Speciation of 1-Alkyl-4-cyanopyridinium Iodide

David A. Binder*,[†] and Maurice M. Kreevoy

Department of Chemistry, University of Minnesota, 207 Pleasant St. S.E., Minneapolis, Minnesota 55455

Received: November 20, 1996[⊗]

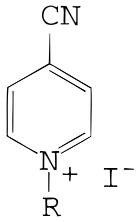
The intensity of the charge-transfer band of 1-alkyl-4-cyanopyridinium iodides was used to estimate the contact ion pair (CIP) concentration in a number of solvents. In several nonhydroxylic solvents with dielectric constant between 4 and 6 the transition dipole moment is very similar, and these values have been averaged. This average value was then used to estimate the intrinsic molar intensity of the CIP in other solvents. The concentration dependence of the intensity of the charge-transfer band was used in a conventional equilibrium formulation to estimate the total ion pair concentration. The solvent-separated ion pair (SSIP) concentration was determined by difference. The results were tested by comparison with conductance measurements. In 2-propanol and in acetonitrile the agreement of ion pair formation constants is within experimental uncertainty. However the agreement is poorer in triethyl phosphate and 2-butanol, with a discrepancy of a factor of 3 in the last solvent. CIP:SSIP concentration ratios of 2:3 in trimethyl phosphate, 1:1 in acetonitrile, 3:2 in 1-propanol, 7:3 in 2-propanol, 2-butanol, and triethyl phosphate, 4:1 in tributyl phosphate, and still higher in the other solvents were estimated. The CIP:SSIP ratio is in general agreement with that determined by Arnold et al. (Arnold, B. R.; et al. *J. Am. Chem. Soc.* **1996**, *118*, 5482) for radical ion pairs. However, the CIP:SSIP ratio is an order of magnitude higher than that estimated by Peters and Li (Peters, K. S.; Li, B. *J. Phys. Chem.* **1994**, *98*, 401) for diphenylcarbonium chloride in acetonitrile. The difference is attributed to a difference in operational definitions of "CIP".

Speciation of 1-Alkyl-4-cyanopyridinium Iodides

Bjerrum[1] first introduced the concept of ion pairs to account for the behavior of ions in solvents with low dielectric constants. The idea that contact ion pairs (CIP) and solvent-separated ion pairs (SSIP) might coexist was introduced by Winstein and coworkers[2] and, independently, at about the same time, by Sadek and Fuoss.[3] It is extremely useful in explaining solvolytic and other sorts of reactivity.[4−7] However, despite the many papers on the speciation of ion pairs and ion aggregates,[8−13] it is still hard to distinguish among CIP, SSIP, free ions, and higher aggregates, when all may coexist in equilibrium.

Spectral changes resulting from the interconversion of ion pairs have been well studied.[14,15] The choice of solvent strongly influences the equilibrium distribution of ion pairs. Relative amounts of ion pairs are also somewhat sensitive to temperature and the structure of the ions. Grunwald[16] suggested that one or both ions carry a solvation shell even in the ion pairs. At large interionic separation the potential energy of the system goes down continuously as the separation is reduced. However the ions must shed some solvent in order to come into direct contact. This increases the energy of the system and facilitates the formation of two distinguishable species, the CIP and the SSIP.[8,17−20] Recent theoretical calculations on ion-paired systems support the CIP/SSIP concept.[21−24] For model systems designed to mimic intermediate polarity aprotic solvents, calculations suggest that the CIP is more abundant than the SSIP. However, a local minimum in the radial dependence of the potential of mean force, due to the SSIP, is clearly observed, in addition to the CIP minimum. Molecular dynamics simulations on the sodium chloride ion pair in water and in dimethyl sulfoxide (DMSO) indicate that in DMSO, the CIP is much stabler than the SSIP. However, such calculations indicate that the SSIP is as stable as the CIP in water.[25] Much additional evidence is consistent with an equilibrium distribution between CIP and SSIP.

Following Bagchi[8] and Jordan and co-workers,[17] we have used the lowest frequency charge-transfer band of 1-alkyl-4-cyanopyridinium iodides, **1**, to characterize the various ionic species. In all the solvents of interest the lowest frequency charge-transfer maximum of **1** is well separated from the π to π^* spectrum. In each solution we have fitted this band to a lognormal 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 have examined the assumption that the integrated intrinsic area of this band is medium-insensitive, and that variations in transition dipole, μ_e, from one solvent to another, primarily reflect variations in the abundance of the CIP. This assumption is clearly not exact, but it seems intuitively reasonable, as does the resulting partition of ion pairs into CIP and SSIP.


1

1-alkyl-4-cyanopyridinium iodide

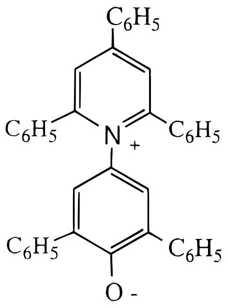
Our assumption is most likely to be valid if the CIP can be regarded as dipoles, interacting with a dielectric continuum. To test this model, the spectrum of Reichardt's betaine dye, **2**, was determined in a number of solvents, spanning the full range of permittivities used in this study. The geometry of **2** is fixed, removing one possible cause of variability in μ_e. The solvent sensitivity of ν_0 for **2** is greater than for **1**.[26] In nonhydroxylic

---

[†] Present address: Lever Brothers Co., 45 River Road, Edgewater, NJ 07020.

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.



2

Reichardt's betaine dye

solvents there is a reasonably good linear relation between ν_0 for **2** and a dielectric measure of solvent polarity.[27] For **1** such a relation is also observed. These observations tend to support our assumption about μ_e, at least as it applies to nonhydroxylic solvents.

