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Conductivity of *N*-Methylpyridinium Iodide and Its Methyl Substituted Derivatives in Water–Ethanol Mixture

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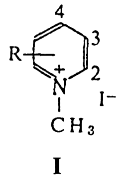
The conductivity of *N*-methylpyridinium iodide (NMPI) and its methyl substituted derivatives at 2-, 3-, and 4-positions in water–ethanol solvent mixtures is reported at 25 °C. The conductivity data are analyzed by the Shedlovsky method to get both Λ_0 and K_A, the association constant, simultaneously. The Λ_0 values decrease or increase with increase or decrease of the viscosity of the solvent mixtures. The values of Λ_0 and K are in the order of H>3->4->2-. The Walden product $\Lambda_0\eta$ for these iodide salts behaves in a manner as is expected for highly hydrogen bonded water-alcohol mixtures. A mole fraction of 0.15 to 0.2 in ethanol indicates maximum interaction between water and ethanol. The values of Λ_0 and K_A indicate greater solvation and hence less ion–ion interaction in case of NMPI and 3-CH_3 salts than 2- and 4-CH_3 salts.

N-Methylpyridinium iodide (NMPI) and its methyl substituted derivatives are formed from reaction of pyridine and picolines with methyl iodide in the form of ionic compounds. Kosower,[1] Roy,[2] Hemmes,[3] Jong-Gi Lee,[4] Bagchi[5] and co-workers have reported spectral, kinetic, and thermodynamic studies on NMPI in 90% and 100% ethanol and acetone solvent mixtures. All these studies point out to formation of solvent shared ion-pairs which is represented as:

$$\underset{\text{Contact ion pair}}{CH_3Py^+I^-} \rightleftarrows \underset{\text{Solvent shared ion pairs}}{CH_3Py^+, I^-} \rightleftarrows \underset{\text{Solvent separated ion pair}}{CH_3Py^+ + I^-} \tag{1}$$

Recently we have carried out the viscosity, apparent molar volume[6] in water at various temperatures and conductance[7] studies in water–methanol mixtures in the entire solvent composition range at 25 °C. All these studies indicate existence of solvent shared ion-pair. A mole fraction of 0.27 in methanol has indicated greater interaction between water and methanol. These studies also indicate difference in the solvation of ions and ion–ion interaction in this solvent system.

Conductance[3] studies of NMPI is only reported in 100% and 90% ethanol–water mixture at 25 °C. The entire solvent composition range has not been studied. In this paper we report conductance measurements of iodide salts of *N*-methylpyridinium ($NMPR^+I^-$) and its methyl substituted derivatives (**I**) in the entire water–ethanol composition range at 25 °C.



I

$NMPR^+I^-$: R=H, CH_3 at 2-, 3-, 4-positions.
When R=H the salt is NMPI.
Short abbreviations for the salts are H, 2-, 3- and 4-.

Experimental

The iodide salts (**I**) were prepared as already described.[6,7] The purity of the salts was checked by gravimetric estimation of iodide as silver iodide.[8] Ethanol was purified by refluxing over calcium oxide. Conductivity water having specific conductivity of $1.2\times10^{-6}\ \Omega^{-1}\,cm^{-1}$ was used. All the solvent mixtures of various composition were prepared by weight at 25 °C. Conductivity measurewments, in triplicate, were carried out as described earlier.[9] The conductivity measurements in the concentration range of 10^{-2} to 10^{-4} M(1 M=1 mol dm^{-3}) of the iodide salts were carried out at 25 °C.

Results and Discussion

NMPI ionizes in solution as

$$CH_3Py^+I^- \rightleftarrows CH_3Py^+ + I^- \tag{2}$$

and the ionization constant K is given by

$$K = \frac{\alpha^2 c}{1-\alpha} f_\pm^2. \tag{3}$$

The symbols have got their usual meaning. By analyzing the conductivity data by the Shedlovsky method[10] we employed

$$\begin{aligned} \alpha &= \frac{\Lambda S(Z)}{\Lambda_0} \\ S(Z) &= \left[\frac{Z}{2} + \left\{1 + \left(\frac{Z}{2}\right)^2\right\}^{1/2}\right]^2 \\ Z &= S\Lambda_0^{-1.5}\,(c\Lambda)^{1/2} \end{aligned} \tag{4}$$

and

$$S = B_1\Lambda_0 + B_2.$$

Both K and Λ_0 were obtained by least-square analysis of Eqs. 5 and 6.

