Speciation of A 1-Alkyl-4-Cyanopyridinium Iodide Using the Charge Transfer Band*[1]

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The intensity of the charge transfer band of 4-cyano-1-(3,7-dimethyloc-tyl)pyridinium iodide (Py^+I^-) has been used to estimate the contact ion pair (CIP) concentration in a number of solvents. In several nonhydroxylic solvents with dielectric constant between 4 and 8 the molar integrated intensity of the low frequency charge transfer band is very similar, and these values have been averaged to estimate the intrinsic molar intensity of the CIP.

A nonlinear concentration dependence of this intensity in 2-propanol shows the presence of a substantial concentration of free ions in that solvent, and an ion association constant, $K_A = 3.9 \times 10^3$, was found. Tributylphosphate gives similar evidence of dissociation, but only at lower concentrations. A value of 3.7×10^6 was estimated for K_A. In the other solvents studied, dissociation is hard to distinguish from other effects which reduce the molar intensity at low concentrations. Both tributyl phosphate and 2-propanol also give molar intensities below the average of less polar solvents at high Py^+I^- concentration. This is regarded as evidence for the presence of solvent separated ion-pairs (SSIP). Solvent separated ion-pairs are not abundant, however, in the solvents studied. The CIP:SSIP concentration ratio seems to be 4–6 in tributylphosphate and 2-propanol, and is still higher in the other solvents.

With increasing concentration the charge transfer band shifts to higher frequency. The magnitude of the shift depends on the solvent, and is most notable in chlorobenzene. A theory is developed which attributes this shift to the increase in the dielectric constant of the medium brought about by the ion-pairs. The effect could be attributed to higher aggregation, but the degree of aggregation would have to increase continuously with concentration, even at concentrations $\sim 10^{-4}$ M. The idea of dielectric modification can also be folded together with aggregation, with the former predominant at low concentration and the latter at higher concentration ($\sim 10^{-3}$ M).

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.
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INTRODUCTION

The idea that contact ion pairs (CIP) and solvent separated ion pairs (SSIP) might coexist appears to have been introduced by Winstein and coworkers,[2] and, independently, at about the same time, by Sadek and Fuoss.[3] It has been extremely useful in explaining solvolytic and other sorts of reactivity.[4-7] However, in spite of the many papers on the speciation of ion pairs and ion aggregates,[8-15] it is still hard to distinguish among CIP, SSIP, free ions, and higher aggregates, when all may coexist in equilibrium. In the present paper spectrophotometric methodology for studying ion pair equilibria is further developed, and applied to 4-cyano-1-(3,7-dimethyl-octyl)pyridinium iodide (Py^+I^-). The interest of M. M. K. was first drawn to the richness of ion pair chemistry when he was an exchange visitor in Prof. D. E. Sunko's laboratory many years ago. This work has a large part of its origins in that visit. It seems very appropriate to dedicate this paper to Prof. Sunko, who has contributed so much to solvolysis chemistry and to our knowledge of the kinetic characteristics of ion pairs, and we are pleased to do so.

Following Bagchi,[14] and Jordon[16] and their coworkers, we have used the long wavelength (low frequency) charge transfer band of Py^+I^- to characterize the various ionic species. In all the solvents of interest the charge transfer bands of Py^+I^- are well separated from the π to π^* spectrum, which is why Py^+I^- was used. In each solution we have fitted the low frequency charge transfer band to a log-normal equation and used this equation to obtain the integrated area of the band. We have assumed that this band is entirely due to the CIP and its aggregates. We examine the assumption that the integrated intrinsic area of this band is solvent-insensitive, and that variations in molar intensity, from one solvent to another, primarily reflect variations in the abundance of the CIP. This assumption is supported by the observation that the molar intensity, corrected for ion pair dissociation, is similar in a number of solvents. The somewhat surprising conclusion is reached that the CIP:SSIP concentration ratio is probably at least 4 in all the solvents studied.

In chlorobenzene the frequency of maximum absorption, ν_0 is quite concentration dependent. This behavior is also observed to a lesser extent in other solvents. It may be due to further aggregation, beyond ion pairs, but a theory based on the effect of the solute on the dielectric constant of the medium, which we introduce, gives a plausible account of the effect, and we prefer it.

It should be possible to evaluate the ion association constant, K_A, from the variation in the molar intensity with concentration, and we have done so in tributylphosphate and in 2-propanol. However, in many solvents it is not clear that the effect of dissociation can be separated from the higher order effect mentioned above, and/or experimental artifacts.

EXPERIMENTAL

Materials. 4-Cyano-1-(3,7-dimethyloctyl)pyridinium iodide was prepared by heating 1-iodo-3,7-dimethyloctane with 4-cyanopyridine at 80 °C, for 24–48 hours in a sealed tube. The resulting brown semi-solid product was recrystallized from a 1:5 mixture of ethyl ether and ethyl acetate to give a yellow, crystalline product in ~15% yield. On heating, this material turned red-brown without liquefying at 110–112 °C. The ^1H NMR spectrum of this substance, in $CDCl_3$ solution, was consistent with its assigned structure. With reference to tetramethylsilane it showed a doublet at 9.57 ppm, 6.2 Hz, rel. wt. of 2; a doublet at 8.35 ppm, 6.2 Hz, rel. wt. of 2 (these two doublets represent the 4 aromatic hydrogens) a multiplet at 5.0 ppm, rel. wt. of 2 (the aliphatic

methylene adjacent to the positive nitrogen) a doublet at 1.03 ppm, 6.5 Hz, rel. wt. of 3 (the 3-methyl group) and a doublet at 0.85 ppm, 6.6 Hz, rel. wt. of 6 (the two methyl groups on the 7-carbon). It also showed several broad bands of unidentified structure between 1.0 and 2.2 ppm, presumably due to the rest of the alkyl group hydrogens. In addition it showed a broad peak at 1.7 ppm, which we believe represents exchangeable hydrogen, mostly water; and a small irregular peak at 3.65 ppm, due to an unidentified impurity.