Kochi and co-workers have shown that the charge-transfer spectra of 4-(carboxymethyl)-1-methylpyridinium iodide and two related compounds are similar in dichloromethane solution and in the crystalline state.[28,29] They draw the important conclusion that the interionic distance is very similar in the two states. It seems likely that the interionic distance in substituted pyridinium iodide CIPs will be similar in any solvent. Higher permittivity solvents will tend to separate the charges, but the CIP will be converted to a SSIP if very much separation occurs.

Recently, Arnold and co-workers[30] reported the relative and absolute free energies of interconversion of contact and solvent-separated radical-ion pairs derived from *p*-xylene and 1,2,4,5-tetracyanobenzene in solvents with dielectric constants ranging from 7 to 25. In solvents of dielectric constant less than 7, they report K_{eq} for the conversion of CRIP to SSRIP to be less than 0.1, that is, more than 90% of the ion pairs are CRIP. At a dielectric constant of ca. 13, the free energies of the two radical-ion pairs become approximately equal ($K_{eq} \cong 1$, $\sim$50% of the ion pairs are CRIP). These results are in general agreement with the work described in this paper.

Peters and Li[31] studied the picosecond dynamics of CIP and SSIP interconversion in the photosolvolysis of diphenylmethyl chloride in acetonitrile. They report rate constants for CIP separation to the SSIP (2.87×10^9 s^{-1}) and SSIP return to the CIP (1.31×10^8 s^{-1}). From this information, an equilibrium constant of 20 was determined for the conversion of CIP to SSIP. About 4% of ion pairs exist as CIP. This is an order of magnitude less than the fraction of CIP which we estimate here and in a recent, related publication.[32] The discrepancy is now attributed to an important difference in the operational definitions.

Experimental Section

Electronic spectra were obtained with a Milton Roy Spectronic 3000 diode array spectrophotometer with a diode spacing of 0.38 nm per diode. Cylindrical cells of 0.20, 2.00, 5.00, and 10.00 cm path length were used.

The iodide ion of **1** is sensitive to air oxidation, giving I_3^- and, presumably, oxygen-derived anions. To avoid oxidation, the solvents were degassed with N_2 before use and up to 3×10^{-2} M thiol (usually dodecanethiol) was incorporated as an O_2 scavenger.[32,33] The concentration of thiol had no affect on the frequency of maximum absorbance up to about 5×10^{-2} M. Triiodide has an intense absorption at 365 nm. Any samples that showed evidence of I_3^-, based on visual inspection of the spectra, were discarded.

In each spectrum the long-wavelength charge-transfer band of **1** was fitted to an analytical lognormal expression to facilitate calculation and comparison. This was done by proceedures that minimize the variance between the experimental and analytical absorbances over the whole charge-transfer band, while constraining ν_0, the frequency of maximum absorbance, to optimize the fit in the near neighborhood of the maximum. These proceedures have been described previously.[32,34−36] The average difference between experimental and calculated absorbances was about 0.4%.

Conductance measurements were made with conventional apparatus and techniques which have been previously described.[32]

Ion Pair Equilibria. Instead of determining K_A using ϵ_0,[37−39] we have used the molar integrated intensity of the long-wavelength charge-transfer transition. For the equilibria

$$\underset{\text{CIP}}{\text{Py}^+,\text{I}^-} \overset{K_i}{\rightleftharpoons} \underset{\text{SSIP}}{\text{Py}^+//\text{I}^-} \overset{K_s}{\rightleftharpoons} \underset{\text{free ions}}{\text{PY}^+ + \text{I}^-} \qquad (1)$$

The overall association constant, K_A, is given by

$$K_A = \frac{[\text{CIP}] + [\text{SSIP}]}{\gamma_{\text{Py}^+}[\text{Py}^+]\gamma_{\text{I}^-}[\text{I}^-]} \qquad (2)$$

For the solution in which the pyridinium iodide is the only solute, $[\text{Py}^+] = [\text{I}^-]$, and the mass balance equation gives

$$C_0 = [\text{Py}^+] + [\text{CIP}] + [\text{SSIP}] \qquad (3)$$

$$f_{\text{CIP}} = \frac{[\text{CIP}]}{[\text{CIP}] + [\text{SSIP}]} \qquad (4)$$

Rearranging eqs 3 and 4 gives

$$C_0 = [\text{P}^+] + [\text{CIP}]/f_{\text{CIP}} \qquad (5)$$

The apparent molar intensity, *I*, of the long-wavelength charge-transfer band was assumed to be given by

$$I = \frac{I_M[\text{CIP}]}{C_0} \qquad (6)$$

where I_M is the intrinsic molar intensity of the contact ion pair.

Substituting eq 5 into eq 2 and rewriting with the substitutions given in eq 6 give eq 7, which relates measured quantities to two independent parameters, K_A and the product, $I_M f_{\text{CIP}}$:

$$IC_0 = \frac{I_M f_{\text{CIP}}}{{\gamma_\pm}^2}\left[\left({\gamma_\pm}^2 C_0 + \frac{1}{2K_A}\right) - \left(\frac{{\gamma_\pm}^2 C_0}{K_A} + \frac{1}{4{K_A}^2}\right)^{0.5}\right] \qquad (7)$$

It is not possible to separate I_M and f_{CIP} without further approximation or assumptions.

