Charge Transfer Complex - Ion Pair Equilibria, Z-values and Exchange Reaction : Proton Magnetic Resonance Studies on 1-Ethyl-4-Carbomethoxy Pyridinium Iodide.

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Summary: Proton magnetic resonance spectra of the charge transfer complex, 1-ethyl-4-carbomethoxy pyridinium iodide were recorded in a number of solvents. It was found that δ (2,6) - δ (3,5) correlated linearly with the solvent polarity parameter Z-values. Through this correlation a (new) Z-value of water, 92, was obtained which agrees with the recently obtained value (91.8).

The equilibrium constant for

$$(\mathrm{PyI})_{\mathrm{CT\ or\ VTIP}} \xrightleftharpoons{K_1} [\mathrm{Py}^+,\ \mathrm{I}^-]_{\mathrm{IP(LIP\ or\ CIP)}}$$

were calculated and found to vary from 0.5 in chloroform to 10.0 in formamide.

The rate for exchange between the CT complex and the ion pair

$$(\mathrm{PyX})_{\mathrm{CT}} + (\mathrm{Py}^+,\mathrm{X}^-)_{\mathrm{IP}} \xrightleftharpoons{\text{exchange}}$$

was calculated to be the order of 10^4 sec^{-1}.

Introduction

1-Ethyl-4-carbomethoxy pyridinium iodide is an interesting compound. It is a charge transfer complex, the solvochromic property of which has been utilized as a solvent polarity parameter, the Z-value [1]. The reduction product - the pyridinyl radical, has been extensively studied by Kosower and his coworkers [2] and Mohammad [3]. It has been shown by Kosower [4] that thhese investigations have relevance to biological reactions. Electrochemical properties of this compound have also been investigated, most extensively by Mohammad and co-workers [5].

Recently conductance studies have been carried out on this compound [6] (1,PyI), but so far NMR studies have been scanty on this interesting compound [7]. The conductance and optical spectroscopic studies [1,5], and ultrasonic studies on related (charge transfer) compound, the methyl pyridinium iodide [8] have established that this class of compound exists as CT complex, ion pair (loose, solvent separated) and free ions, depending upon the solvent; e.g. in water 1 is almost completely dissociated (complete absence of a CT band) while in nonaqueous but highly polar solvent, it (1) exists as CT complex (or very tight ion pair) and loose ion pair [6,8] and in methyl tetrahydrofuran (MTHF) and $CHCl_3$ it exists mostly as CT complex [9]. The magnetic resonance spectroscopy (both ESR and NMR) can distinguish between a tight or contact and loose ion pair through the ion pair's hyperfine splittings [10]. Thus proton magnetic resonance studies on 1-ethyl 4-carbomethoxy pyridinium iodide in various solvents can give information regarding the nature of moieties present in the solvent.

In this report we present the results of the proton magnetic resonance spectroscopic studies on this compound to obtain the following information (a) any correlation between the Z-values (the solvochromic property) and NMR δ-value (b) the correct Z-value of water (c) the equilibrium constant between the CT complex (or very tight (VT) ion pair) and loose ion pair (d) the exchange rate between a CT complex (or VT ion pair) and loose ion pair.

Results

NMR spectra of the CT complex 1 were recorded in various solvents with Z-values ranging from 92.0 (D_2O, see "Discussion" for the Z-value of water) to 63.2 ($CHCl_3$). Also the NMR spectra of 1-ethyl-4-carbomethoxy pyridinium perchlorate (also called pyridinium perchlorate $PyClO_4$ here) and their mixtures were recorded in $CHCl_3$. A representative NMR spectrum of 1, $PyClO_4$ and 1:1 mixture in $CHCl_3$ are shown in Figs.1,2,3. Representative NMR data in some solvents are collected in Table 1.

