- = BF_4^-$
HMIM BF_4	$R^1 = C_6H_{13}$	$R^2 = H$	$X^- = BF_4^-$
OMIM BF_4	$R^1 = C_8H_{17}$	$R^2 = H$	$X^- = BF_4^-$
DMIM BF_4	$R^1 = C_{10}H_{19}$	$R^2 = H$	$X^- = BF_4^-$
BMPyrr TF_2N	$R^1 = CH_3$	$R^2 = C_4H_9$	$X^- = TF_2N^-$



and relatively high enol contents,[13] which can be directly measured by different techniques (NMR and UV spectroscopy).

In RTILs, the tautomeric interconversion reaction proceeds faster than in conventional solvents, even if no special "ionic liquid effect" can be evidenced as one comprehensive linear solvation energy relationship for both organic solvent and RTILs can be obtained if different solvent parameters are considered.[14] The rate acceleration on changing from molecular solvents to RTILs has been ascribed to the stabilization of the enolate-like transition state in RTILs.

The kinetics of a number of other common organic reactions have been extensively studied in RTILs, such as Diels–Alder cycloadditions,[15] nucleophilic substitutions,[16,17] and electrophilic additions.[18]

In spite of the fact that the investigation of the influence of ionic liquids upon chemical kinetics has been the topic of much interest, quantitative studies of chemical equilibria in RTILs are scarce.

We have measured the equilibrium constants at 25 °C for the keto–enol interconversion of 2-nitrocyclohexanone (2-NCH) in water,[19] some organic solvents, and ionic liquids.[11] The tautomeric equilibrium is displaced toward the keto form upon transfer from apolar organic solvents to RTILs as the cavitational and nonspecific electrostatic effects that stabilize the ketone overwhelm the specific electrostatic contributions that stabilize the enol.

This work aims to provide insight into the investigation on the effect of RTILs on the concentration of solutes in equilibrium. In particular, we have determined the tautomeric equilibrium constants for 2-NCH in some RTILs at different temperatures to separate the thermodynamic parameters, $\Delta G°$, $\Delta H°$, and $\Delta S°$, for the reaction. The results are compared with those obtained in some conventional organic solvents, and the influence of the ionic composition of the ionic liquids is discussed.

■ RESULTS AND DISCUSSION

The position of a chemical equilibrium is determined by the Gibbs free energy change of the reaction according to eq 1

$$\Delta G = -RT \ln K \tag{1}$$

Because ΔG is sensitive to the solute–solvent interactions, which, in turn, depend on the nature of the solvent, the relative concentrations of reagents and products at equilibrium change when the solvent is changed.

The values of the equilibrium constant (K_T = [EH]/[KH]) for the keto–enol interconversion of 2-NCH, a general base-catalyzed reaction that can be conveniently investigated by UV–vis spectroscopy, have been determined in pure organic solvents (C_6H_{12}, CCl_4, $CHCl_3$, and CH_3CN) and solvent mixtures, spanning a wide range (from 2 to 35.9) of permittivity values, ε.

K_T values have also been measured in some RTILs as reported in Scheme 1.

The UV–vis spectrum of a 1×10^{-4} M solution of 2-NCH in each investigated solvent, registered immediately after dissolution, is characterized by two absorption maxima, one at higher wavelengths (319–330 nm, depending on the solvent) and the other at lower wavelengths (~205 nm), which can be attributed to the enol and keto forms, respectively.

As time elapses, the intensity of one of the bands increases (or decreases) whereas that of the other band decreases (or increases) until the equilibrium is reached. The absorption spectra of a 1×10^{-4} M solution of 2-NCH in the ionic liquid EMIM TF_2N, registered at different times, are reported in Figure 1 as an example. The decrease in the intensity of the absorption band at 332 nm is due to the ketonization reaction of the enol form.

The attainment of equilibrium is accelerated when triethylamine is used as the basic catalyst.