$$\frac{1}{\Lambda S(Z)} = \frac{1}{K\Lambda_0^2}\Lambda C f_\pm^2\, S(Z) + \frac{1}{\Lambda_0}, \tag{5}$$

$$\mathrm{Log} f_\pm = -\frac{A\sqrt{I}}{1+\sqrt{I}}, \tag{6}$$

where $I=\alpha C$ and A, B_1, and B_2 are Debye-Hückel and Onsager constants. The values of the physical constants of water–ethanol system[11] are set out in Table 1. In all the calculations the correlation coefficient was found to lie between 0.99 and 1 and the error of estimate

Table 1. Physical Constants[a] of Water+Ethanol Mixture at 25 °C

% Ethanol w/w	ε	η CP	B_1 $\mathrm{mol^{-1/2}\,dm^{3/2}}$	B_2 $\mathrm{mol^{-3/2}\,\Omega\,cm^2\,dm^{3/2}}$	A
0	78.3	0.8904	0.2299	60.57	0.51108
10	72.8	1.323	0.2564	42.28	0.57008
20	67.0	1.815	0.2904	32.12	0.64569
30	61.1	2.180	0.3335	28.00	0.74143
40	55.0	2.350	0.3905	27.38	0.86814
50	49.0	2.400	0.46437	28.41	1.03238
60	43.4	2.240	0.55902	32.34	1.23851
70	38.0	2.037	0.67996	38	1.51168
80	32.8	1.748	0.84791	47.67	1.88505
90	28.1	1.424	1.06931	63.22	2.37725
100	24.3	1.096	1.32970	88.33	2.95614

a) Data from Ref. 11.

Table 2. Values of Λ_0 of Compounds I in Water+Ethanol Mixture at 25 °C

% Ethanol	Λ_0/ Ohm^{-1} cm^2 mol^{-1}			
w/w	H	2-	3-	4-
0	174.91	153.85	160.53	158.11
10	125.47	104.61	111.77	108.57
20	95.76	77.70	82.99	80.93
30	80.05	65.83	71.96	68.82
40	72.12	59.60	66.30	62.55
50	65.76	54.62	63.76	58.67
60	66.62	53.44	62.50	57.53
70	67.33	54.24	65.36	59.07
80	71.53	57.27	66.77	61.59
90	78.49	61.38	73.84	67.78
100	84.41 (62.6)[a]	68.05	80.58	72.60

Error of estimate is 0.02% and r lies between 0.99 and 1.
a) Data from Ref. 3.

Table 3. Values of K_A of Compounds I in Water+Ethanol Mixture at 25 °C

% Ethanol	K_A/ dm^3 mol^{-1}			
w/w	H	2-	3-	4-
0	1.12	5.44	1.80	3.76
10	5.03	12.29	5.69	9.77
20	10.73	16.19	12.14	13.61
30	14.40	20.17	15.78	17.85
40	19.24	25.15	20.58	22.96
50	23.39	30.59	25.79	28.49
60	30.85	38.40	32.27	36.76
70	35.42	46.15	39.48	44.37
80	49.98	61.27	52.50	57.22
90	69.67 (41.7)[a]	86.1	73.07	79.02
100	98.49 (107)[a]	122.14	105.65	112.74

Error of estimate is 0.02% and r lies between 0.99 and 1.
a) Data from Ref. 3.