Anal. Calcd for $C_{16}H_{25}N_2I$: C 57.62, H 6.77, N 7.53, I 34.09; found:[17] C 51.88, H 6.61, N 7.42, I 33.87.

The general method of Fieser[18] was used to prepare 1-iodo-3,7-dimethyloctane from 3,7-dimethyl-1-octanol, NaI, and H_2SO_4. 3,7-Dimethyl-1-octanol and 4-cyanopyridine were purchased from Aldrich Chemical Co., as were tetrabutylammonium iodide, 1-dodecanethiol and all the organic solvents used. The solvents were carefully redistilled before use, and all of them had appropriate boiling points. Tetrabutylammonium iodide was recrystallized before use.

Methods. Electronic spectra were obtained with a Milton Roy Spectronic 3000 diode array spectrophotometer with a diode spacing of 0.38 nm per diode. Cells of 0.10, 1.00, 2.00, and 5.00 cm path length were used. The 0.10 and 1.00 cm cells were rectangular. The 2.00 and the 5.00 cm cells were cylindrical.

The iodide ion of Py^+I^- is sensitive to air oxidation, giving I_3^- and, presumably, oxygen-derived anions. The pyridinium ion appears to catalyze this reaction. It is easy to detect, because of the intense absorption of I_3^- at 365 nm. To avoid air oxidation, solvents were degassed with N_2 before use and solutions were protected from air as well as reasonably possible. Nevertheless, to obtain spectra free of the triiodide absorption it was necessary to include small concentrations of thiols in the test solutions. Typically 3×10^{-3} to 3×10^{-2} M 1-dodecanethiol was used. The concentration of thiol did not affect ν_0 up to $\sim 5 \times 10^{-2}$ M in chlorobenzene, and the molar integrated intensity was nearly constant, increasing by $\sim 3\%$. Thiols are known to be photochemically activated oxygen scavengers.[19]

The long wavelength charge transfer band of Py^+I^- has wave length of maximum absorption, λ_{max}, between 390 and 600 nm in the solvents of present interest. It is overlapped by the second charge transfer band[20] and, in the more polar solvents, the short wavelength tail of the band of interest may be overlapped by the long wave-length tail of the π to π^* spectrum of Py^+. The band of interest was separated from the rest of the spectrum, and its integrated intensity estimated, by fitting the measured molar absorptivities, $\varepsilon(\nu)$ to a log-normal equation in frequency, ν, shown in Eq. (1),[21,22] from the shortest wavelength still judged to be free of interference to a wavelength at which absorbance is essentially zero. A total of ~ 700 $\varepsilon(\nu)$ values, obtained from

$$\varepsilon(\nu) = \frac{\varepsilon_0 b}{\nu - a} \exp\left\{ -\frac{c^2}{2} - \frac{1}{2c^2} \left[\ln\left(\frac{\nu - a}{b}\right) \right]^2 \right\} \quad \text{for} \quad \nu > a \quad (1)$$

$$\varepsilon(\nu) = 0 \quad \text{for} \quad \nu \leq a$$

$$\nu \equiv \text{frequency}; \qquad a \equiv \nu_0 - H\left(\frac{\rho}{\rho^2 - 1}\right); \qquad b \equiv H\left(\frac{\rho}{\rho^2 - 1}\right)\exp(c^2); \qquad c \equiv \frac{\ln \rho}{\sqrt{2\ln 2}}$$

$$H \equiv \nu_b - \nu_r; \qquad \rho \equiv \frac{\nu_b - \nu_0}{\nu_0 - \nu_r}$$

$\nu_b \equiv$ high frequency of half-maximum absorbtivity

$\nu_r \equiv$ low frequency of half-maximum absorbtivity

$\nu_0 \equiv$ frequency of maximum absorbtivity; $\qquad \varepsilon_0 \equiv$ absorbtivity at $\nu = \nu_0$

$$I = \varepsilon_0 c H \sqrt{2\pi} \left(\frac{\rho}{\rho^2 - 1}\right) \exp\left(\frac{c^2}{2}\right) \quad (2)$$
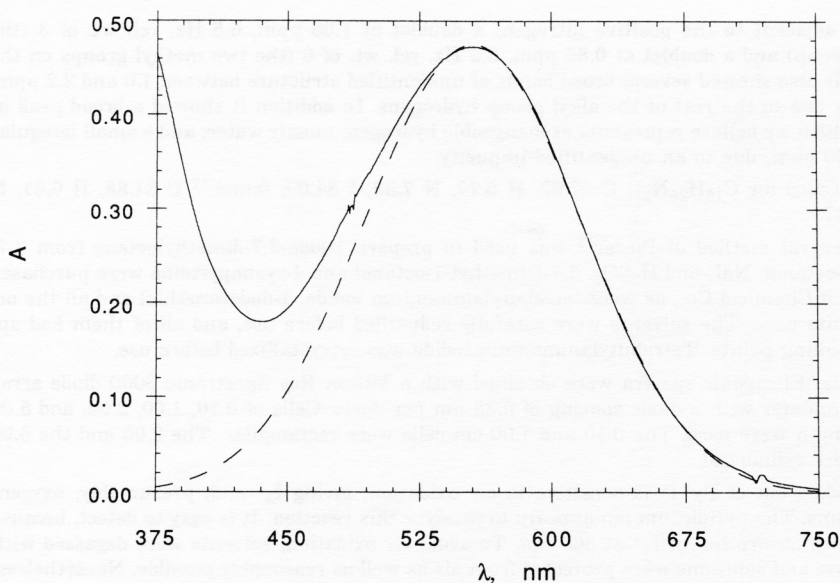
Figure 1. Plots of measured absorbance (solid line) and absorbance calculated from the $\varepsilon(\nu)$ values given by Eq. (1) – as a function of wavelength. The small irregularities in the experimental spectrum are instrumental artifacts. The spectrum is that of a 5.49×10^{-5} M solution of Py^+I^- in chlorobenzene, in a 5.0 cm cell.