Equation 7 was used to determine best values of $I_M f_{\text{CIP}}$ and K_A. All suitable spectra in a given solvent were used. Parameters were selected by iteration so as to minimize the sum of the squares of the discrepancies between all observed and calculated *I* values. The activity coefficients of ions by the Debye−Hückel theory,[40−42] with the radius, *R*, given by Bjerrum's characteristic distance,[35,43,44] were used. Ion pair activity coefficients were taken as 1.0. These assignments are suspect, and some of their possible consequences in comparing association constants based on conductance with association constants based on spectroscopic measurements are discussed in our recent paper[35] and below. The resulting values of K_A

TABLE 1: Transition Dipole Moment, μ_e, Determined from Eq 8, for the 1-Alkyl-4-cyanopyridinium Iodide Long-Wavelength Charge-Transfer Transition

solvent[a]	D	$\nu_0/10^4$ (cm^{-1})	$\bar{\nu}_0/10^4$ (cm^{-1})	$I_M/10^6$ (M^{-1} cm^{-2})	μ_e[f]	μ_e[g]
anisole[b]	4.33[h]	1.839	1.910	6.79	1.84	1.81
anisole[c]	4.33	1.839	1.900	6.89	1.85	1.82
anisole[c,d]	4.33	1.830	1.878	6.91	1.86	1.84
butyl acetate[c]	4.94[h]	1.868	1.939	7.94	1.97	1.94
butyl acetate[c,d]	4.94	1.869	1.947	7.69	1.94	1.90
chlorobenzene[b]	5.62[h]	1.780	1.859	8.84	2.14	2.09
chlorobenzene[c,e]	5.62	1.764	1.807	9.30	2.20	2.17
ethyl benzoate[b]	5.91[h]	1.921	1.972	6.11	1.71	1.69
ethyl benzoate[b,d]	5.91	1.922	1.976	6.25	1.73	1.70
trioctyl phosphate[c]	4.5[j]	1.839	1.900	6.95	1.86	1.83
p-chlorotoluene[c]	6.08[h]	1.770	1.824	6.72	1.87	1.84

[a] In these solvents, we believe that all ion pairs are CIP and that $I = I_M$. [b] 4-Cyano-1-(3,7-dimethyloctyl)pyridinium iodide. [c] 4-Cyano-1-(2-ethylhexyl)pyridinium iodide. [d] Added salt: tetra-*n*-heptylammonium iodide. [e] Added salt: 4-cyano-1-(2-ethylhexyl)pyridinium perchlorate. [f] Calculated from eq 8, subsituting ν_0 for $\bar{\nu}$. [g] Calculated from eq 8, using $\bar{\nu}$. [h] Reference 72. [j] Reference 73.

TABLE 2: Transition Dipole Moment, μ_e, Determined from Eq 8, for the Long-Wavelength Charge-Transfer Transition of Reichardt's Betaine Dye (2)

solvent	$C_0 \times 10^5$ (M)	$\nu_0/10^4$ (cm^{-1})	$I/10^7$ (M^{-1} cm^{-2})	μ_e[a] (from ν_0)
chlorobenzene	15.95	1.310	1.507	3.25
ethyl benzoate	105.1	1.334	2.936	4.49
triethyl phosphate	118.9	1.440	2.382	3.90
acetone	124.7	1.482	2.608	4.02
2-butanol	113.8	1.640	2.408	3.67
acetonitrile	115.3	1.652	2.111	3.42
2-propanol	126.9	1.681	1.695	3.04
methanol	113.8	1.926	1.851	2.97

[a] Calculated from eq 8, substituting ν_0 for $\bar{\nu}$.

and $I_M f_{CIP}$ are given in Table 3. They do not depend on the assumption that μ_e is solvent-independent. They only require that I_M be concentration-independent.

Evaluation of f_{CIP}. An independent method was needed to determine I_M and f_{CIP} in each solvent of interest. To solve this problem, f_{CIP} was assumed to be unity in a number of low-permittivity solvents and the transition dipole of the charge-transfer band, μ_e, was assumed to be independent of solvent. I_M is related to μ_e according to eq 8.[45,46] Theoretical work by

$$I_M = \bar{\nu}(\mu_e/0.0958)^2 \tag{8}$$

Mulliken[47] and by Demtröder[48] suggests that μ_e should be constant if the structure of the chromophore is constant. For charge-transfer transitions in 1-alkyl-4-cyanopyridinium iodides, we also expect that μ_e is approximately independent of the alkyl group, as long as the alkyl group does not block access of the iodide to the ring. The acceptor orbital is an unoccupied π orbital. The effect of alkyl groups on neighboring functional groups is small and roughly independent of the nature of the alkyl group.[49] The best value of μ_e was obtained by averaging the values for a group of low-permittivity solvents, in which it was approximately constant.

For each higher permittivity solvent the values of I_M was obtained from eq 8 using $\bar{\mu}_e$ from the low permittivity solvents. (The difference between $\bar{\nu}$ and ν_0 is discussed below). Using eq 6, C_0, and the experimentally measured intensity, I, then gave [CIP] at each concentration. From C_0 and K_A the total ion pair concentration, [CIP] plus [SSIP], was obtained, and f_{CIP} was obtained from its definition, eq 4.