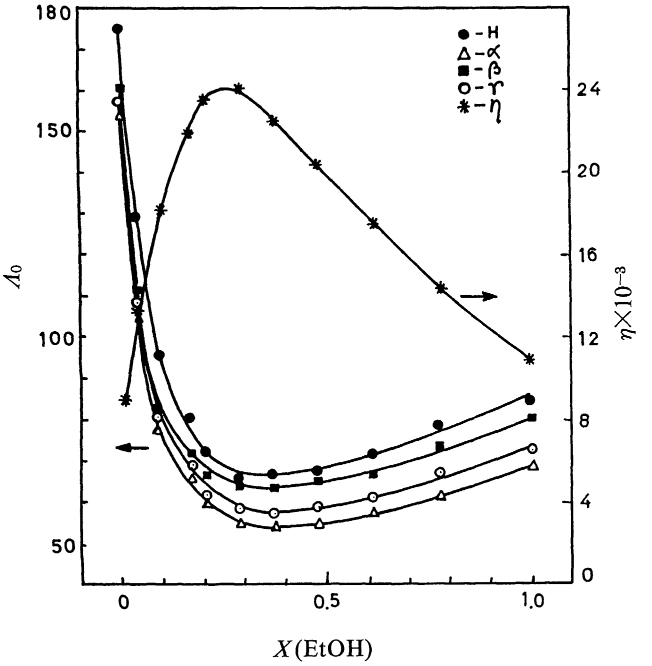


Fig. 1. Variation of Λ_0 and η against mole fraction of ethanol.

was 0.02%. The initial value of Λ_0 needed for calculation was obtained from the plot of Λ against $\sqrt{C}$. The results of such calculations are set out in Tables 2 and 3.

The variation of Λ_0 of these compounds and the η of the solvent mixtures with the mole fraction of ethanol are shown in Fig. 1. The viscosity of water–ethanol mixtures increases up to a mole fraction of 0.31 and then gradually decreases. The Λ_0 values of these iodide salts decrease up to this mole fraction and then increase in ethanol-rich region, showing opposite behavior to the viscosity of the medium. The association constant, K_A, of these salts gradually increases with increase in ethanol composition (Fig. 2). The association constants are in the order H<3-<4-<2-. The Λ_0 values are in the order H>3->4->2-. These results indicate that the viscosity of the medium plays an important role on the mobility of ions in solution.

Fuoss[12] has pointed out that the plot of $\log K_A$ vs. $1/\varepsilon$ should be linear in the vicinity of the dielectric constant, lying below 40. This prediction by Fuoss is obeyed by NMPI and its methyl substituted derivatives in alcohol-rich region where the dielectric constant lies

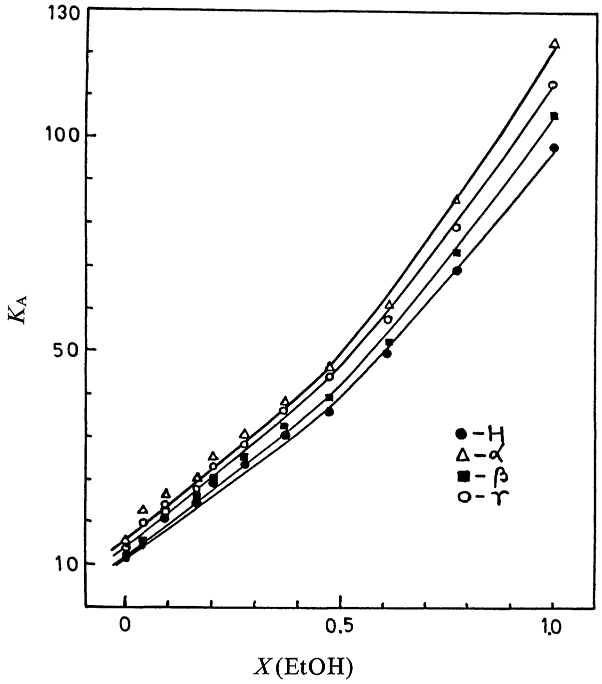


Fig. 2. Variation of K_A with mole fraction of ethanol.