The assignment of proton resonance lines are straight forward and

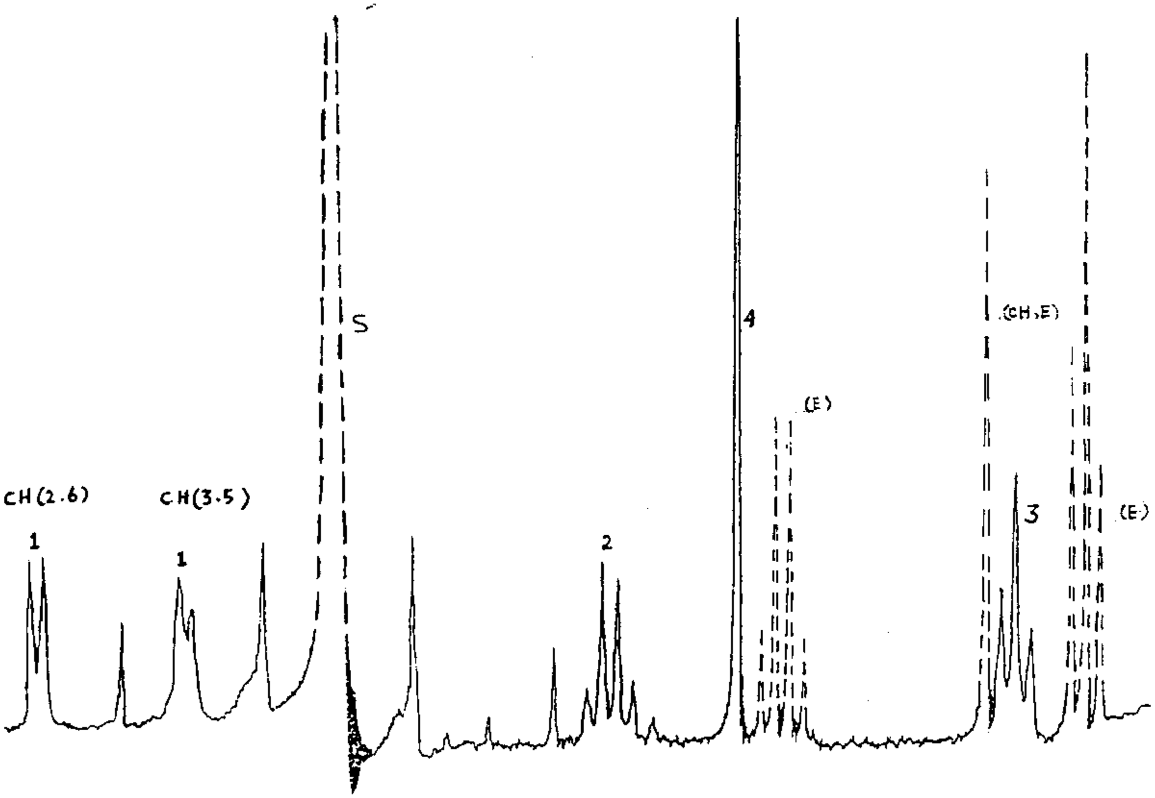

Fig.1: NMR spectrum of 1-ethyl-4-carbomethoxy pyridinium iodide in $CHCl_3$ (Peaks S = Solvent $CHCl_3$, E = Ethanol present in $CHCl_3$ as stabilizer)

