

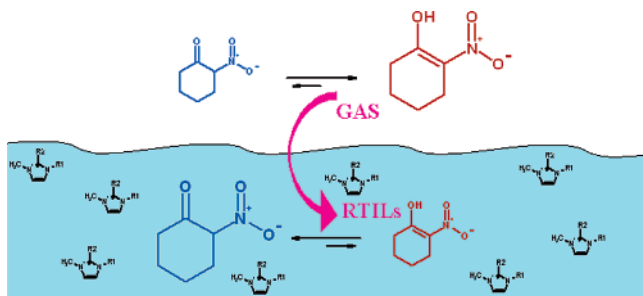
Determination of the Polarities of Some Ionic Liquids Using 2-Nitrocyclohexanone as the Probe

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Solute–solvent interactions on the keto–enol tautomerism of 2-nitrocyclohexanone in several organic solvents and room-temperature ionic liquids (RTILs) have been analyzed in terms of multiparameter equations. Permittivity and cohesive pressure values of the RTILs, unavailable by direct measurements, have been derived.

Nitrocarbonyl compounds have recently attracted considerable interest both from the synthetic¹ and commercial² points of view. Although nitroketones represent a rare example of monocarbonyl derivatives with appreciable quantities of the enol form, EH, in equilibrium with the keto form, KH, kinetic^{3–5} studies of tautomerization and, particularly, studies of solvent effects on the tautomeric equilibrium constant, $K_T = [EH]/[KH]$, are very scarce. We have measured the tautomeric equilibrium constant of 2-nitrocyclohexanone (2-NCH) in several organic solvents at 25.0 ± 0.1 °C. Determinations carried out in cyclohexane (C₆H₁₂) by a combination of IR, ¹H NMR, and UV techniques show that, after dissolution of 2-NCH, equilibrium is established between KH and EH.

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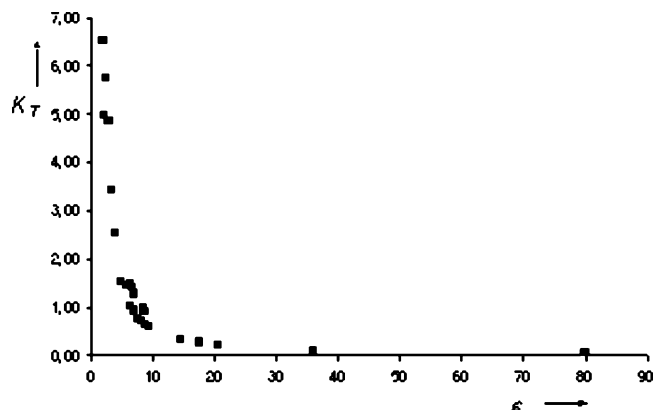


FIGURE 1. Plot of K_T against the permittivity (ϵ) of the solvent.

Preliminary kinetic measurements carried out on the keto–enol interconversion of 2-NCH in aprotic apolar solvents clearly show that bases (e.g., triethylamine, TEA, or substituted pyridines) catalyze the tautomerization process without affecting the final value of the absorbance, A_{∞} , of the enol form. Therefore, catalytic amounts of TEA (i.e., $[TEA]/[2-NCH] \approx 10^{-3}$) were added to speed up the establishment of the equilibrium. Appreciable amounts of the nitronic form (the so-called “aci” form) could not be detected at equilibrium (see Supporting Information). The absence of the aci form is also shown by the occurrence of one isosbestic point in the UV spectra registered at different time intervals after dissolution. K_T values in 5 pure organic solvents (C₆H₁₂, CCl₄, CHCl₃, CH₂Cl₂, CH₃CN) and 18 binary solvent mixtures spanning a wide range (from 2 to 37.5) of permittivity values have been measured by UV–visible and ¹H NMR spectrometry. There is a good agreement between the values measured by the two techniques (Table 1 in Supporting Information). The value of K_T in water has been determined using a previously reported kinetic procedure.³ The results obtained show a strong dependence of K_T on the permittivity of the solvent (Figure 1).