the individual diodes were fitted. The four independent parameters of Eq. (1) are ν_0, the frequency of maximum absorption; ε_0, the molar absorptivity at $\nu = \nu_0$; H, the total width at half height; and ρ, a skewness parameter, defined above. These parameters were adjusted to minimize the sum of the squares of the discrepancies between the observed and calculated $\varepsilon(\nu)$ values. The average discrepancy between calculated and observed absorbances varied between $\sim 5 \times 10^{-4}$ for absorbances below 0.1 to $\sim 3 \times 10^{-3}$ for absorbances above 1.0. These values are not larger than the instrumental uncertainties, so the use of Eq. (1) does not introduce additional error where the band is not overlapped by other absorptions. The correspondence between Eq. (1) and the experimental spectrum in a typical case is shown in Figure 1. It was assumed that Eq. (1) also fits in the region of overlap. The integrated intensity of the band, I, was obtained from Eq. (2). It was reproducible with an average deviation from the mean value of $\pm 5\%$ when measurements were repeated from the beginning. A good deal of this scatter is thought to originate in errors of weighing small samples of Py^+I^-.

RESULTS AND DISCUSSION

Table I shows the four parameters which characterize the band of interest in each solvent for a number of concentrations. The results shown in Table I were selected as representative points from much larger bodies of data. They span the full concentration range studied in each solvent. For chlorobenzene and anisole it is evident that the parameters are concentration dependent. Figure 2 shows the appearance of spectra which are subject to the effect.

For chlorobenzene and tributylphosphate, spectra were also made from solutions containing low, fixed concentrations of Py^+I^-, and varying concentrations of tetra-

TABLE I

Log-Normal Parameters of the Charge Transfer Band in Solvents of Dielectric Constant K_E

C_0	$10^{-4}\nu_0/cm^{-1}$	$10^{-3}\varepsilon_0/M^{-1}cm^{-1}$	H/cm^{-1}	ρ
Chlorobenzene (CB, K_E = 5.62[a])				
1.12×10^{-5}	1.777	1.50	4256	1.23
2.24×10^{-5}	1.780	1.74	4313	1.24
3.35×10^{-5}	1.787	1.68	4466	1.26
7.82×10^{-5}	1.808	1.50	4967	1.34
1.68×10^{-4}	1.859	1.34	6370	1.53
2.79×10^{-4}	1.911	1.14	7835	1.70
Anisole (A, K_E = 4.33[a])				
1.33×10^{-5}	1.840	1.34	4398	1.22
2.00×10^{-5}	1.849	1.45	4465	1.21
3.33×10^{-5}	1.846	1.42	4490	1.23
6.66×10^{-5}	1.852	1.38	4619	1.25
9.99×10^{-5}	1.860	1.38	4783	1.28
1.67×10^{-4}	1.877	1.35	5137	1.32
Trioctylphosphate (TOP, K_E = 4.5[b])				
1.81×10^{-5}	1.853	1.09	4790	1.25
4.51×10^{-5}	1.852	1.27	4769	1.24
9.03×10^{-5}	1.855	1.33	4774	1.22
1.35×10^{-4}	1.861	1.35	4871	1.25
2.26×10^{-4}	1.868	1.38	4976	1.26
Tetrachloroethane (TCE, K_E = 8.20[a,c])				
2.14×10^{-5}	2.024	1.22	4700	1.13
5.35×10^{-5}	2.019	1.36	4651	1.15
1.07×10^{-4}	2.018	1.42	4655	1.16
1.61×10^{-4}	2.017	1.44	4632	1.16
2.68×10^{-4}	2.020	1.46	4700	1.17
Tributylphosphate[e] (TBP, K_E = 7.95[a,d])				
1.85×10^{-5}	1.979	0.92	5291	1.20
3.70×10^{-5}	1.985	0.98	5458	1.22
9.24×10^{-5}	1.980	1.00	5331	1.23
1.85×10^{-5}	1.985	1.98	5314	1.23
2.77×10^{-5}	1.984	1.01	5336	1.24
4.62×10^{-4}	1.984	1.04	5402	1.25
Parachlorotoluene (PCT, K_E = 6.08[a,c])				
8.2×10^{-6}	1.770	0.86	4404	1.25
1.20×10^{-5}	1.766	0.71	4362	1.24
2.04×10^{-5}	1.771	1.01	4558	1.29
4.08×10^{-5}	1.776	1.10	4684	1.31
8.06×10^{-5}	1.791	1.00	5083	1.37
1.50×10^{-4}	1.816	0.86	5816	1.47
2-Propanol (IPA, K_E = 18.3[a])				
1.02×10^{-4}	2.513	0.202	7329	1.13
2.02×10^{-4}	2.497	0.291	7001	1.14
4.04×10^{-4}	2.505	0.394	7251	1.17
8.34×10^{-4}	2.505	0.476	7198	1.19
2.08×10^{-3}	2.496	0.551	7083	1.21
4.17×10^{-3}	2.499	0.598	7035	1.24
1.04×10^{-2}	2.503	0.807	6809	1.13