Results and Discussion

In solvents of low permittivity (dielectric constant less than 7) it is very unlikely that there is any significant fraction of SSIP or dissociated ions.[50] This assumption is supported by the recent study of radical ion pairs by Arnold and co-workers,[30] who reported that in solvents of dielectric constant less than 7, more than 90% of the ion pairs exist as CIP. At concentrations above ~3 × 10^{-5} M there is a gradual increase in I'_M, the experimentally measured intensity, and a tendency for I'_M to level off at concentration well above 10^{-3} M. The increase in I'_M is accompanied by an increase in ν_0. Two examples of the increase in intensity are shown in Figure 1. The gradual increase and ultimate leveling can be regarded as the consequences of aggregation, with the monomer and the dimer as the only significant species at concentrations below ~3 × 10^{-4} M.[34] At concentrations below ~2 × 10^{-5} M, we were unable to obtain reproducible data. To obtain I_M, the molar intensity of the unaggregated ion pair, from the data we have used a formalism based on an ion pair monomer−dimer equilibrium. (The dimer is a quadrupole.) The molar intensities of the ion pairs in isolation, I_M, and in the dimer were treated as parameters.

TABLE 3: Best-Fit Values of K_A and f_{CIP} Using Eqs 7 and 8

solvent	D	K_A (M^{-1})	$I_M f$ (M^{-1} cm^{-2})	ν_0 (cm^{-1})	f_{CIP}[a]	$\bar{\nu}$ (cm^{-1})	f_{CIP}[b]
tributyl phosphate[d]	8.10[e]	$1.28 \times 10^6 \pm 4.1 \times 10^5$	6.18	1.971	0.79	2.057	0.78
triethyl phosphate[c]	13.05[f]	$2.51 \times 10^3 \pm 360$	8.62	2.088	1.04	2.148	1.05
triethyl phosphate[d]	13.05	$6.93 \times 10^3 \pm 114$	5.56	2.088	0.67	2.148	0.68
2-butanol[c]	15.8[e]	$2.09 \times 10^4 \pm 700$	5.29	2.455	0.54	2.489	0.55
2-butanol[d]	15.8	$6.74 \times 10^3 \pm 120$	6.79	2.455	0.70	2.489	0.71
2-propanol[c]	19.41[g]	$4.45 \times 10^3 \pm 48$	6.98	2.507	0.70	2.581	0.71
2-propanol[d]	19.41	$4.94 \times 10^3 \pm 590$	6.75	2.507	0.68	2.581	0.68
1-propanol[d]	20.33[h]	$1.19 \times 10^3 \pm 10.6$	5.86	2.560	0.58	2.623	0.58
trimethyl phosphate[d]	21.26[i]	271 ± 6.4	3.60	2.239	0.44	2.344	0.44
acetonitrile[c]	36.7[e]	88.3 ± 4.7	3.22	2.313	0.35	2.366	0.36
acetonitrile[d]	36.7	57.2 ± 1.4	4.40	2.313	0.48	2.366	0.48

[a] Obtained using ν_0 in eq 8, in place of $\bar{\nu}$. [b] Obtained from eq 8, as written. [c] K_A is fixed at the conductance value and $I_M f_{CIP}$ is the only adjustable parameter in eq 7. [d] Both K_A and $I_M f_{CIP}$ are adjustable parameters in eq 7. [e] Reference 72. [f] Reference 74. [g] Reference 44. [h] Reference 75. [i] Reference 76.

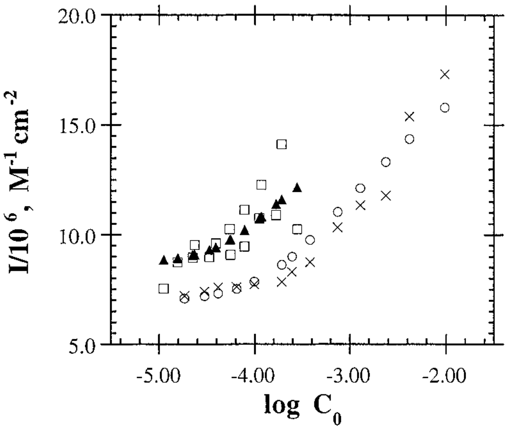


Figure 1. log C_0 vs I for 4-cyano-1-(2-ethylhexyl)pyridinium iodide charge-transfer spectra in anisole and for 4-cyano-1-(3,7-dimethyloctyl)-pyridinium iodide in chlorobenzene. For anisole × are from the lognormal best fit of the experimental spectra at each concentration. ○ are from the lognormal best fit of the calculated spectra determined from an ion-pair monomer−dimer equilibrium formalism with the equilibrium constant equal to 1.19×10^3 M^{-1}. For chlorobenzene □ and ▲ are the experimental and calculated values, respectively, with the equilibrium constant equal to 1.25×10^3 M. In both cases, the calculated spectra were obtained by adding the contributions of the monomer and the dimer to the charge-transfer band. The lognormal parameters of the monomer and of the dimer were treated as concentration-independent parameters and adjusted to optimize the fit, as described in the text.

Modeling the results with a monomer−dimer formalism is the equivalent of fitting I'_M to the first two terms of an even-power series in C_0. This would be likely to approximate the results even if the model was not correct, and it is used, here, only to extract the value of I_M. A more detailed description of this model and its fit to the experimental data is discussed elsewhere.[34] Figure 1 shows typical fits of the formalism to the data. Equation 8 was used to calculate μ_e from I_M.The resultant values of I_M and μ_e for low-permittivity solvents are shown in Table 1.