The transfer of the tautomeric equilibrium to solvents of increasing polarity is accompanied by a progressive bathochromic shift of λ_{max} in the UV spectrum of EH. This positive solvatochromism of EH has been used to assign a normalized polarity index, T_N (see Supporting Information), to the investigated solvents (analogous to the well-known^{6–8} indexes π^* , π_{azo}^* , and E_T). The large amount of experimental data collected allows an in depth regression analysis of the solvent effects in terms of different multiparameter equations.⁹ Various linear combinations of one, two, and three descriptors have been considered according to the general eq 1

$$\Delta G_x^0 = \Delta G_{gas}^0 + \sum f_i D_i \quad (1)$$

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TABLE 1. Tautomeric Constants, K_T , for 2-NCH in Different Solvents and Physical Properties of the Solvents

solvent	ϵ	δ (cal ^{1/2} cm ^{-3/2})	$F(\epsilon)$	T_N	K_T
C ₆ H ₁₂	2	8.2	0.200	0.03 ± 0.02	6.51 ± 0.57
CCl ₄	2.2	8.6	0.222	0.25 ± 0.02	5.97 ± 0.47
CHCl ₃	4.8	9.3	0.358	0.67 ± 0.02	1.53 ± 0.06
CH ₂ Cl ₂	8.9	9.7	0.420	0.67 ± 0.02	0.64 ± 0.02
CH ₃ CN	35.9	11.8	0.479	0.67 ± 0.02	0.110 ± 0.006
1	10.0 ± 1.5	13.1 ± 0.1	0.429 ± 0.010	0.82 ± 0.02	0.091 ± 0.012
2	22.5 ± 7.4	11.8 ± 0.1	0.467 ± 0.010	0.77 ± 0.02	0.138 ± 0.007
3	16.2 ± 3.8	12.2 ± 0.1	0.455 ± 0.010	0.77 ± 0.02	0.120 ± 0.007
4	25.7 ± 9.6	11.5 ± 0.1	0.471 ± 0.009	0.75 ± 0.02	0.157 ± 0.017
5	29.7 ± 13.3	11.5 ± 0.1	0.475 ± 0.009	0.77 ± 0.02	0.156 ± 0.002

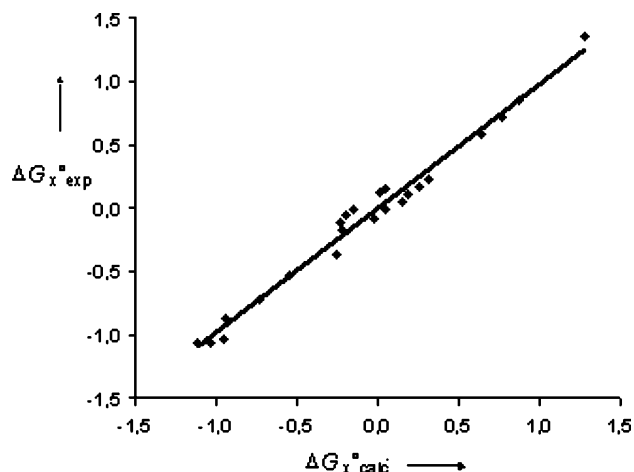
where ΔG_x^0 represents the standard free energy change associated with the tautomeric equilibrium of 2-NCH in solvent x, D_i represents the i selected descriptors of solvent polarity, and f_i represents the corresponding regression coefficients. The above correlation analysis has been initially limited to the five pure organic solvents, as the corresponding D values are available from the literature. It turns out that the two best correlations ($R^2 > 0.999$, Table 3 in Supporting Information) are those obtained from the three-parameter equations that use Kirkwood's function $F(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$, the cohesive pressure δ^2 , and E_T or T_N [eqs 2 and 3] as the descriptors of the observed solvent effects.