Spectrophotometric equilibrium constants, K_T^x, in the different solvents have been calculated from eq 2.

$$K_T^x = \frac{1}{\frac{[\text{2-NCH}]a_x^{EH}}{A_x^{eq}} - 1} \tag{2}$$

where A_x^{eq} is the absorbance of EH at equilibrium and the molar absorptivity of the enol form, EH, in solvent x, a_x^{EH}, has been calculated as reported in the Experimental Section. K_T values determined in each solvent at 25 °C are listed in Table 1.

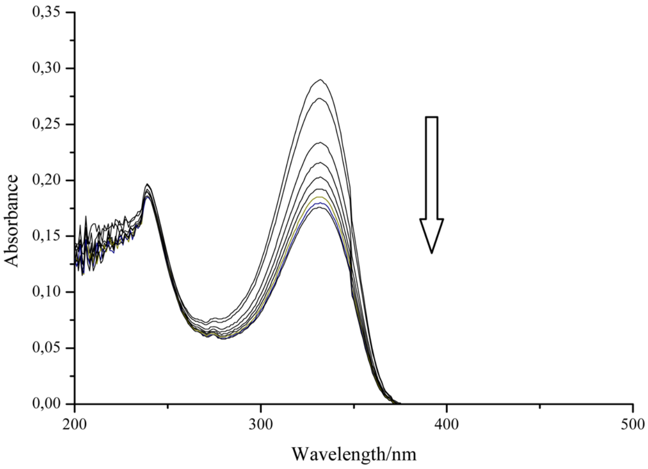


Figure 1. Absorption spectra of a 1×10^{-4} M solution of 2-NCH in the ionic liquid EMIM TF_2N, registered at different times.

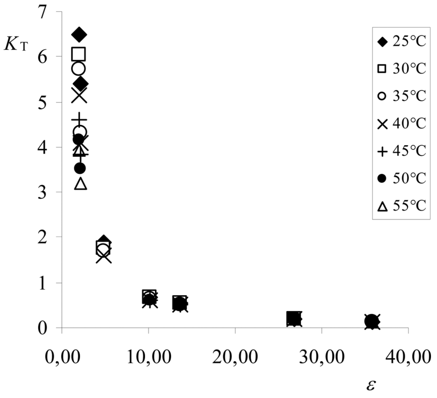


Figure 2. Dependence of K_T on the permittivity of the solvent, at each temperature.

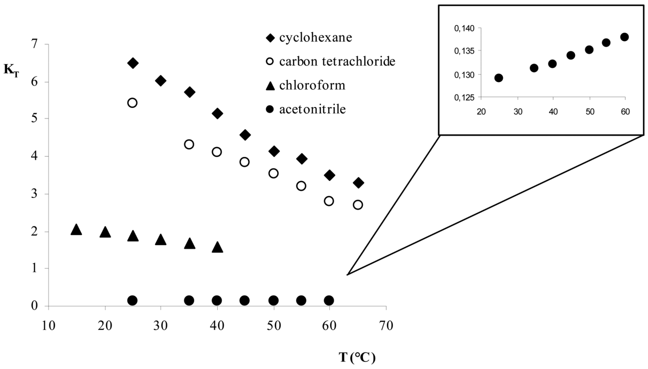


Figure 3. Effect of temperature on the K_T values calculated in organic molecular solvents.

Thermodynamics of the Keto–Enol Interconversion in Molecular Organic Solvents. As expected, the enol tautomer of 2-NCH is favored in aprotic solvents while the keto tautomer, which has a higher dipole moment, is favored in polar solvents. Indeed, a good correlation exists between K_T and the solvent permittivity, ε, at each temperature, K_T, becoming unitary at an ε of ~8 (Figure 2).

The K_T variations, as a function of temperature, appear to be much more marked in the less polar solvents and almost negligible in acetonitrile where, however, this variation is in the sense of an increase, albeit minimal, with an increase in temperature (Figure 3).

The keto–enol interconversion reaction of 2-NCH has been investigated in the temperature range of 25–60 °C except in chloroform (15 °C $\leq T \leq$ 40 °C).