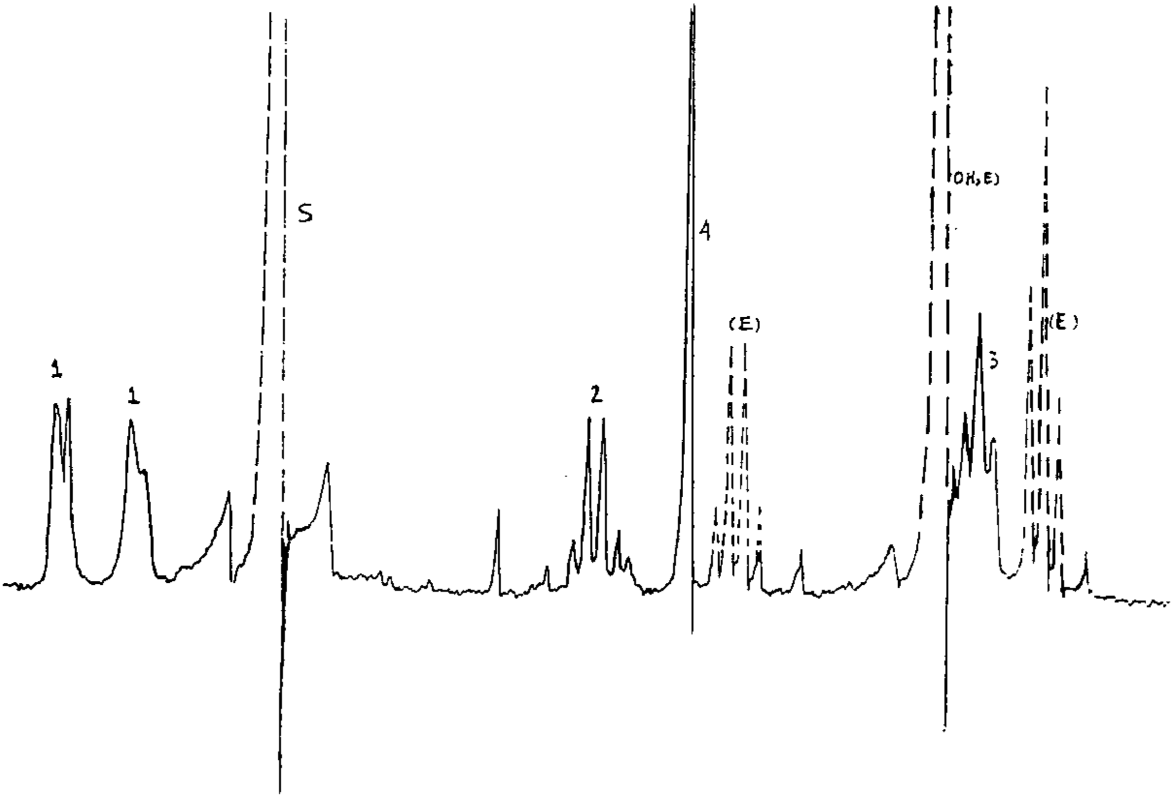

Fig.2: NMR spectrum of the perchlorate salt in $CHCl_3$ (For S & E, see fig.1)

are indicated in the figures (1-3) and in the Table 1. $\delta(2,6)$ and $\delta(3,5)$ are doublets, the difference between their centre of gravities changes with the solvent (Table 2) and correlates with the Z-value of the solvent (see fig.4). The greatest value of $\Delta\delta = 1.20$ is for $CHCl_3$ ($Z = 63.2$) while the smallest one of $\Delta\delta = 0.58$ is for (deuterated) water. It was also noted that $\Delta\delta$ for $PyClO_4$ in $CHCl_3$ as well as in D_2O remains constant as 0.58.

NMR spectra of the mixture of pyridinium iodide $\underline{1}$ and pyridinium perchlorate, in the ratio 1:5; 1:2; 1:1; 2:1; 5:1 were recorded. Interestingly instead of observing NMR spectrum one of each compound, only one spectrum consisting two doublets (aromatic protons), CH_2-quartet, CH_3-triplet and CH_3COO singlet were observed, the positions and $\Delta\delta$ of which depended upon the ratio of the two components (fig.3 and Table 3).

Discussion

The charge transfer complex $\underline{1}$ in solution can be expressed in equilibria:

$$(PyI)_{CT\ or\ VTIP} \underset{}{\overset{K_1}{\rightleftharpoons}} [Py^+, I]_{LIP\ or\ CIP} \quad (1)$$

$$\overset{K_2}{\rightleftharpoons} [Py^+ \| I^-]_{SSIP} \overset{K_3}{\rightleftharpoons} Py^+ + I^-$$

Where VTIP = very tight ion pair, LIP = loose ion pair, CIP = contact/caged ion pair, SSIP = solvent separated ion pair. Here the CT and very tight ion pair moieties are lumped together and contact/caged ion pair

Table-1: Proton NMR Spectra of Pyridinium Salts in Some Solvents[a].

Solvent/Position[b]	CH (2,6)	CH(3,5)	CH_2(7)	CH_3COO(10)	CH_3(8)
$CHCl_3$	9.72 ; 9.62	8.59 ; 8.49	5.35;5.21;5.18;4.98	4.08	1.97;1.84;1.60
DMSO[c]	9.30 ; 9.20	8.45 ; 8.35	4.83;4.70;4.60;4.47	3.60	(f)
d-MeCN[d]	9.29 ; 9.19	8.37[g]	4.96;4.83;4.72;4.60	3.98	(h)
DMF[e]	9.40 ; 9.29	8.38 ; 8.24	4.92;4.81;4.68;4.56	3.95	(i)

(a) 1-ethyl 4-carbomethoxy pyridinium iodide. Here representative NMR data in some solvents are given (b) δ - values (c) - (e) dimethyl sulphoxide, acetonitrile, dimethylformamide (f) under DMSO (g) broad (h) under MeCN (i) under DMF.