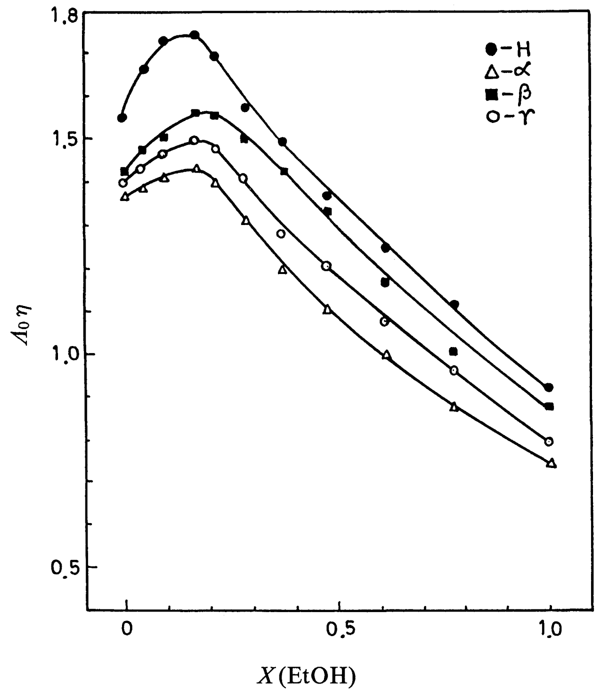


Fig. 4. Variation of Walden product with mole fraction of ethanol.

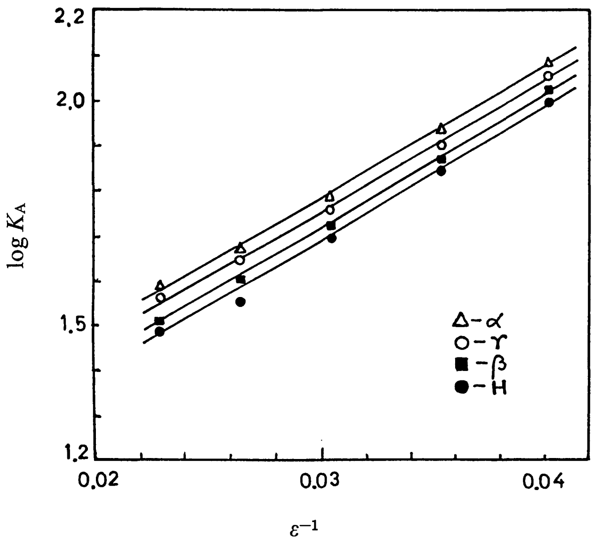


Fig. 3. Variation of log K_A with $1/\varepsilon$.

Table 4. Values of $\Lambda_0\eta$ of Compounds **I** in Water+Ethanol Mixture at 25 °C

% Ethanol	$\Lambda_0\eta$			
w/w	H	2-	3-	4-
0	1.557	1.370	1.429	1.408
10	1.660	1.384	1.479	1.436
20	1.738	1.410	1.506	1.469
30	1.745	1.435	1.569	1.500
40	1.695	1.401	1.558	1.470
50	1.578	1.311	1.500	1.408
60	1.492	1.197	1.424	1.289
70	1.372	1.105	1.331	1.203
80	1.250	1.001	1.167	1.077
90	1.118	0.874	1.051	0.965
100	0.925	0.746	0.883	0.796

below 40 (Fig. 3).

The Walden product $\Lambda_0\eta$ for the entire solvent range for these salts is given in Table 4 and shown in Fig. 4 as a function of mole fraction of ethanol. The Walden product passes through a maximum which lies between 0.15 and 0.2 in ethanol mole fraction and then decreases at higher ethanol content. It has been pointed out[13] that the Walden product of water–alcohol mixtures passes through a maximum and the values are quite high as expected for highly hydrogen-bonded solvents. Both cation $NMPR^+$ and anion I^- can move through the solutions overcoming the viscous forces in the solvent system. The structure of water determines the Walden product in water–ethanol mixtures. The trend in the Walden product of these salts in water–ethanol solvent mixtures clearly indicates strong interaction between water and ethanol.

The Λ_0 and K values indicate that NMPI and 3-CH_3 salts are more close to each other than 2- and 4-salts. The ion–ion interaction takes place between $NMPR^+$ and I^- to form ion-pairs through preferential solvation of these ions in both water-rich and ethanol-rich regions. The electron donating capacity of methyl group at 2- and 4-positions partially neutralizes the positive charge in the pyridinium ion. Such partial neutralization is not possible in NMPI and 3-CH_3 salts. Therefore the 2- and 4-salts are less solvated than NMPI and 3-CH_3 salts. This results in greater ion–ion interaction between $NMPR^+$ and I^- ions of 2- and 4-salts is reflected in the low values of Λ_0 and high values of K_A than the corresponding values of NMPI and 3-CH_3 salts. All these data favor the existence of solvent shared ion-pairs of these salts in water–ethanol solvent mixtures.

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