$\Delta G°$ values have been calculated from the K_T values at different temperatures according to eq 1. $\Delta H°$ and $-\Delta S°$ values can be determined as the slope and intercept, respectively, of a plot of $\Delta G°/T$ versus $1/T$. The free energy variations at 25 °C, enthalpies, and entropies calculated in the different solvents are listed in Table 1. $\Delta H°$ and $\Delta S°$ values cannot be calculated for the reaction in the ionic liquid OMIM TF_2N for which only the K_T value at 25 °C has been obtained.

In molecular solvents, as expected, the tautomeric equilibrium is enthalpically disfavored and entropically favored by the increase in the permittivity of the solvent. This is consistent

Table 1. K_T Values (at 25°C) for the Keto–Enol Interconversion of 2-NCH and Calculated Free Energy Variations (at 25 °C), Enthalpies, and Entropies in Different Solvents[a]

solvent	ε	β	δ	K_T(25 °C)	$\Delta G°$(25 °C)	$\Delta H°$	$T\Delta S°$
C_6H_{12}	2	0.000	8.20	6.49	−1.108	−3.540	−2.415
CCl_4	2.2	0.100	8.60	5.41	−1.000	−3.500	−2.504
$CHCl_3$	4.8	0.100	9.30	1.88	−0.374	−1.877	−1.521
78:22 $CHCl_3/CH_3CN$	10.1	0.166	9.85	0.680	0.225	−1.032	−1.252
65:35 $CHCl_3/CH_3CN$	13.6	0.205	10.18	0.536	0.370	−0.359	−0.716
25:75 $CHCl_3/CH_3CN$	26.8	0.377	11.18	0.183	1.006	0.386	−0.626
CH_3CN	35.9	0.400	11.80	0.129	1.213	0.390	−0.835
BMIM PF_6	11.9	0.207	12.88	0.097	1.382	3.340	1.968
EMIM TF_2N	19.2	0.280	12.00	0.129	1.213	0.506	−0.716
BMIM TF_2N	25.6	0.243	11.51	0.157	1.097	0.649	−0.239
OMIM TF_2N	15.6	0.280	12.03	0.128	1.218		
BM_2IM TF_2N	18.0	0.239	12.09	0.125	1.232	1.871	0.656
BMPyrr TF_2N	24.6	0.370	11.32	0.171	1.046	0.768	−0.268
BMIM BF_4	33.7	0.376	11.70	0.145	1.144	−1.717	−2.594
HMIM BF_4	34.5	0.414	11.06	0.194	0.972	−1.218	−2.176
OMIM BF_4	30.3	0.435	10.62	0.250	0.821	−0.508	−1.342
DMIM BF_4	27.1	0.451	10.33	0.309	0.696	−0.611	−1.312

[a] $\Delta G°$ and $\Delta H°$ are expressed in kilocalories per mole. The ε, β, and δ parameters of the solvents are also reported.

DOI: 10.1021/jo502898s
J. Org. Chem. 2015, 80, 2333–2338

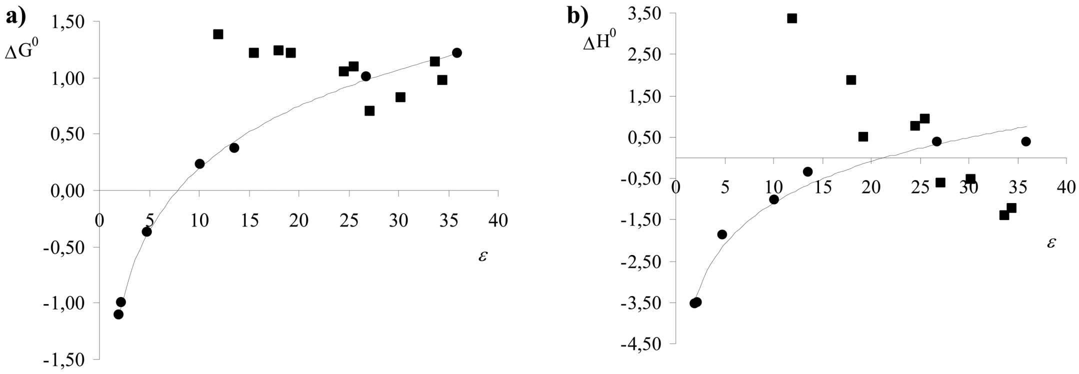


Figure 4. (a) Plot of $\Delta G°$ vs ε and (b) plot of $\Delta H°$ vs ε for the tautomerization reaction of 2-NCH in organic solvents (●) and RTILs (■).

with a more efficient solvation of the keto form by more polar solvents and a higher level of organization of the solvent molecules around the keto with respect to the enol tautomer.