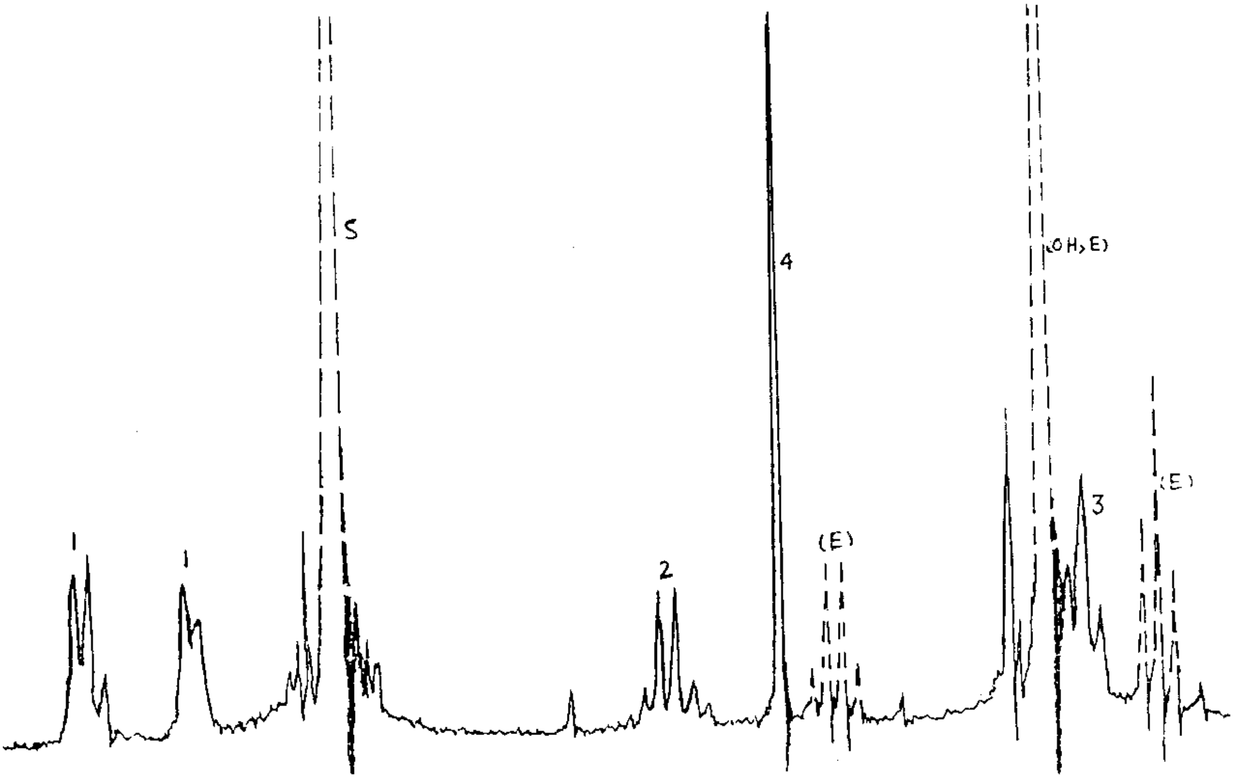

Fig.3: The 1:1 mixture of the 1 and the perchlorate salt in $CHCl_3$ (For S and E see fig.1)

and loose ion pair are lumped together. However, other workers lump VTIP and CIP together, and LIP and SSIP together (see e.g. ref. 11 page 353, ref.12 page 256 and ref [12b]), or combinations thereof [12b].

Keeping in view the above mentioned properties of a charge transfer complex in solution an attempt can be made to explain the above mentioned experimental observations.

(i) Z-correlations and the correct Z-value of water.

As is evident from fig.4, there is a linear correlation between Z-value and Δδ i.e. both manifest the same structural changes in pyridinium iodide in various solvents. These structural changes can be qualitatively explained by the standard charge-transfer-ion pair potential energy diagrams in non polar and polar solvents [11,12].

Table-2: NMR parameters $\Delta\delta^a$, the equilibrium constant K_1 the charge transfer parameter Z-values and other solvents polarity parameters of some solvents.