$$\Delta G_x^0 = \Delta G_{\text{gas}}^0 + a\delta^2 + bF(\epsilon) + cE_T^N \quad (2)$$

$$\Delta G_x^0 = \Delta G_{\text{gas}}^0 + a\delta^2 + bF(\epsilon) + cT_N = \Delta G_{\text{gas}}^0 + \Delta G_{\text{sol}}^0 \quad (3)$$

It should be considered that these three parameters express different and complementary properties of the solvent, namely, the electrostatic shielding of partial or full charges [$F(\epsilon)$], the cavitation energy (δ^2), and aspecific as well as lone pair donor-acceptor and hydrogen bonding interactions (E_T or T_N). We have then extended the regression analysis to the above-mentioned 18 binary solvent mixtures (see Table 4 in Supporting Information) in terms of eq 3, where T_N represents experimental values, $F(\epsilon)$ has been calculated from Kirkwood's theory,¹⁰ and δ^2 has been calculated from the known values in the pure solvents taking into consideration the appropriate volume fractions in the examined binary mixtures.¹¹ The obtained correlation is good ($\Delta G_{\text{gas}}^0 = -3.53 \pm 0.12$ kcal/mol, $R^2 = 0.9815$, $n = 23$), and the average difference between the experimental values of ΔG_x^0 and those estimated from eq 3 is of only 0.075 kcal/mol (Figure 2).

Room-temperature ionic liquids (RTILs) are emerging as convenient, reusable, environmentally benign, and versatile solvents for a variety of organic reactions.¹² An attractive feature of RTILs is that their physical properties can be fine-tuned by structural variations within the cationic or anionic components.^{13,14a-c} Although several efforts have been made to determine the polarity of RTILs using solvatochromic dyes and partition methods,^{14,15} neither direct measurement of permittivities, ϵ , which would require a nonconducting medium, nor cohesive

**FIGURE 2.** Comparison between the values of ΔG_x^0 calculated from eq 3 ($\Delta G_x^0_{\text{calc}}$) and the experimental values ($\Delta G_x^0_{\text{exp}}$).

pressure values, δ , due to the absence of volatility, are available. However, we note that a paper¹⁶ has recently appeared on the estimates of internal energies of vaporization of some RTILs determined on the basis of kinetic measurements for the reaction of singlet oxygen with 1,4-dimethylnaphthalene. Empirical polarity scales, developed using solvatochromic dyes, suggest that imidazolium RTILs are more polar than acetonitrile and less polar than or of comparable polarity to that of lower alcohols.¹⁴ However, polarity is the sum of all possible, nonspecific

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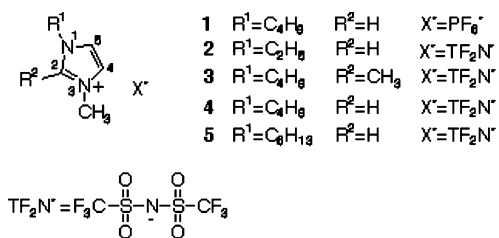
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SCHEME 1. Structures of the Investigated RTILs



and specific, interactions between the solute ions or molecules and the solvent molecules. These interactions involve a number of different intermolecular forces with the consequence that no single probe molecule is capable of providing a reliable polarity scale. To separate specific effects of the local electric fields from the hydrogen bonding effects, Welton has recently determined¹⁷ the polarity of some RTILs applying the classical approach of Abboud–Kamlet–Taft. Dipolarity/polarizability (π^*), hydrogen bond basicity (β), and hydrogen bond acidity (α) of some RTILs have been determined by using three solvatochromic dyes. The data obtained show that all the examined RTILs are characterized by π^* values higher than those of most nonaqueous molecular solvents. Depending upon the anion the examined, RTILs can have a significant hydrogen bond basicity and, depending upon the cation, a hydrogen bond acidity comparable to or lower than that of aniline, although the latter parameter is also affected by the anion.¹⁷ More recently, the use of pentane-2,4-dione as a possible indicator of polarity for RTILs has been proposed¹⁸ by Seddon. Within this context, we have measured the tautomeric equilibrium constant, K_T , of 2-NCH also in the five RTILs of Scheme 1 to obtain quantitative estimates of the polarities of 1–5.