(a) Reference 28.
(b) J. Gibson, *Solvent Extraction and Liquid Membrane Properties of Trioctylphosphate*. University of Minnesota M.A. Thesis, 1982, p 55. The dielectric constant determined was that of tri-*n*-octylphosphate, but that of the branched compound would be very similar.
(c) Measured at 20 °C. The value would be slightly lower at 25 °C.
(d) Measured at 30 °C. The value would be slightly higher at 25 °C.
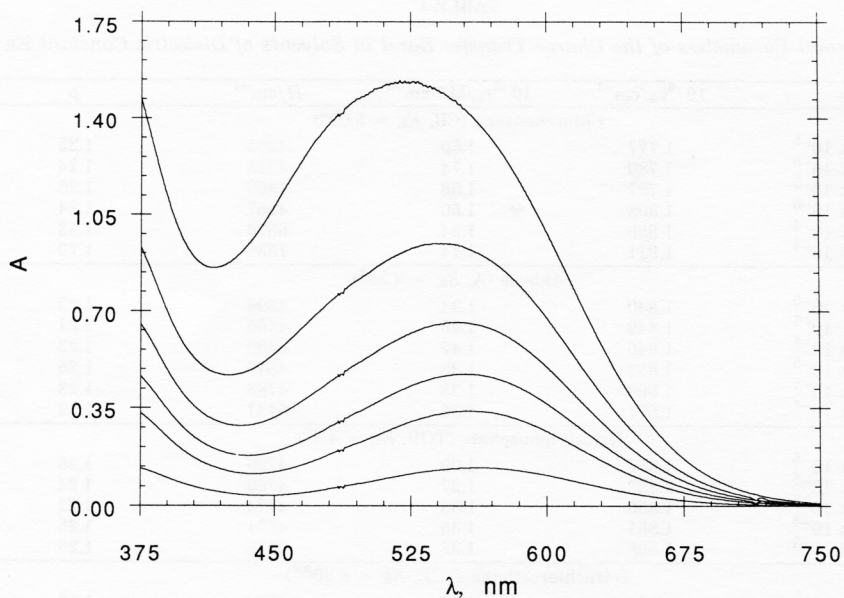(e) Provisional results.

Figure 2. Spectra of Py^+I^- in chlorobenzene, in a 5.0 cm cell. The concentrations are 1.57×10^{-5}, 3.92×10^{-5}, 5.49×10^{-5}, 7.84×10^{-5}, 1.18×10^{-4}, and 1.92×10^{-4} M. The irregularities around 487 nm and 717 nm are instrumental artifacts.

TABLE II

Log-Normal Parameters of the Charge Transfer Band with Fixed Concentrations of Py^+I^- and Varying Concentration of TBAI.

(TBAI)/M	$10^{-4}\nu_0/cm^{-1}$	H/cm^{-1}	ρ	$10^{-6}I/M^{-1}\,cm^{-2}$
CB; $(Py^+I^-) = 2.41 \times 10^{-5}M$				
0	1.781	4221	1.22	6.28
2.53×10^{-5}	1.786	4317	1.23	6.53
5.07×10^{-5}	1.800	4642	1.28	7.82
1.52×10^{-4}	1.842	5515	1.39	9.36
3.04×10^{-4}	1.895	6381	1.45	10.80
7.60×10^{-4}	1.970	6188	1.26	11.59
1.17×10^{-3}	1.998	5833	1.17	11.03
TPB; $(Py^+I^-) = 3.16 \times 10^{-5}$ M				
0	1.983	5387	1.27	5.63
3.00×10^{-5}	1.986	5437	1.26	6.05
1.50×10^{-4}	1.988	5503	1.27	6.33
3.00×10^{-4}	1.991	5550	1.30	6.64
1.50×10^{-3}	1.995	5569	1.27	6.45
3.00×10^{-3}	2.005	5749	1.29	6.97
6.60×10^{-3}	2.020	5870	1.28	6.80

butylammonium iodide (TBAI). Parameters characterizing these spectra are shown in Table II. They show changes with total salt concentration very similar to those seen when only Py$^+$I$^-$ is present. With the larger concentration range made possible by the greater solubility of TBAI it becomes clear that spectra made from solutions in tributylphosphate show trends in the same directions as those from chlorobenzene solution, though they are much weaker. Trioctylphosphate solutions show similar trends though they are attenuated compared to chlorobenzene. The systematic changes are attributed to interactions between ion pairs, the nature of which will be discussed below.

In any given medium the fraction of ion-pairs which are solvent separated was considered constant. For each solvent, therefore, the ion-pair charge transfer band should have a characteristic integrated molar intensity, I_M. With increasing dilution, however, the observed molar intensity, I, may diminish due to ion pair dissociation. Tables III and IV show the results for tributylphosphate and chlorobenzene. Neglecting the interaction between ion-pairs, and activity coefficients, Eq. (3) should account for the variation in I with C_o, where C_o is the stoichiometric concentration of Py$^+$I$^-$. Equation (3) follows

$$IC_o = I_M [(C_o + 1/2K_A) - (C_o/K_A + 1/4K_A^2)^{1/2}] \tag{3}$$

straight forwardly from the mass-action expression, Eq. (4), and the assumption that the fraction of ion pairs which are in contact is concentration-independent in any given solvent, which leads to Eq. (5). Both solvent separated and contact ion pairs are included in Py$^+$I$^-$. Activity coefficients are neglected in Eqs. (3) and (4), because we

TABLE III

Experimental Areas and Accuracy of Fit for Various Solute Concentrations in Tributylphosphate.