It can be seen that the derived values of μ_e are fairly constant, despite a substantial variation of solvent types and alkyl groups. However, the scatter is larger than the expected experimental error, which is around 5%, and it was concluded that μ_e is only approximately constant. The average value of μ_e, $\bar{\mu}_e$, determined from eq 8, is 1.87 $M^{-1/2}$ $cm^{-1/2}$, with a standard deviation from the mean of 0.14. If ν_0 is used instead of $\bar{\nu}$, μ_e, is essentially the same, 1.91 $M^{-1/2}$ $cm^{-1/2}$, again with a standard deviation of 0.14. The results in Table 1 suggest that μ_e may show a small, systematic decrease with increasing ν_0. It is not possible to determine if this trend is real, because the choice of solvents is very limited. Solvents used to determine μ_e were required to have a dielectric constant less than 7. In many such solvents the probes were not adequately soluble. If real, the trend is slight and I_M can probably be estimated in other solvents using $\bar{\mu}_e$, with an uncertainty of ∼10%. However great significance should not be ascribed to small differences between calculated and observed values.

To test our assumption that μ_e is constant in the absence of solvent separation and ion dissociation, Reichardt's betaine dye, **2**, was studied in a variety of solvents. Like **1**, **2** has a strongly solvatochromic charge-transfer transition, but the donor and acceptor are connected by a rigid, covalent framework, so that the structure of the chromophore cannot vary from one solvent to another, and neither dissociation nor solvent separation can occur. Despite this constraint, some scatter and possibly a systematic trend to lower values of μ_e with increasing ν_0 were observed, as shown in Table 2. Analysis of the results of Kjaer and Ulstrup reveals a similar trend.[51] The apparent intensity is very sensitive to certain oxidizing impurities in the solvents, and there is some loss of intensity with time.[35] These problems may account for some or all of the scatter, although we have tried to minimize them in the usual ways. The apparent decrease in μ_e with increasing ν_0 may be due to intensity transfer between the charge-transfer band and $\pi \rightarrow \pi^*$ transitions. It may also be an indication that μ_e has some solvent dependence. Despite these problems, it is clear that the large falloff in intensity that occurs for **1** in ion-separating solvents is absent in **2**. The smallest observed values of μ_e, 3.0, for methanol and 2-propanol, are ∼0.8 of the average of the chlorobenzene and ethyl benzoate values. And no anomalously high values of I_M and μ_e were observed in high ν_0 solvents. We conclude that estimates of the intrinsic μ_e of **1** in ion-separating solvents based on the average of values in less polar solvents are uncertain by ∼20%, and such estimates are more likely to be high than low. This will still permit us to make useful estimates of the relative abundance of contact ion pairs and solvent-separated ion pairs of **1** in ion-separating solvents.

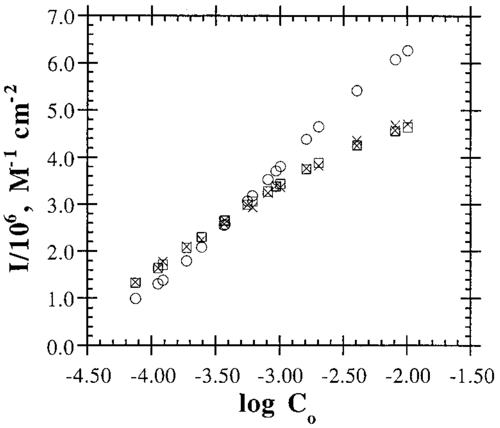


Figure 2. I vs log C_0 for 4-cyano-1-(3,7-dimethyloctyl)pyridinium iodide in triethyl phosphate. × are experimental data. □ best fit of eq 7 with K_A and $I_M f_{CIP}$ as adjustable parameters. ○ best fit of eq 7 with K_A determined by conductance.

A dielectric measure of solvent polarity is given by

$$F(D,n) = \frac{D-1}{D+2} - \frac{\nu^2-1}{\nu^2+2} \qquad (9)$$

where D is the static dielectric constant and n is the optical refractive index of the solvent. This reaction field factor comes from dielectric continuum theories of solvatochromic shifts[52−57] and has been discussed in detail in a recent article by Horng et al.[58] A linear relationship between ν_0 and F indicates that the solute dipole moment between the ground and excited states remains unchanged as a function of solvent. Figures 8 and 9 show the data for **1** and **2**, respectively. These plots show that in nonhydroxylic solvents there is a reasonable linear relationship between ν_0 and F for both the betaine and the pyridinium iodide. This indicates that the structure of the two chromophores do not change in these solvents. These observations support our assumption that μ_e, for the alkylpyridinium iodide, is independent of solvent, at least as it applies to nonhydroxylic solvents.

The values of K_A and f_{CIP} in dissociating solvent were derived from the decrease in I on dilution, using eq 7. In the most dilute 2-propanol solutions, for example, I reaches a value only ∼30% of I_M and dissociation is clearly significant. The two parameters of eq 7, K_A and the product, $I_M f_{CIP}$, were adjusted so as to minimize the squares of the discrepancies between

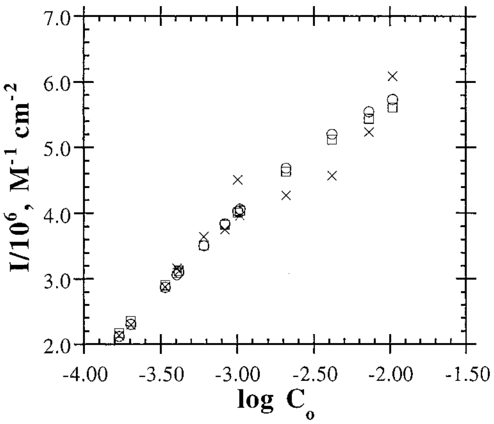


Figure 3. I vs log C_0 for 4-cyano-1-(3,7-dimethyloctyl)pyridinium iodide in 2-propanol. × are experimental data. □ best fit of eq 7 with K_A and $I_M f_{CIP}$ as adjustable parameters. ○ best fit of eq 7 with K_A determined by conductance.