Good correlations were found by simply plotting $\Delta G°$ or $\Delta H°$ values against the solvent permittivity, ε (Figure 4). From Figure 4b, it can be evinced that at an ε of ≈20 the reaction turns from exoergonic to endoergonic.

The relative contributions of $\Delta H°$ and $T\Delta S°$ to $\Delta G°$, calculated on a percentage basis, show that in the molecular solvents the contribution of $\Delta H°$ decreases with increasing permittivity up to an ε of ~15 (Figure 5). On the other hand, the contribution of $T\Delta S°$ increases in the same range of ε values. The $\Delta H°$ contribution prevails in the less polar solvents, while the $T\Delta S°$ contribution becomes predominant in the more polar solvents.

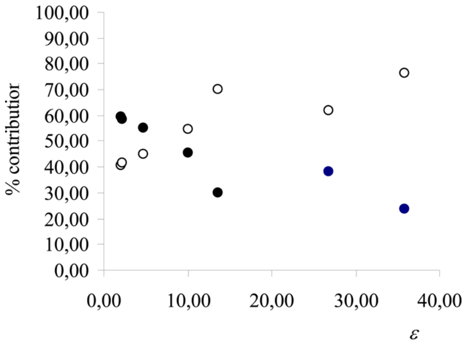


Figure 5. Percent contribution of $\Delta H°$ (●) and $T\Delta S°$ (○) to $\Delta G°$ for the tautomerization reaction of 2-NCH in solvents with different permittivities, ε.

Thermodynamics of the Keto–Enol Interconversion in Ionic Liquids. The attempt to include the ionic liquids in the same correlations obtained for organic molecular solvents fails (Figure 4). However, via insertion of the new data into the previously described[11] multiparameter equation (eq 3), a good correlation between the calculated and experimental $\Delta G°$ values is obtained (Figure 6)

$$\Delta G^{\circ}_{x} = \Delta G^{\circ}_{gas} + a\delta^2 + bF(\varepsilon) + cT_N \qquad (3)$$

This supports the reliability of the multiparameter approach we have previously developed and confirms that no special "ionic liquid effect" could be evidenced if other parameters, besides the permittivity of the solvent, are taken into account.

Effect of Changing the RTIL Anion. To investigate how changing the anion can affect the position of the tautomeric equilibrium, the values of $\Delta H°$ and $T\Delta S°$ (Table 1) obtained for the reaction in the three ionic liquids (BMIM PF_6, BMIM TF_2N, and BMIM BF_4) have been considered as a function of anion type.

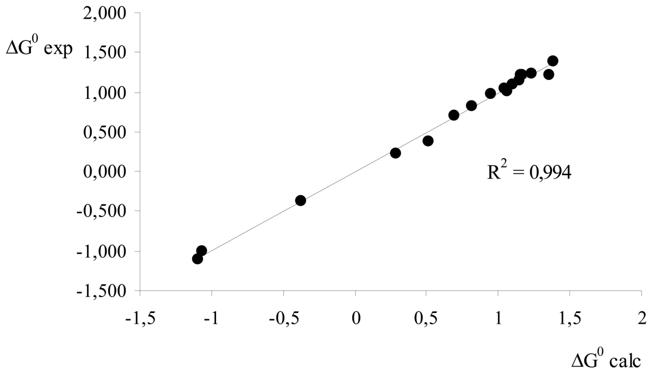


Figure 6. Comparison between the values of $\Delta G°$ calculated from eq 3 ($\Delta G°_{calc}$) and the experimental values ($\Delta G°_{exp}$).

Indeed, as the three RTILs contain the same $BMIM^+$ cation, clearly changing the anion is the cause of any observed effects.