C_o/M	$10^{-6}I$/M^{-1} cm^{-2}	Δ^a/%	Δ^b/%	Δ^c/%
1.85×10^{-5}	5.02	7	8	8
2.54×19^{-5}	5.81	−5	−5	−5
3.70×10^{-5}	5.73	−2	−2	−2
5.07×10^{-5}	5.92	−3	−4	−4
9.24×10^{-5}	5.75	2	1	1
1.27×10^{-4}	6.00	−1	−2	−3
1.48×10^{-4}	5.08	17	16	16
1.85×10^{-4}	5.77	4	3	2
2.77×10^{-4}	5.87	3	2	−1
2.96×10^{-4}	5.80	4	3	2
3.80×10^{-4}	6.27	−3	−4	−5
4.62×10^{-4}	6.06	0	−1	−1
7.25×10^{-4}	6.13	0	−1	−2
8.57×10^{-4}	5.87	5	3	2
1.48×10^{-3}	6.21	−1	−2	−3
1.72×10^{-3}	6.06	2	1	0

(a) All the data points were used in evaluating I_M and K_A.
(b) Only data for (Py$^+$I$^-$) $\leq 3.8 \times 10^{-4}$ M was used in evaluating I_M and K_A, but calculated and observed areas are compared for all data points
(c) Only data for (Py$^+$I$^-$) $\leq 2.8 \times 10^{-4}$ M was used in evaluating I_M and K_A, but calculated and observed areas are compared for all data points.

TABLE IV

Experimental Areas and Accuracy of Fit for Various Solute Concentrations in Chlorobenzene.

C_0/M	$10^{-6}I$/M^{-1} cm^{-2}	Δ^a/%	Δ^b/%	Δ^c/%
1.12×10^{-5}	6.86	-1	6	6
1.57×10^{-5}	7.90	-6	-3	-3
2.24×10^{-5}	8.06	-1	-1	0
2.35×10^{-5}	8.64	-6	-7	-1
3.35×10^{-5}	8.07	7	4	4
3.92×10^{-5}	8.60	3	-2	-8
5.49×10^{-5}	8.96	4	-3	2
5.59×10^{-5}	8.00	17	9	10
7.82×10^{-5}	8.05	21	11	12
7.84×10^{-5}	9.43	3	-5	-4
1.12×10^{-4}	9.05	11	1	2
1.18×10^{-4}	10.51	-4	-13	-12
1.68×10^{-4}	9.42	11	-1	0
1.92×10^{-4}	14.15	-25	-34	-33
2.79×10^{-4}	10.08	7	-6	-5

(a) All the data points were used in evaluating I_M and K_A.
(b) Only data for $(Py^+I^-) \leq 1.12 \times 10^{-4}$ M was used in evaluating I_M and K_A, but calculated and observed areas were compared for all data points.
(c) Only data for $(Py^+I^-) \leq 5.6 \times 10^{-5}$ M was used in evaluating I_M and K_A, but calculated and observed areas are compared for all data points.

$$K_H = (Py^+I^-) / (Py^+)(I^-) \qquad (4)$$

$$IC_o = I_M(Py^+I^-) \qquad (5)$$

doubted the applicability of the Debye-Hückel equation to liquids of such low dielectric constant, especially in the presence of substantial ion-pair concentrations, and lacked any other way to evaluate them. As a result, K_A is not a real equilibrium constant, and may be expected to vary somewhat with C_o. We have nevertheless, assumed it to be concentration independent.

A variant of Eq. (3) was used to determine best values of I_M and K_A. These parameters were systematically varied and used to calculate I values. Parameters were selected so as to minimize the sum of the squares of the discrepancies between observed and calculated I values.[23] The values of the parameters are shown in Table V. For tributylphosphate and chlorobenzene Tables III and IV show the correspondence between calculated and observed area. For tributylphosphate the average discrepancy is 4%, which approximates the reproducibility of the measurements. For chlorobenzene the average discrepancy was 9%; roughly twice that expected. For chlorobenzene there is a marked tendency for the discrepancies to be larger at higher solute concentrations.

Since there is also a change in ν_o at higher concentrations in chlorobenzene, both data sets were truncated. The highest one-third of concentrations were eliminated for both solvents, and the least-squares fitting procedure was repeated. Then a further third of the concentrations were removed, and the least-squares fitting procedure was applied only to the lowest third of the concentrations studied. In chlorobenzene the first truncation removes the concentrations which give rise to most of the concentra-

TABLE V

Values of I_M *and* K_A

Solvent	Cutoff Conc./M	K_A/M^{-1}	$10^{-6} I_M/M^1 cm^2$
TBP	1.7×10^{-3}	2.2×10^6	6.3
TBP	3.8×10^{-4}	2.9×10^6	6.2
TBP	2.8×10^{-4}	3.7×10^{6b}	6.1[b]
CB	2.8×10^{-4}	3×10^5	12.2
CB	1.1×10^{-4}	8×10^5	10.1
CB	5.6×10^{-5}	7×10^5	10.3
A	1.7×10^{-4}	3×10^6	7.4
A	8.9×10^{-5}	9×10^6	7.0
A	4.1×10^{-5}	7×10^6	71.[b]
TOP	2.3×10^{-4}	3×10^5	8.3
TOP	9.0×10^{-5}	4×10^5	8.1[b]
TCE	3.0×10^{-4}	8×10^5	6.9
TCE	1.1×10^{-4}	4×10^5	7.7[b]
PCT	1.5×10^{-4}	2×10^5	7.4
PCT	8.1×10^{-4}	4×10^5	6.6
PCT	4.1×10^{-4}	4×10^5	6.5[b]
IPA	1.0×10^{-2}	4.3×10^{3b}	6.3[b]
IPA	1.0×10^{-3}	3.9×10^3	6.6

(a) Except where rated as a preferred value, K_A, values are not considered physically significant.