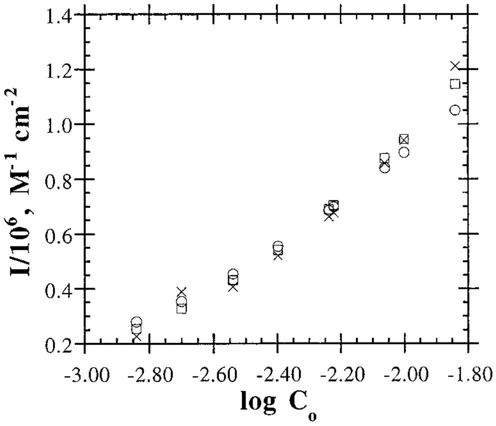


Figure 4. I vs log C_0 for 4-cyano-1-(3,7-dimethyloctyl)pyridinium iodide in acetonitrile. × are experimental data. □ best fit of eq 7 with K_A and $I_M f_{CIP}$ as adjustable parameters. ○ best fit of eq 7 with K_A determined by conductance.

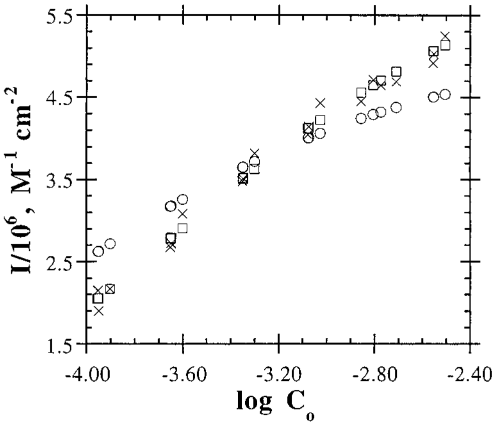


Figure 5. I vs log C_0 for 4-cyano-1-(3,7-dimethyloctyl)pyridinium iodide in 2-butanol. × are experimental data. □ best fit of eq 7 with K_A and $I_M f_{CIP}$ as adjustable parameters. ○ best fit of eq 7 with K_A determined by conductance.

calculated and observed values of I. The quality of the fits obtained are shown in Figure 2−5. The parameters are given in Table 3.

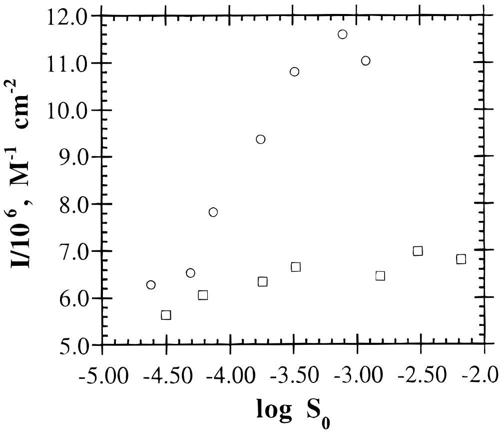


Figure 6. ○ I vs log S_0 for 4-cyano-1-(3,7-dimethyloctyl)pyridinium iodide in chlorobenzene, with tetra-*n*-butylammonium iodide as the added salt. The pyridinium iodide concentration is 2.407×10^{-5} M for all solutions. □ I vs log S_0 for 4-cyano-1-(3,7-dimethyloctyl)-pyridinium iodide in tributyl phosphate, with tetra-*n*-butylammonium iodide as the added salt. The pyridinium iodide concentration is 3.159×10^{-5} M for all solutions.

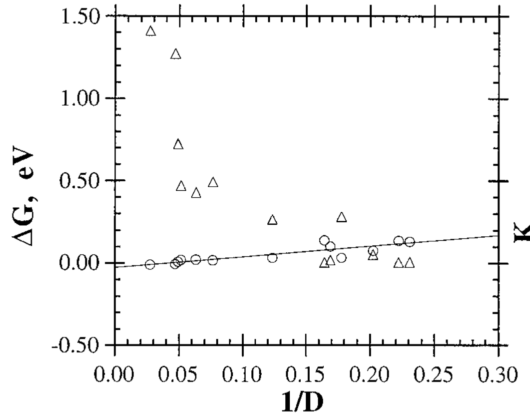


Figure 7. ○ are the free energy of formation of SSIP from CIP vs the recipricol of solvent dielectric constant (in debyes). The best linear fit to the data is $\Delta G = -0.026 + 0.65\ (1/D)$. Δ are the equilibrium constants $K_{SSIP/CIP}$ (K_i in eq 1) vs $1/D$. The ordinate scale is the same for both sets of data.

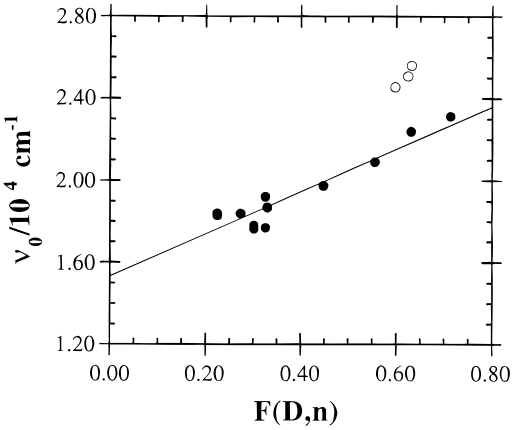


Figure 8. ν_0 vs the reaction field factor $F(D,n)$ for 1-alkyl-4-cyanopyridinium iodide. ● are the values in nonhydroxylic solvents. ○ are in hydroxylic solvents. The line drawn through the filled circles is $\nu_0 = 15\,310\ \text{cm}^{-1} + 1.034F(D,n)$ with $R = 0.89$.