The values of K_T in RTILs 1–5 (Table 1) are generally close to those measured in solvents of relatively high polarity such as acetonitrile, where the more polar keto tautomer, KH, is favored over the less polar enol tautomer, EH, and $K_T < 1$.

The experimentally determined T_N values for RTILs of Scheme 1 are also of interest. Although the [PF₆]⁻ anion of 1 displays strong interactions with EH (as shown by the large value of T_N), the overall effect of 1 is a stabilization of KH, as shown by the lowest measured value of K_T . On the other hand, for RTILs 2–5, which have the [TF₂N]⁻ anion in common, the highest formal polarity, as measured by the corresponding K_T value, should be assigned to 3, despite the larger apolar portion of its cationic surface. Smaller variations of K_T and T_N have been measured for the remaining RTILs 2, 4, and 5, which can be easily accounted for by the different size of their alkyl groups in position 1.

The absence of strong acidic hydrogen atoms¹⁹ in all of the investigated RTILs and the fact that the highest formal polarity should be assigned to 3 (the RTIL lacking the H atom at C-2) suggest that the solute–solvent interactions on the keto–enol equilibrium of 2-NCH are comparable to those observed in aprotic organic solvents.

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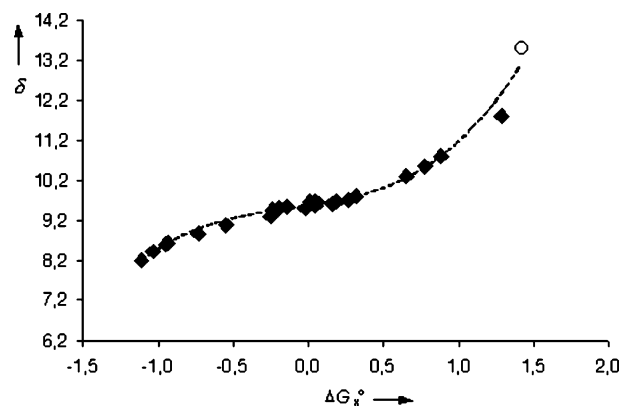


FIGURE 3. Plot of Hildebrand's δ values against free energy change (ΔG_x^0) for the tautomeric equilibrium of 2-NCH in the 23 organic solvents (\blacklozenge) and RTIL 1 (\circ).

TABLE 2. Physical Properties of RTILs 1–5

RTIL	δ^2 (cal cm ⁻³)	V_m (cm ³ mol ⁻¹)	U_{vap} (kcal mol ⁻¹)
1	171.7 ± 2.4	208.9 ± 1.2	35.8 ± 0.4
2	139.9 ± 2.4	256.4 ± 4.2 ^a	35.7 ± 1.2
3	149.3 ± 2.4	299.0 ± 4.9 ^a	44.5 ± 1.5
4	132.4 ± 2.4	287.2 ± 4.7 ^a	38.0 ± 1.2
5	132.8 ± 2.4	317.4 ± 5.2 ^a	42.0 ± 1.4

^a Estimated by molecular mechanics.

An excellent sigmoidal correlation (Figure 3) exists between the Hildebrand's δ values¹¹ of the 23 organic media and the corresponding ΔG_x^0 associated with the keto–enol tautomerism of 2-NCH. By inserting a previously calculated²⁰ δ^2 value of 182 cal cm⁻³ ($\delta = 13.5$) at 25 °C for 1 into the correlation of Figure 3, eq 4 ($R^2 = 0.9814$, $n = 24$) can be obtained, which provides the set of δ of RTILs 1–5 reported in Table 1. The comparison between the δ data points of Figure 3 and the values of δ from eq 4 gives a standard deviation of 0.1.

$$\delta = 0.778(\Delta G_x^0)^3 + 0.258(\Delta G_x^0)^2 + 0.565\Delta G_x^0 + 9.551 \quad (4)$$