The three anions mainly affect the ionic liquid basicity, quantitatively expressed by the value of the solvent parameter β. It is reasonable to suppose that the greater the ability of the anion to act as an H-bond acceptor, the greater the stabilization of the enol form (H-bond donor) through H-bond formation. This is supported by the finding that in the most basic BMIM BF_4 ($\beta = 0.376$) the reaction has a favorable enthalpy (negative value of $\Delta H°$) while it is endothermic in the other two ionic liquids with the highest $\Delta H°$ value in the least basic, BMIM PF_6 ($\beta = 0.207$). Indeed, this hypothesis is consistent with the results obtained by Wang et al.,[20] who reported for water the formation of dimer with BF_4^- anion via H–O–H···BF_4···H–O–H, but they did not find stable complexes for PF_6^- anion with water molecules.

The BF_4 anion, which has coordination ability that is better than that of the charge-diffused and weakly coordinating TF_2N and PF_6 anions, acting as a good H-bond acceptor, stabilizes the enol form rather than the keto form. An opposite trend is observed for entropy changes with $T\Delta S°$ values decreasing in the following order: $PF_6 > TF_2N > BF_4$. The increase in the degree of order of the system, because of the higher level of organization around the enol form than around the keto form, could be responsible of the unfavorable entropy change on going from a less basic to a more basic RTIL.

The relative contributions of $\Delta H°$ and $T\Delta S°$ to $\Delta G°$ show that in BMIM PF_6 and in the TF_2N-based ILs the contribution of $\Delta H°$ prevails versus the contribution of $T\Delta S°$ to $\Delta G°$ except when $EMIM^+$ is the cation, while in BF_4-based ILs, the solvent effect is predominantly entropic in origin [the entropic contribution always overwhelms the enthalpic contribution to $\Delta G°$ (see Table 2)].

Table 2. Relative Contributions of $\Delta H°$ and $T\Delta S°$ to $\Delta G°$ Calculated on a Percentage Basis

	%$\Delta H°$	%$T\Delta S°$
BMIM PF_6	62.93	37.07
EMIM TF_2N	41.40	58.60
BMIM TF_2N	86.36	13.64
BM_2IM TF_2N	74.04	25.96
BMPyrr TF_2N	74.10	25.90
BMIM BF_4	35.30	64.70
HMIM BF_4	35.88	64.12
OMIM BF_4	27.85	72.15
DMIM BF_4	31.78	68.22

Contrary to what has been observed in conventional solvents (Figure 5), the contributions of $\Delta H°$ and $T\Delta S°$ are not affected by the ε in ILs.

Effect of Changing the RTIL Cation. For a fixed anion, the change in cation primarily causes a variation of the RTIL acidity. The cation ability to act as an H-bond donor is quantitatively expressed by the solvent parameter α. It has been demonstrated[21] that imidazolium cation can strongly interact with acetone via H-bond formation between the hydrogen at C2 and the carbonyl oxygen, especially in the presence of an anion with dispersed charge and a weak H-bond acceptor character such as TF_2N anion. Instead, solutes like water and alcohols give place to weak interactions with the proton of the imidazolium ring.[22] In analogy with these findings, the keto tautomer can be considered a better H-bond acceptor than the enol so that the lowest K_T value is expected in the most acidic IL and the highest K_T value in the less acidic IL; i.e., the tautomerization reaction would be enthalpically favored and entropically disfavored on passing from BMIM TF_2N (α = 0.617) to BM_2IM TF_2N (α = 0.381) where the replacement of the hydrogen at C2 with a methyl group reduces the cation acidity. Moreover, as the H-bond donor ability of the cation decreases, the strength of the H-bond between the enol form and the anion would increase because of a reduced level of competition between the cation and the enol for H-bonding the anion. However, experimental results in the most acidic BMIM TF_2N (Table 1) do favor the enol form over the keto form. A possible explanation of the unexpected correlation between K_T and the cation acidity could be that, in this specific case, the enol is a push−pull system in which the delocalization of the oxygen lone pair toward the resonance electron acceptor NO_2 group causes the $-NO_2$ to become superbasic in H-bonding. This resonance effect is lacking in the keto tautomer so that H-bond formation between $BMIM^+$ and the super basic $-NO_2$ group stabilizes the enol form more than H-bond formation between $BMIM^+$ and the carbonyl oxygen stabilizes the keto form. The stabilization of the enol through H-bonding is missing in BM_2IM TF_2N. On the other hand, enol is entropically disfavored in BMIM TF_2N because of the higher level of organization of the solvent around the enol than the keto tautomer. However, this explanation is no longer reliable when comparing the $\Delta H°$ values in BMIM TF_2N and BMPyrr TF_2N. The highest enol content was obtained in the latter IL in spite of the fact that $BMPyrr^+$ cation is less able to act as an H-bond donor than $BMIM^+$. This result suggests that even if there is evidence of a specific cation H-bonding effect, it cannot be the only factor responsible for the observed changes, so other contributions have to be considered.