Solvents/ Parameters	$ChCl_3$	$MeCl^b$	DMF^c	DMSO	MeCN	$IP\text{-}OH^d$	$E\text{-}OH^e$	Me-OH	Fmd^f	D_2O
$\Delta\delta$	120	118	104	93	90	88	80	74	66	60
K_1	0.50	0.54	1.00	1.63	1.86	2.07	3.17	4.88	10.11	-
Z-values^a	63.2	64.2	68.4	71.1	71.3	76.3	79.6	83.3	84.0	94.6
ε^g	5.6	9.0	37	46.6	36.2	18.3	24.3	32.6	109.5	78.4
μ^h	1.02	1.54	3.82	4.30	3.84	1.60	1.69	1.70	3.25	1.85

(a) See Table 1 for footnotes: $\Delta\delta \times 10^2$ = ; Solvent polarity parameter Z-values are taken from Ref 11. errors ir $\Delta\delta = \pm 2$ (b-f) methylene chloride, dimethyl formamide, isopropanol, ethanol, formamide (g-h) dielectric constant and dipole moment respectively, taken from literature such as "Handbook of Chemistry and Physics", Chemical Rubber Co. and A.J. Parker, Chem.Rev. 69, 1 (1969).

Table-3: Proton NMR Parameters δ for PyI - $PyClO_4$ mixture in $CHCl_3^{(a)}$

$PyI/PyClO_4$ Ratio	
5 : 1	110
2 : 1	102
1 : 1	85
1 : 2	77
1 : 5	70
1 : 1 (in D_2O)	58

a) See Table 1 and 2 for foot notes.

Chloroform having low dielectric constant (ε =4.6) will not assist in converting charge transfer complex into ion pairs - the thermal as well as the photochemical energy required for such conversion is too large to be supplied by the thermal (kT) or electrostatic (Born charging) energies. In fact, earlier, it had been assumed that in $CHCl_3$ the association of PyI (into very tight ion pair or CT complex formation) was virtually complete [11,13].

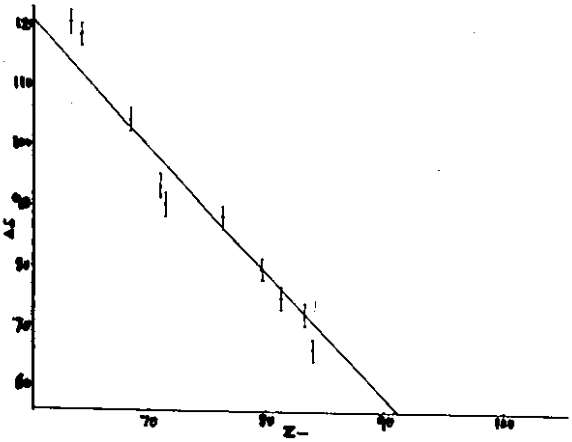

Fig.4: $\Delta\delta$ vs Z-value (scale $\Delta\delta$ x 100)

In terms of the ionic equilibria given above, in water this equilibrium is displaced towards right i.e. K_2 and K_3 being dominant, as the solvation free energies for the ion pair is large enough to affect the charge transfer complex structure, on the other hand, in a solvent like MTHF, the equilibrium will be totally displaced towards the left i.e. there will be no (loose or caged) ion pair but only the CT complex (or very tight ion pair). In $CHCl_3$, the conductance studies of PyI (1) has established that $[Py^+, I]_{SSIP}$ and free ions are negligible [6], hence the CT complex is in equilibrium with CIP or loose ion pair. It becomes then necessary to evaluate this equilibrium constant K_1, which is described in the next section.

From the above discussions and the Δδ-values of 1 and the perchlorate salt, it is clear that, in water, 1 and the perchlorate salt must have the same structure (Δδ=0.58 for both), i.e. pyridinium iodide 1 in water, as mentioned above, does not have CT structure and hence charge transfer complex transition for 1 in water has never been observed [14]. An earlier reported Z-value (94.6) for water was obtained indirectly [1,11] by extrapolation of a linear correlation with Winstein Y-value. In the present work, a (hypothetical) Z-value of 92 is obtained for water from correlation of Δδ and Z-value of various solvents (fig.4). Incidentally the recently new determined Z-values of water is 91.81 [15].

(ii) Evaluation of Equilibrium constant K_1:

Referring to the equilibria depicted in (1), it has been established by the earlier work of Kosower [1] and Hommes [8], and recently Mohammad [6], that in non aqueous and aprotic solvents. $[Py^+ I^-]_{SSIP}$ and the free Py^+ and I^- exist in negligible quantities. Thus in most of the solvents used in the present study, it is K_1 which is relevant. It may be recalled that in solvents like water, acetone or ethanol, the electrostatic contribution is dominant [1,8], (See also Table 2, K_1 values), while in solvents like methyl tetrahydrofuran, (MTHF), dimethoxyethane, chloroform etc, it is the charge transfer contribution which is dominant [1,9] (the extinction coefficient of the CT transition is $>5x10^3$). Also since Δδ manifest these structural changes in various solvents, this quantity can be used for the calculation of K_1.