(b) Preferred value, for reasons discussed in the text.

tion-dependent change in v_o. Table V shows the effect of truncation on the parameters and the discrepancies generated by the new parameters are shown in Tables III and IV. Discrepancies are tabulated for the full data sets even though truncated sets were used in evaluating the parameters. For tributylphosphate neither I_M nor the discrepancies are much changed by the truncations. However for chlorobenzene the first truncation changes I_M by ~20%. The second truncation produces little further change, but there is some question as to whether the remaining concentration range – 1.1×10^{-5} to 5.6×10^{-5} – is sufficient to reliably assign the parameters. In both solvents the K_A values vary substantially with truncation.

In these calculations K_A is being evaluated from the decrease in I at high dilution. Tables III and IV show that this is small in both solvents. In tributylphosphate I approaches an approximately constant value at higher concentration, so a value of K_A can be estimated from the small decrease in more dilute solutions. Although K_A cannot be evaluated from I values obtained from the mixed salt solutions, the solutions in TBP also show a sharp increase in I when TBAI is added, as shown in Table II. This tends to confirm the origin of the effect. In chlorobenzene I increases with concentration at the higher concentrations, presumably for the same reason that v_o changes. This introduces a significant uncertainty into I_M, and makes it impossible to evaluate K_A reliably.

Data for the other solvents were treated in the same way, and the I_M and K_A values so determined are summarized in Table V. Since it seems likely that I_M shows some drift toward higher values at higher C_o in all solvents we prefer the I_M values derived from the truncated data sets except in the case of 2-propanol, where the higher concentrations are needed to avoid extensive dissociation. Anisole and *p*-chlorotoluene behave like chlorobenzene; tetrachloroethane behaves like tributylphosphate, and tri-

octylphosphate is intermediate. 2-Propanol is unique, in that it has a much higher dielectric constant than the other solvents, and supports much more dissociation. For this reason there is a much larger concentration-related reduction in I on dilution, and K_A is much more reliable. Chlorobenzene, anisole, trioctylphosphate, and p-chlorotoluene all have dielectric constants significantly lower than that of tributylphosphate, and would be expected to have higher values of K_A. The determined values are lower, which makes them further suspect. Thus, the only values of K_A in Table V that we regard as physically significant are those for tributylphosphate and 2-propanol. The others are useful in the determination of I_M values, but are probably seriously affected by artifacts, such as minor amounts of oxidation of I^- in the most dilute solutions, and the inaccuracies in our assumptions. It is our intention eventually to redetermine the K_A values by conductance. On the other hand, apart from that for chlorobenzene solutions, the I_M values are not much altered by truncation, the changes that do occur do not appear to be systematic, and the determined values are not very sensitive to the K_A values used. We, therefore, believe that the I_M values are reliable, even though most of the K_A values are not.

It was suggested above that the intrinsic molar intensity of the charge transfer band of the CIP, I_M°, would be approximately constant. If this is so, I_M should approach a common value, I_M°, in solvents which do not support a significant concentration of SSIP. If the chlorobenzene results are set aside because we may not have succeeded in separating out a higher order effect, it is not clear that the remaining values of I_M differ from their average by more than their uncertainties. However, earlier work provides convincing evidence for the existence of SSIP,[2-7] and intuition suggests that it should be most abundant in 2-propanol and tributylphosphate. Triethylphosphate has a hydrogen bond acceptor parameter of 0.77,[24] indicating that phosphate esters should be good cation solvents, and tributylphosphate has one of the higher dielectric constants among our solvents. 2-Propanol has the highest dielectric constant among our solvents, and is a relatively good solvent for both cations and anions.[24] These two solvents do, indeed, have the lowest values of I_M. For TBP, values of I higher than the preferred value of I_M can be observed by adding TBAI to the solution, as shown in Table II. However, we believe that the gradual increase in I for total salt concentrations above 10^{-4} M is due to the higher order effect mentioned above and discussed below.

A value of 7.4×10^6 M^{-1} cm^{-2} was obtained for I_M° be averaging the I_M values for anisole, trioctylphosphate, tetrachloroethane, and p-chlorotoluene. Chlorobenzene was omitted because of the difficulties described above, and because it varies so widely from the others. If this value of I_M° is accepted the CIP:SSIP concentration ratio in tributylphosphate is 4.7 and in 2-propanol is 5.7. The other solvents probably support small concentrations of SSIP as well, and this may be one reason for the variation of their I_M values. In all of these solvents the observed proportion of SSIP is unexpectedly low.

The K_A values are essentially derived from the decrease in I on dilution. In 2-propanol I reaches a value only ~30% of I_M in our most dilute solutions, and K_A is clearly significant. The present value, 3.9×10^3, can be compared with the value, 3.2×10^3, which can be calculated for 1-ethyl-4-cyanopyridinium iodide from the data of Mackay and Poziomek.[25] We believe that K_A is also significant in tributylphosphate, because of the good fit to Eq. (4) (Table III) and the large body of data we collected (85 points). In addition, although the mixed salt data cannot be treated quantitatively, the fact that the value of I rises to its high concentration value when tetrabutylam-

monium iodide is added to dilute solutions of Py^+I^- in tributylphosphate is very supportive of our general treatment of this solvent.