The length of the alkyl side chain linked to the imidazolium cation may also influence the outcome of a reaction. Indeed, the aggregation of the side alkyl chains give rise to nonpolar domains, whose size depends upon the chain length, which is responsible of the structured nature of RTILs.[8,23]

The existence of polar and nonpolar domains influences the solvation of solutes and hence may influence the position of chemical equilibria.

The results obtained for the tautomerization reaction of 2-NCH in the four imidazolium RTILs of the type C_nMIM BF_4 (where n = 4, 6, 8, or 10) showed that $\Delta G°$ values linearly decrease with the increasing length of the alkyl chain of the substituent on the imidazolium ring (Figure 7).

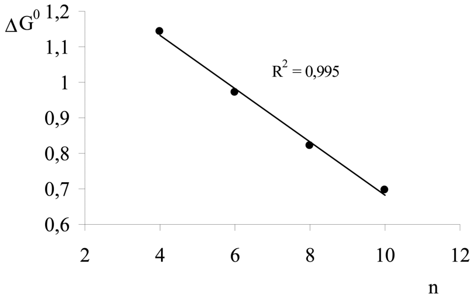


Figure 7. Values of $\Delta G°$ for the tautomeric reaction of 2-NCH in BF_4-based RTILs at 25 °C as a function of the number (n) of carbon atoms in the alkyl side chain of the imidazolium ring.

The analysis of the contribution of $\Delta H°$ and $T\Delta S°$ to $\Delta G°$ revealed that the reaction is enthalpically disfavored and entropically favored up to n = 8. The plateau reached by $\Delta H°$ and $T\Delta S°$ values with a further increase in n could be interpreted as a change in the structuration of ILs as the number of nonpolar domains increases, in agreement with the trend observed for other properties of RTILs such as surface tension,[24] density, and viscosity.[25]

The data obtained suggest that the enol form of 2-NCH interacts not only with the polar but also with the nonpolar domains of the ILs. The energetic price paid to break the van der Waals interactions between the side alkyl chains of the imidazolium ring is more than offset by the entropic reward because of the increase in the degree of disorder of the system, in agreement with the predominantly entropic origin of the solvent effect observed in these RTILs (Table 2).

■ CONCLUSIONS

The thermodynamic analysis of the keto−enol interconversion reaction performed in some conventional media and ionic liquids with different cation−anion combinations has shown that RTILs exhibit behavior different from that of molecular solvents even if, according to our previous report, a comprehensive linear solvation energy relationship (LSER) for both organic and IL media can be obtained when more solvent parameters are taken into consideration. However, $\Delta G°$ values derive from quite different combinations of $\Delta H°$ and $\Delta S°$ values depending on the nature of the solvent. In conventional solvents, as expected, a direct correlation exists between thermodynamic parameters and the solvent polarity expressed in terms of permittivity, ε, and the reaction is enthalpically driven. A different and more complex behavior was detected in RTILs in which the anion seems to dominate the thermodynamics of the reaction with the cation playing a secondary role. Indeed, the strongest H-bond is between the H of the enol hydroxyl group and the anion, while a weaker H-bond exists between the H at C2 of the imidazolium ring and enol and/or ketone. The alkyl chain segregation in the heterogeneous organization of RTILs can also influence the position of the tautomeric equilibrium. Thus, the comprehension of how reactants and products involved in a chemical equilibrium can be coordinated within ionic liquids is fundamental in understanding how these media can influence the outcome of the reaction.