As the obtained δ values of the investigated RTILs lie in the interval $13.1 > \delta > 11.5$, a superficial analysis would lead to the conclusion that two of them are less polar than acetonitrile ($\delta = 11.8$). However, it should be recalled that δ^2 and internal vaporization energy, U_{vap} , are related by eq 5 as follows

$$\delta^2 = \Delta U_{\text{vap}}/V_m \quad (5)$$

where V_m is the molar volume of the solvent. Using the literature²¹ V_m value of 208.9 cm³ mol⁻¹, we calculated a U_{vap} of 35.8 kcal mol⁻¹ for 1. The U_{vap} values for RTILs 2–5 have been estimated from the approximate V_m values calculated as described in Supporting Information. The results obtained are reported in Table 2.

The U_{vap} value calculated for acetonitrile is only 7 kcal mol⁻¹, and this result is of course in full agreement with the larger V_m s and the extremely low vapor pressures of RTILs. The values of Kirkwood's function, $F(\epsilon)$, and consequently those of ϵ for 1–5 can be obtained from eq 3 by using the same regression coefficients ΔG_{gas}^0 , a , b ,

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and c found with the 23 apolar organic solvents. Only a few permittivity values, ϵ , for some imidazolium-based RTILs have been reported^{13,22} so far. The ϵ values, determined^{13,22} indirectly by fluorescence experiments, generally range between 10 and 13. More particularly, the ϵ value of 10.0 (± 1.5) estimated from eq 3 for **1** is in good agreement with those of about 10–11 reported for **1** in the previous studies.^{13,22} The ϵ values of **1–5** (Table 1) are unexpectedly low, if compared with known ϵ values of polar organic solvents generally considered^{14a} similar to RTILs. It should be recalled though that the permittivity, ϵ , of a given solvent depends on the dipolar character of the solvent, which should be absent in ideal RTIL salts. In real RTIL systems, ion-pair formation,²³ with associated dipole moments²⁴ much higher than those of the molecules of common organic solvents, might well give rise to substantial ϵ values. To generalize, the following four points clearly emerge from the present study: (i) The tautomeric equilibrium of 2-NCH, which is in favor of the enol form in the gas phase ($\Delta G_{\text{gas}}^0 = -3.53$ kcal/mol), is displaced toward the keto form upon transfer to relatively polar organic solvents and RTILs **1–5**. This is essentially due to the fact that the cavitation and nonspecific electrostatic contributions by the solvent, which strongly stabilize KH, more than offset the specific electrostatic contribution which stabilizes EH. (ii) RTILs with the $[\text{TF}_2\text{N}]^-$ anion and $\text{R}^2=\text{H}$ (Scheme 1) display solvation effects similar to that of acetonitrile, albeit with a somewhat higher ability to stabilize the enol tautomer. (iii) RTILs having a methyl group at C-2 or $[\text{PF}_6]^-$ as the counteranion are characterized by higher values of the cohesive pressure and more effectively stabilize the keto tautomer of 2-NCH. Finally, (iv) comparison of the polarities of **1–4** with those of **3** and **4** suggests that the anionic portion affects the polarity of RTILs more than the cationic portion.

Interestingly, the values of δ reported by Gordon et al.¹⁶ for **1**, **3**, and **4** are in good agreement with those of the present work. This supports the reliability of our approach and of the values of permittivity (ϵ) of RTILs **1–5**.

Experimental Section

Instruments. ¹H NMR spectra were recorded with a Bruker Avance 400 spectrometer. Chemical shifts (δ) in Figure 1 of Supporting Information are given in parts per million relative to TMS. IR spectra were recorded on a Jasco FT/IR-430 spectrophotometer. UV–vis spectra were recorded with a Varian Cary 1E spectrophotometer with a spectral resolution set to 0.333 nm.