The origin of the concentration-dependent change in ν_0 particularly in chlorobenzene, remains to be discussed. It could, of course, be caused by further aggregation. If so, however, this is probably not a simple equilibration with one additional species. Neither an equilibration with ion-pair dimers nor an equilibration with inverted micelles of fixed composition seem to explain the results. If an equilibration with one additional species were involved, spectra made after dividing each absorbance by the total ion-pair concentration in the solution generating it would show an isosbestic point. Figure 3 shows that they do not if K_A is used to calculate the ion-pair concentrations. As pointed out above, the value of K_A is unreliable, and probably low. However, neither a higher value of K_A, nor equating the ion-pair concentration to the total salt concentration produces an isosbestic point. Non-isosbestic behavior could be explained if the ion-pairs were equilibrating with a series of oligomers; dimers, trimers, *etc.* In that case the average aggregation number would increase steadily with concentration, and the observed spectra could be produced. However, in the absence of hydrophobic forces, such an explanation seems intuitively unattractive for these dilute solutions.
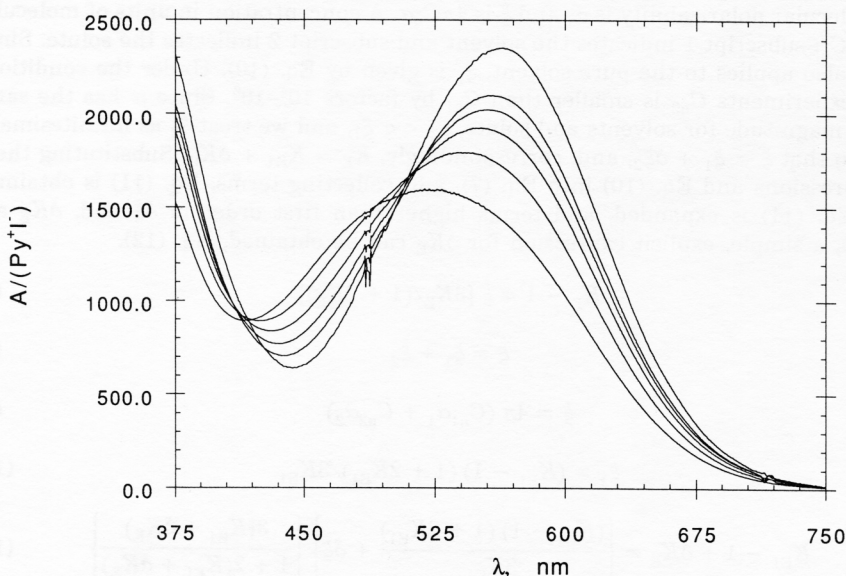

Figure 3. Spectra of Py^+I^- in chlorobenzene, each absorbance divided by the total ion-pair concentration, calculated from the stoichiometric salt concentration and $K_A = 7 \times 10^5$ M^{-1}. The stoichiometric salt concentrations, followed by the ion-pair concentrations are: 1.57×10^{-5}, 1.16×10^{-5}; 3.92×10^{-5}, 3.24×10^{-5}; 5.49×10^{-5}, 4.67×10^{-5}; 7.84×10^{-5}, 6.85×10^{-5}; 1.18×10^{-4}, 1.05×10^{-4}; 1.92×10^4, 1.76×10^{-4}. The solution of lowest concentration has the highest value of $A/(Py^+I^-)$ at 600 nm and the lowest value at 450 nm and the others are in regular order of increasing concentration at these wave lengths. The small irregularities at 487 nm and 717 nm are instrumental artifacts.

An alternative sort of explanation begins by noting that the increase in ν_o for this solvatochromic substance implies that the contribution of solvation energy to the Frank-Condon excitation energy increases with increasing concentration of ion pairs. If the Py^+I^- ion-pair is regarded as a spherical dipolar molecule with effective radius, R, and dipole moment, μ, embedded in a continuous medium, the dipolar solvation energy of the ground state U, is given by Eq. (6), in which K_E is the dielectric constant.[26]

$$U = \mu^2/3K_E R^3 \qquad (6)$$

The excited state is also dipolar,[27] and, at equilibrium, would have a solvation energy given by an expression analogous to Eq. (6). However, the orientation of the excited state dipole is thought to be roughly perpendicular to that of the ground state dipole.[27] Thus, the dipolar solvation energy of the Frank-Condon excited state is probably much smaller than that of the ground state. For purpose of this approximate calculation it is taken as zero, so that the change in solvation energy accompanying Frank-Condon excitation is $-U$.

In solutions of finite concentration, K_E is not simply the dielectric constant of the solvent, but, in a two constituent solution, is related to the composition by Eqs. (7)–(9). The molecular polarizability is α, and ξ is $4\pi C_n \alpha$. A concentration in units of molecules cm^{-3} is C_n; subscript 1 indicates the solvent and subscript 2 indicates the solute. Since Eq. (7) also applies to the pure solvent, ξ_1 is given by Eq. (10). Under the conditions of our experiments C_{n2} is smaller than C_{n1} by factors 10^4–10^6. Since α has the same general magnitude for solvents and solute, $\xi_2 << \xi_1$, and we treat ξ_2 as infinitesimally small, so that $\xi = \xi_1 + \delta\xi_2$, and, correspondingly, $K_E = K_{E1} + \delta K_E$. Substituting these two expressions and Eq. (10) into Eq. (7), and collecting terms, Eq. (11) is obtained. When Eq. (11) is expanded, and terms higher than first order in $\delta\xi$ and, δK_E are dropped, a simple, explicit expression for δK_E can be obtained, Eq. (12).

$$K_E - 1 = \xi \left[3K_E/(1 + 2K_E)\right] \qquad (7)$$

$$\xi = \xi_1 + \xi_2 \qquad (8)$$

$$\xi = 4\pi \left(C_{n1}\alpha_1 + C_{n2}\alpha_2\right) \qquad (9)$$

$$\xi_1 = (K_{E1} - 1)(1 + 2K_{E1})/3K_{E1} \qquad (10)$$

$$K_{E1} - 1 + \delta K_E = \left\{\frac{(K_{E1} - 1)(1 + 2K_{E1})}{3K_{E1}} + \delta\xi\right\}\left\{\frac{3(K_{E1} + \delta K_E)}{1 + 2(K_{E1} + \delta K_E)}\right\} \qquad (11)$$

$$\delta K_E = [3K_{E1}^2/(1 + 2K_{E1}^2)]\delta\xi \qquad (12)$$

From Eq. (6) the change in $-U$ accompanying an infinitesimal change in K_E is given by Eq. (13), and substitution of the value of δK_E from Eq. (12) gives Eq. (14).