■ EXPERIMENTAL SECTION

Materials. The organic solvents (cyclohexane, carbon tetrachloride, dichloromethane, chloroform, and acetonitrile), 2-nitrocyclohexanone, and trifluoroacetic acid were commercial samples of AnalaR grade and used without further purification. Triethylamine was distilled in the presence of NaOH, and commercial RTILs shown in Scheme 1 were dried for 2 h at 80 °C under vacuum before each experiment.The purity of imidazolium salts was checked by ESI-MS and UV spectrophotometry (purified $[\text{bmim}]^+$ salts containing <0.1 ppm of Cl^- or Br^- have no absorption band in the 250−300 nm region).

Instruments. The UV−vis spectra were recorded with a UV−vis spectrophotometer with a spectral resolution set to 0.333 nm. The spectrophotometer was provided with a thermostated cell holder.

UV/Vis Measurements. The molar absorptivity of the enol form, EH, in solvent x, a_{x}^{EH}, has been calculated from the previously reported equations:[11]

$$a_{\text{x}}^{\text{EH}} = a_{\text{x}}^{\text{R}} a_{\text{cyclohexane}}^{\text{EH}}$$

where

$$a_{\text{x}}^{\text{EH}} = \frac{a_{\text{x}}^{\text{EH}}}{a_{\text{cyclohexane}}^{\text{EH}}}$$

by diluting the standard solution of 2-NCH in solvent x containing trifluoroacetic acid to stop the interconversion of the tautomers.

Tautomeric equilibrium constants, K_{T}, have been determined by adding a small aliquot of a stock solution of 2-NCH in CH_2Cl_2 to a cuvette containing TEA dissolved in the appropriate solvent. The concentration of the substrate was kept constant at 1×10^{-4} mol dm^{-3} in all experiments. The absorbance at the λ_{max} of the enol has been registered at different temperatures, and K_{T} values have been calculated.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: siani@unich.it.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was conducted with support from the Università "G. d'Annunzio" of Chieti-Pescara and MIUR (PRIN 2010-11, prot. 2010N3T9M4). A.D.C. thanks MIUR (PRIN 2010-11, prot. 2010N3T9M4) that funded his biennial postdoctoral fellowships.

■ REFERENCES

(1) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.

(2) (a) Wheeler, C.; West, K. N.; Liotta, C. L.; Eckert, C. A. *Chem. Commun.* **2001**, 887−888. (b) Lancaster, N. L.; Welton, T.; Young, G. B. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2267−2270. (c) Lancaster, N. L.; Welton, T. *J. Org. Chem.* **2004**, *69*, 5986−5992. (d) Chiappe, C.; Pieraccini, D.; Saullo, P. *J. Org. Chem.* **2003**, *68*, 6710−6715. (e) Creary, X.; Willis, E.; Gagnon, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 18114−18120. (f) D'Anna, F.; Frenna, V.; Noto, R.; Pace, V.; Spinelli, D. *J. Org. Chem.* **2006**, *71*, 5144−5150. (g) D'Anna, F.; Frenna, V.; Pace, V.; Noto, R. *Tetrahedron* **2006**, *62*, 1690−1698.

(3) MacFarlane, D. R.; Pringle, J. M.; Jonansson, K. M.; Forsyth, S. A.; Forsyth, M. *Chem. Commun.* **2006**, 1905−1917.

(4) Crowhurst, M. L.; Falcone, R.; Lancaster, N. L.; Mestre, V. L.; Welton, T. *J. Org. Chem.* **2006**, *71*, 8847−8853.

(5) Crowhurst, M. L.; Lancaster, N. L.; Arlandis, J. M. P.; Welton, T. *J. Am. Chem. Soc.* **2004**, *126*, 11549−11555.

(6) Reichardt, C. *Green Chem.* **2005**, *7*, 339−351.

(7) (a) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377−383. (b) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027−6038. (c) Kamlet, M. J.; Abboud, J. L.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877−2887.