From fig.4 it is clear that on extrapolation of Δδ to Z=54, one obtains a value of 1.50, which can be considered Δδ for $(PyI)_{CT}$ in "vacuum" [11]. At the same time, Δδ for the $(PyI)_{LIP\ or\ CIP}$ may be taken as 0.58, the same value which PyI has in water or $PyClO_4$ has in $CHCl_3$ or water. Thus the equilibrium constant K_1 can be calculated from the general relationship:

$$K_1 = \frac{R_L - R_S}{R_S - R_R}$$

where R_L and R_R are some physical properties of the pure species (here CT and ion pair respectively) on the left and right of the equilibrium with K_1 as the equilibrium constant; while R_S is the property of the system under observation. Thus R_L and R_R to be taken as $(\Delta\delta)_{vacuum}$ and $(\Delta\delta)_{water}$ thus for PyI in chloroform it is

$$K_1 = \frac{1.50 - 1.20}{1.20 - 0.58}$$

For other solvents, including MeCN, DMF etc. K_1 can be calculated since K_2 and K_3 for these solvents are small as mentioned before [6]. These K_1 are collected in Table 2. The value ranges from 0.5 for $CHCl_3$ to 10 for formamide.

iii) Rate of Exchange:

As mentioned before, for various mixtures of PyI-$PyClO_4$ only one spectrum was observed. The positions of the resonating protons depended upon the ratio of the two compounds and follow the equation [16]

$$\delta = P_1\,\delta_1 + P_2\,\delta_2$$

where P_1 and P_2 being the relative population. This means a time average phenomenon is being observed, the life time of which can be calculated from the theory of "jumping spins" [17]. For fast jumping process with $T < \frac{1}{\Delta W_0}$ (where T is the "averlage life time" and ΔW_o is the frequency difference of the two chemical shifts in the absence of exchange) a single line appears [18]. The rate of the jumping of the spins can be calculated from ΔW_o and the half width of the single line δW by [17,18]

$$W_e \text{ (jumping frequency)} = \frac{(\Delta W_0)^2}{\delta W} \qquad (3)$$

For the pyridinium iodide - pyridinium perchlorate mixture, where pyridinium iodide is to quite an extent in CT or very tight ion pair form and pyridinium perchlorate is in loose or caged ion pair form, we have the pyridinium ring in two environments

$$(Py^+)_{CT} + (Py^+)_{IP} \xrightleftharpoons{\text{exchange}}$$

Of course, in chloroform, some Py^+I^- is already in (contact/caged-loose) ion pair form, nevertheless an idea or order of magnitude of the jumping frequency can be obtained. Thus (in chloroform since δ w≈2-Hz and ΔW_o = 134 Hz, the jumping frequency W_o = 9000 sec^{-1}. For vacuum i.e. using the extrapolated value, assuming the half width remaining the same, it comes out to be about 13000 sec^{-1}. It is seen that the rate of exchange is quite large i.e. in the order of 10^4 sec^{-1}. In other solvents the calculation of jumping frequency is complicated because of larger values of K_1.

In conclusion, through NMR studies of <u>1</u> in various solvents, we have obtained (a) a correlation between $\Delta\delta$ and Z-value and a new Z-value of water has been estimated (b) the equilibrium constants for CT complex (very tight ion pair)-ion pair (equilibrium) in various solvents and (c) the exchange rate for the process described in (b).

Experimental

All the NMR spectra were recorded on JEOL 60 MHz proton magnetic resonance spectrometer. Tetramethylsilane was used as an internal reference, however, the solvent peaks were also used as secondary reference.

The concentration of 1-ethyl-4-carbomethoxy pyridinium iodide, in all solvents, was 0.2M. However, in $CHCl_3$, chemical shifts were also recorded for various concentration of <u>1</u> (down to 0.04M, δ =9.93). The spectra were recorded at ambient (30°C) temperature.

1 and the perchlorate salt were synthesised according to the standard procedure [19]. The solvents were purified according to the standard procedure [20].

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