The present K_A value in 2-propanol, 4.9×10^3 M^{-1} can be compared with the value, 3.2×10^3 M^{-1}, which can be calculated for 1-ethyl-4-cyanopyridinium iodide from the results of Mackay and Poziomek.[59] Mackay and Poziomek ignored activity coefficients. Ignoring activity coefficients in eq 7 leads to a value of 3.9×10^3 M^{-1}, which is even closer to the Mackay and Poziomek result. Mackay and Poziomek[59] obtained 96 M^{-1} for K_A in acetonitrile. This can be compared to the present value of 58 M^{-1} (88 M^{-1} if activity coefficients are ignored). These appear to be the only available comparisons with previous

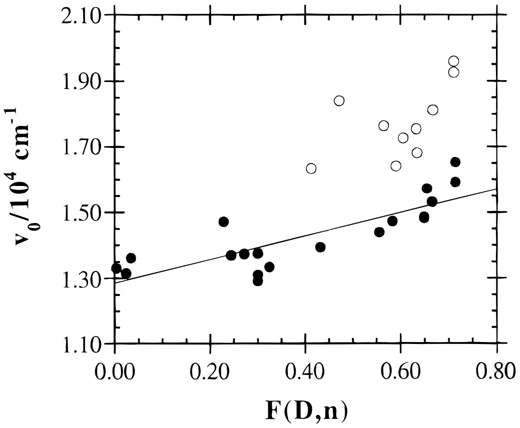


Figure 9. ν_0 vs the reaction field factor $F(D,n)$ for Reichardt's betaine dye. ● are the values in nonhydroxylic solvents. ○ are in hydroxylic solvents. The line drawn through the filled circles is $\nu_0 = 12\,860$ cm^{-1} + $0.3560F(D,n)$ with $R = 0.82$. The data are taken from Kjaer and Ulstrup.[51]

results for 1-alkyl-4-cyanopyridinium iodides. The agreement appears to be quite satisfactory.

Among the solvents listed in Table 3, the one supporting the least dissociation is tributyl phosphate, which gives only about 15% dissociation at a concentration around 3×10^{-5} M. These are the most dilute in which we regard the results as reliable. Nevertheless, because of the large number of self-consistent data (85 points) and because addition of tetrabutylammonium iodide to dilute solutions of **1** in tributyl phosphate causes an increase in I (discussed below) we believe that the apparent dissociation is real.

To further test our K_A values, comparison values have been obtained from conductance for four of our solvents using the Lee and Wheaton equations.[40−42] The comparison is shown in Table 3. In addition, the experimental intensities were fitted to eq 7 using the conductance based K_A and adjusting only $I_M f_{CIP}$. The quality of the fits is shown in Figures 2−5 and compared with the fits obtained when both parameters were adjusted. For 2-propanol and acetonitrile the fits are almost equally good. The two K_A values are somewhat discrepant in acetonitrile, but the fit of the intensity values to eq 7 is insensitive to the difference because little association occurs. In triethyl phosphate and, particularly, 2-butanol the calculated plots show significant deviations from the experimental results when the conductance K_A values were used. In these solvents the probe is significantly associated at all concentrations and the best spectrophotometric value of K_A differs substantially from the conductance value.

While the disagreement between the spectrophotometric and conductance results is probably too large to be explained only in terms of activity coefficients, errors in activity coefficients could be quite significant since the ionic concentrations were not the same in the two types of experiments.[43,60−63] There are comparisons in the literature between K_A values determined from spectrophotometric and conductance data. In some cases, the agreement is good. Gilkerson[43,44,64] determined K_A values for group I picrates and tetraphenylborates in 2-butanone and group I picrates in 2-propanol using both spectrophotometric and conductance data and found the disagreement to be less than 20% in most cases. In other cases, where the spectroscopic K_A has been determined by NMR, there is disagreement by at least a factor of 2 between the spectroscopic and conductance values.[43,65−67] The significance of such differences has been discussed by Gilkerson and Kendrick.[43]

In the present case there are additional possible sources of error. In deriving eq 7, it was assumed that the ratio of CIP:SSIP remains constant over the entire concentration range studied. Interaction of the ion pairs with neighboring ions or dipoles may promote the conversion of CIP to SSIP. The Debye−Hückel equation ignores ion−dipole interactions and leads to the assumption that activity coefficients for ion pairs are unity in dilute solutions. This assumption is highly suspect. Ion pair activity coefficients can be substantially less than unity at low concentrations in weakly polar solvents.[34] Ion−dipole and dipole−dipole interactions also increase the intrinsic intensity of the charge-transfer absorption band, which has the effect of increasing the spectroscopic K_A. For triethyl phosphate the spectrophotometric value of K_A is clearly preferable to the conductometric value, since the latter leads to unacceptable values of f_{CIP}. For 2-butanol, we have less basis for preference. The f_{CIP} would be expected to be larger for 2-butanol than for 2-propanol because the functional group is the same and 2-butanol has a lower dielectric constant. Therefore, for 2-butanol, the spectrophotometric value of K_A is probably also preferable to the conductometric value. In any event, the conductance-based values of K_A tend to confirm the conclusion that f_{CIP} is generally between 0.3 and 1.0 and does not decrease rapidly with increasing permittivity of the solvent.

