Ultrasonic Relaxation Evidence for Two Types of Ion Pairs in *N*-Methylpyridinium Iodide Solutions

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Summary The two ultrasonic relaxations found in 95% (v/v) aqueous acetone solutions of *N*-methylpyridinium iodide were assigned to formation of solvent separated (concentration dependent) and contact ion pairs (concentration independent relaxation).

As part of an investigation of the rate and mechanism of charge-transfer complex formation we have investigated solutions of *N*-methylpyridinum iodide (MPI). This compound has been shown by Kosower[1] to possess a charge-transfer band in its electronic spectrum.

In our attempts to define the rate constants for the ionic association process of MPI, employing ultrasonic relaxation measurements, we discovered that not one but two molecular events occur in 95% aqueous acetone (v/v) manifested by the observation of two distinct relaxation processes. (This solvent mixture was chosen to assure solubility of substrate; it has an interpolated dielectric constant of 22·1).[2] The instrumentation used has been described.[3]

For a system showing n ultrasonic relaxations the excess absorption μ is given by equation (1) where μ_{max} is the

MPI concentration (M)	B^a $\times 10^{17}$	$fr_1 \times 10^{-6}$ (s^{-1})	$fr_2 \times 10^{-6}$ (s^{-1})	fr_1(calc.) $\times 10^{-6}$ (s^{-1})	fr_2(calc.) $\times 10^{-6}$ (s^{-1})
0·30	50	120	20	120	20
0·20	46	100	20	100	20
0·15	40	90	20	91	19
0·10	38	72	—	68	16

[a] B has units of neper s^2 cm^{-1}.

$$\mu = \sum_{i=1}^{n} \frac{2\mu_{\max} f/fr_i}{1 + (f/fr_i)^2} \qquad (1)$$

maximum value of μ for the ith process, fr_i is the relaxation frequency for the ith process, $\mu = (\alpha - \alpha_0)u/f$, α is the sound absorption coefficient of the solution, α_0 is the absorption coefficient in the absence of chemical relaxation and is obtained by data fitting, f is the frequency, and u is the velocity of sound, 1225 m s^{-1}.

The Figure presents the essential results. A 0·1M solution of the salt exhibits only one relaxation: increased concentration brings on a second relaxation process. While the high-frequency relaxation is strongly concentration dependent the lower-frequency process is nearly concentration independent. The low-frequency relaxation is not found in NaI solution.

To interpret the above data a two-step Eigen type[4] mechanism is proposed for the association process [equation (2)] where MP^+ (solv) is a solvated cation, I is the anion,

$$MP^+(solv) + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MP(solv)I \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MPI \qquad (2)$$

MP(solv)I is the solvent separated ion pair, and MPI is the contact ion pair.

Equations for the two relaxation frequencies and the method of data treatment were taken from the literature.[4,5]

Conductance measurements gave an association constant of 220 ± $20M^{-1}$. This value was used in calculating the free-ion concentrations.[5]

The Table presents the results, giving observed and caculated relaxation frequencies. The rate constants derived from the data fitting are: $k_1 = 3{\cdot}0 \pm 0{\cdot}3 \times 10^{10}\ M^{-1}\,s^{-1}$, $k_{-1} = 1{\cdot}4 \pm 1{\cdot}0 \times 10^7\,s^{-1}$, $k_2 = 1{\cdot}6 \pm 0{\cdot}8 \times 10^7\,s^{-1}$, $k_{-2} = 1{\cdot}0 \pm 0{\cdot}5 \times 10^8\,s^{-1}$. The value of k_1 is in reasonable agreement with the estimated (Debye equation) diffusion controlled rate constant ($8{\cdot}7 \times 10^{10} M^{-1}\,s^{-1}$ calculated from experimental values of Λ_0).[6] As is often the case the experimental value of k_1 is lower than the Debye estimate.

The Table indicates that the kinetic agreement is excellent. K_T calculated from the rate constants (these derived solely from kinetic results) is some ten times larger than the conductance value. One should point out that k_{-1} especially is subject to error since it is obtained as a small difference between two larger numbers in the data fitting process and only its order of magnitude is certain.

In summary, under the conditions of our experiment, the concentrations of the two species, which we suggest are the solvent separated and contact ion pairs, are very similar since no ultrasonic effect would be observed if one species were highly favoured. It will be of great interest to see if the processes here described bear any relationship to the u.v. spectral changes quoted by Kosower.

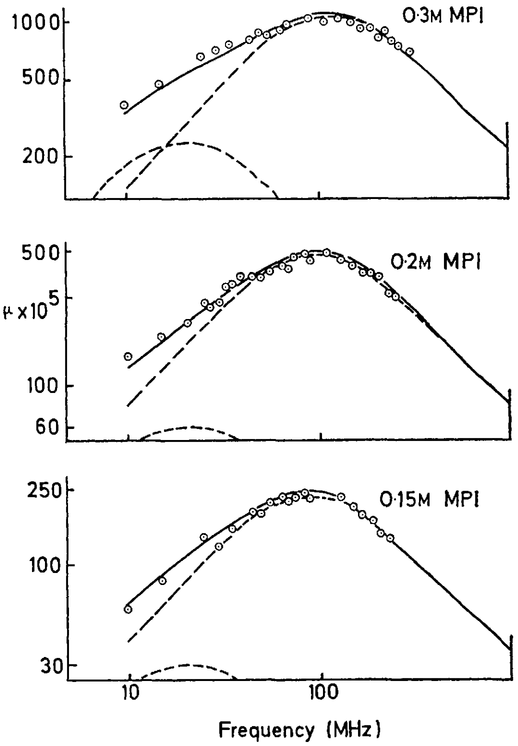

FIGURE. Plot of excess absorption per wavelength *vs.* frequency.

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