(8) Canongia Lopes, J. N. A.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 3330−3335.

(9) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413−3474.

(10) D'Anna, F.; Frenna, V.; Noto, R.; Pace, V.; Spinelli, D. *J. Org. Chem.* **2006**, *71*, 9637−9642.

(11) Angelini, G.; Chiappe, C.; De Maria, P.; Fontana, A.; Gasparrini, F.; Pieraccini, D.; Pierini, M.; Siani, G. *J. Org. Chem.* **2005**, *70*, 8193−8196.

(12) (a) Russell, P. B. *J. Am. Chem. Soc.* **1952**, *74*, 2654−2656. (b) Bell, R. P.; Smith, P. W. *J. Chem. Soc. B* **1966**, 241−243. (c) Dubois, J.-E.; El-Alaoui, M.; Toullec, J. *J. Am. Chem. Soc.* **1981**, *103*, 5393−5401. (d) Mills, S. G.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216−1224. (e) Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1988**, *110*, 1993−1995. (f) Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 4862−4868.

(13) Fontana, A.; De Maria, P.; Siani, G.; Pierini, M.; Cerritelli, S.; Ballini, R. *Eur. J. Org. Chem.* **2000**, 1641−1646.

(14) Angelini, G.; De Maria, P.; Chiappe, C.; Fontana, A.; Gasbarri, C.; Siani, G. *J. Org. Chem.* **2009**, *74*, 6572−6576.

(15) Bini, R.; Chiappe, C.; Mestre, V. L.; Pomelli, C. S.; Welton, T. *Org. Biomol. Chem.* **2008**, *6*, 2522−2529.

(16) Lancaster, N. L.; Salter, P. A.; Welton, T.; Young, G. B. *J. Org. Chem.* **2002**, *67*, 8855−8861.

(17) Crowhurst, L.; Falcone, R.; Lancaster, N. L.; Llopis-Mestre, V.; Welton, T. *J. Org. Chem.* **2006**, *71*, 8847−8853.

(18) Chiappe, C.; Pieraccini, D. *J. Org. Chem.* **2004**, *69*, 6059−6064.

(19) Angelini, G.; De Maria, P.; Fontana, A.; Pierini, M.; Siani, G. *J. Org. Chem.* **2007**, *72*, 4039−4047.

(20) Wang, Y.; Li, H.; Han, S. *J. Phys. Chem. B* **2006**, *110*, 24646−24651.

(21) Ruiz, E.; Ferro, V. R.; Palomar, J.; Ortega, J.; Rodriguez, J. J. *J. Phys. Chem. B* **2013**, *117*, 7388−7398.

(22) (a) Danten, Y.; Cabac, M. I.; Besnard, M. *J. Phys. Chem. A* **2009**, *113*, 2873−2889. (b) Fazio, B.; Triolo, A.; Di Marco, G. *J. Raman Spectrosc.* **2008**, *39*, 233−238. (c) Canongia Lopes, J. N. A.; Costa Gomes, M. F.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 16816−16818.

(23) (a) Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Farrar, D. H.; Lough, A. J.; Loh, W.; da Silva, L. H. M.; Dupont, J. *J. Phys. Chem. B* **2005**, *109*, 4341−4349. (b) Hayes, R.; Imberti, S.; Warr, G. G.; Atkin, R. *J. Phys. Chem. C* **2014**, *118*, 13998−14008.

(24) Almeida, H. F. D.; Freire, M. G.; Fernandes, A. M.; Lopes-da-Silva, J. A.; Morgado, P.; Shimizu, K.; Filipe, E. J. M.; Canongia lopes, J. N.; Santos, L. M. N. B. F.; Coutinho, J. A. P. *Langmuir* **2014**, *30*, 6408−6418.

(25) Rocha, M. A. A.; Neves, C. M. S. S.; Freire, M. G.; Russina, O.; Triolo, A.; Coutinho, J. A. P.; Santos, L. M. N. B. F. *J. Phys. Chem. B* **2013**, *117*, 10889−10897.

DOI: 10.1021/jo502898s
J. Org. Chem. 2015, 80, 2333−2338