$$\delta(-U) = (\mu^2/3R^3K_E^2)\,\delta K_E \qquad (13)$$

$$\delta(-U) = (\mu^2/3R^3K_E^2)\,[3K_{E1}^2/(1 + 2K_{E1}^2)]\delta\xi \qquad (14)$$

It is our intention to apply these ideas to solutions in the limit of infinite dilution, in which case $K_E = K_{E1}$; from Eq. (9), $\delta\xi = 4\pi\alpha_2\delta C_{n2}$; and Eq. (14) leads to Eq. (15). The polarizability, α, of a dipole in an electric field arises from its ability to orient itself in that field. It is diminished by thermal randomization at higher temperature, so, for a permanent dipole, $\alpha = \mu^2/3kT$. This expression is inserted in Eq. (15), as are a number of unit conversions which cast the equation into a more easily used form. The final result, in which μ_D is the dipole moment expressed in Debye, R_A is the radius expressed in Å (10^{-8} cm) and C is the molar salt concentration.

$$\frac{\delta(-U)}{\delta C_{n2}} = \frac{4\pi\alpha_2\mu^2}{R^3(1 + 2K_{E1}^2)} \tag{15}$$

$$\frac{\delta\nu_0}{\delta C} = \frac{1.64 \times 10^5\,\mu_D^4}{R_A^3(1 + 2K_{E1}^2)} \tag{16}$$

To test the plausibility of Eq. (16) it will be used to calculate a value of R_A from the variation of ν_0 with the concentration of salt in chlorobenzene, which shows the effect most clearly. Figure 4 shows a plot of ν_0 against the total stoichiometric concentration of salt. It has a slope of 4.2×10^6 cm^{-1} M^{-1} at zero concentration, easily determined with sufficient accuracy by inspection, and essentially the same with and without added TBAI. When this value, along with the dielectric constant of chlorobenzene (5.26^{28}) and the dipole moment of Py$^+$I$^-$ ($14D^{27b}$) are inserted into Eq. (16) a value
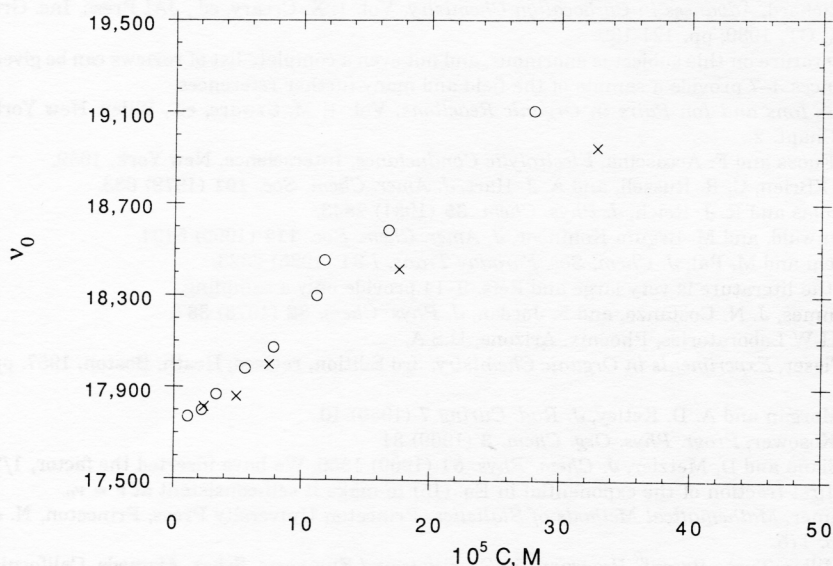

Figure 4. The relation between salt concentration and the frequency of maximum absorption, ν_0, for Py$^+$I$^-$ solutions in chlorobenzene, with (x) and without (o) added TBAI. C is the total stoichiometric salt concentration.

of 2.9 Å is calculated for R_A. This is clearly a value of appropriate molecular scale, and demonstrates the plausibility of the theory.

The dielectric modification theory and the aggregation theory are capable of merging into one another if the ion-pairs are attracted to one another, and the solution gradually partitions itself into regions of high ion-pair concentration and depleted regions as their concentration increases. In this way the solutions would change from random distributions of ion pairs, as assumed in the dielectric modification theory, in very dilute solutions; to somewhat segregated solutions; to very loose aggregates; to solutions of conventional aggregates at sufficiently high concentrations. We believe that this view of ion-pair »aggregation« is consistent with that of Petrucci and Eyring.[29] It is also consistent with the fact that the charge transfer bond renarrows at the highest TBAI concentration, and the increase in I_M saturates, as shown in Table II.

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SAŽETAK

Specijacija 1-alkil-4-cijanopiridinijeva jodida pomoću vrpce prijenosa naboja

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Na primjeru 4-cijano-1-(3,7-dimetiloktil)piridinijeva jodida ilustrirana je mogućnost karakterizacije ionskih parova u solvolitskim uvjetima iz intenziteta vrpci u spektrima prijenosa naboja. Utvrđeno je da povećanje koncentracije polaznog spoja uzrokuje pomak vrpce prema višim frekvencijama, što je pripisano porastu dielektrične konstante uslijed nastajanja ionskih parova.