Materials. RTILs of Scheme 1 were prepared from the corresponding halides, following reported procedures.^{13,25} The purity of imidazolium salts was checked by ESI-MS and UV spectrophotometry (purified $[\text{bmim}]^+$ salts containing $[\text{Cl}]^-$ or $[\text{Br}]^- < 0.1$ ppm have no absorption band in the 250–300 nm region).²⁶ After drying (2 h at 80 °C

under vacuum), the water content of RTILs was determined by the Karl Fisher technique using an apparatus composed of a stand titrator and a coulometer. A water content within 120–150 \pm 20 ppm was found for ionic liquids **2–5**, whereas a water content of 348 \pm 25 ppm was found for **1**.

Determination of the Tautomeric Equilibrium Constant of 2-NCH. Tautomeric equilibrium constants, $K_{\text{T}}^{\text{x(NMR)}}$, of 2-NCH have been determined in pure organic solvents x by ¹H NMR using peak area ratios for the acidic hydrogens of the enol and the keto tautomers.

The molar absorptivities of EH in the different solvents x , $\epsilon_{\text{x}}^{\text{EH}}$, have been calculated by eqs 6 and 7

$$\epsilon_{\text{x}}^{\text{R}} = \frac{A_{\text{x}}^{\text{EH}}}{A_{\text{cyclohexane}}^{\text{EH}}} \quad (6)$$

$$\epsilon_{\text{x}}^{\text{EH}} = \epsilon_{\text{x}}^{\text{R}} \epsilon_{\text{cyclohexane}}^{\text{EH}} \quad (7)$$

where A_{x}^{EH} is the absorbance at $\lambda_{\text{max}}^{\text{EH}}$ of a solution obtained by diluting 200 times with solvent x a standard solution of 2-NCH in CHCl_3 containing about 0.04 M trifluoroacetic acid (TFA) in order to stop the interconversion of the tautomers. The required $\epsilon_{\text{cyclohexane}}^{\text{EH}}$ value has been obtained from a best fit of eq 8 to experimental $K_{\text{T}}^{\text{x(NMR)}}$ data determined in C_6H_{12} , CHCl_3 , CH_2Cl_2 , $\text{CH}_3\text{-CN}$ ($R = 0.99$, $\epsilon_{\text{cyclohexane}}^{\text{EH}} = 8321 \pm 86$)

$$K_{\text{T}}^{\text{x(UV)}} = \frac{1}{\frac{[\text{2-NCH}]_{\text{x}}^{\text{R}} \epsilon_{\text{cyclohexane}}^{\text{EH}}}{A_{\text{x}}^{\text{eq}}} - 1} \quad (8)$$

where A_{x}^{eq} is the absorbance of EH at equilibrium in solvent x . Spectrophotometric equilibrium constants of 2-NCH, $K_{\text{T}}^{\text{x(UV)}}$, in the different solvents have been calculated from eq 8. $K_{\text{T}}^{\text{x(UV)}}$ and ϵ^{EH} are collected in Table 1 and Table 4 of Supporting Information as average values of three to four determinations.

Determination of Permittivity Values. Permittivity values of RTILs **1–5** were obtained from a rearranged form of eq 3 as follows:

$$F(\epsilon) = (\Delta G_{\text{x}}^0 - \Delta G_{\text{gas}}^0 - a\delta^2 - cT_{\text{N}})/b$$

$$\epsilon = (F(\epsilon) + 1)/(1 - 2F(\epsilon))$$

The uncertainty of the $F(\epsilon)$ values was estimated by the treatment of propagation of errors. It should be outlined that error on ϵ increases exponentially as the value of $F(\epsilon)$ increases (see Figure 2 in Supporting Information).

Acknowledgment. We thank MIUR-Rome for the financial support (PRIN 2003 and 2004).

Supporting Information Available: Spectrophotometric identification of the tautomers of 2-NCH in cyclohexane; tautomeric constants for 2-NCH in different solvents; standard free energy change associated with the tautomeric equilibrium; calculation of the polarity index T_{N} ; and calculation of the molar volume of RTILs **1–5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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