To furthur test the foregoing ideas, spectra were also made from solutions containing low, fixed concentrations of **1**, and varying concentrations of tetrabutylammonium iodide (TBAI) in chlorobenzene and tributyl phosphate. The results are shown in Figure 6. They show changes with total salt concentration very similar to those seen when the concentration of **1** is raised. With the larger concentration range made possible by the greater solubility of TBAI it becomes clear that spectra made from solutions in tributyl phosphate show trends in the same directions as those from chlorobenzene solution. The increases in I at higher salt concentrations are attributed to interactions between ion pairs,[32,35] which are most simply regarded as higher aggregation. However, addition of TBAI to very dilute solutions of **1** in tributyl phosphate also increases I. There is roughly a 20% increase in I when the total salt concentration increases from 3×10^{-5} to 3×10^{-4} M. Higher agregation seems intuitively unlikely in such dilute solutions in a solvent with a polar functional group. We believe this increase at low concentrations is primarily due to the suppression of dissociation, as indicated above. In solvents such as chlorobenzene, with very low dielectric constants, theory anticipates very large values of K_A and very small fractions of free ions.[10,68] The increase in I_M with salt concentration makes it impossible to reliably interpret small changes in I. Together, these factors make it impossible to determine K_A spectrophotometrically in such solvents.

Theory suggests that SSIP are more prevalent in hydroxylic solvents than in nonhydroxylic solvents of comparable permittivity.[25] However, f_{CIP} which were determined from eqs 7 and 8 and are shown in Table 3, show no such trend. Earlier work provides convincing evidence for the existence of SSIP.[3−7] Theory[25] and intuition suggest that f_{CIP} should decrease, and the relative abundance of SSIP should increase, as the permittivity of the solvent increases. Figure 7 provides support for this idea. There is probably some functional group specificity as well.[69]

Both the integrated intensity and the frequency of the low-energy charge-transfer transition increase with increasing electrolyte concentration, particularly in solvents of low permittivity. These effects have been attributed to electrostatic interaction between ion pair dipoles.[32] These interactions are dominated by the interactions of very near neighbors,[32] and they can be regarded as due to aggregation, which we have done, above, in

TABLE 4: Slopes of Plots of I vs ν_0 for 1-Alkyl-4-cyanopyridinium Iodides in the Indicated Solvent

solvent	$\Delta I/\Delta\nu_0$ (M^{-1} cm^{-1})	$\Delta C \times 10^4$ (M)	solvent	$\Delta I/\Delta\nu_0$ (M^{-1} cm^{-1})	$\Delta C \times 10^4$ (M)
anisole[a]	4330	1.5	chlorobenzene[a]	4810	2.6
anisole[b]	3490	13	chlorobenzene[b,d]	4730	5.2
anisole[b,c]	2230	13	ethyl benzoate[a]	2340	5.7
butyl acetate[b]	2920	5.4	ethyl benzoate[a,c]	2900	9.1
butyl acetate[b,c]	2850	8.7	trioctyl phosphate[b]	4370	2.4

[a] 4-Cyano-1-(3,7-dimethyloctyl)pyridinium iodide. [b] 4-Cyano-1-(2-ethylhexyl)pyridinium iodide. [c] Added salt: tetra-*n*-heptylammonium iodide. [d] Added salt: 4-cyano-1-(2-ethylhexyl)pyridinium perchlorate.

TABLE 5: Best-Fit Values of K_A and f_{CIP} Using Modifications to Eq 7

solvent	$K_A{}^a$ (M^{-1})	f_{CIP}	K_A (M^{-1})	f_{CIP}	K_A (M^{-1})	f_{CIP}
method	A[a]	A[a]	B[b]	B[b]	C[c]	C[c]
tributyl phosphate	1.28×10^6	0.78	5.34×10^6	0.68	6.23×10^5	0.84
triethyl phosphate	6.93×10^3	0.68	1.03×10^4	0.53	596	0.73
2-butanol	6.74×10^3	0.55	7.41×10^3	0.68	5.49×10^3	0.78
2-propanol	4.94×10^3	0.68	5.22×10^3	0.67	4.10×10^3	0.75
1-propanol	1.19×10^3	0.58	1.23×10^3	0.56	1.02×10^3	0.64
trimethyl phosphate	271	0.44	284	0.39	235	0.50
acetonitrile	57.2	0.48	64.1	0.43	40.0	0.67

[a] Both K_A and $I_M f$ are adjustable parameters in eq 7. These values are the same as those given in Table 3. [b] Equation 7 with I_M replaced by $I_M + 5000\Delta\nu_0$. [c] Equation 7 with f_{CIP} replaced by $f_{CIP}(1 - 0.10C_0/C_{0,max})$.

calculating μ_e. Table 4 shows the slope of plots of I_M vs ν_0 for 1-alkyl-4-cyanopyridinium iodides for several low permittivity solvents. The upper limit of the slope appears to be $\sim$5000 M^{-1} cm^{-1}. Equation 8 predicts that I_M increases as $\bar{\nu}$ (or, presumably, ν_0) increases, but $(\mu_e/0.1)^2$, the slope predicted by eq 8, is $\sim$400 M^{-1} cm^{-1}, so the increase in $\bar{\nu}$ is not the major cause of the increase in I_M. A detailed model of these interactions will be discussed in a future paper. To evaluate the possible effect of an increasing I_M on the calculated values of f_{CIP} we have replaced I_M with $I_M + 5000\Delta\nu_0$ in eq 7. This allows for an upper-limit estimate of the changes in K_A and f_{CIP} due to electric field effects. These results are presented in Table 5. Generally there is only a slight increase in K_A and a decrease in f_{CIP} of only a few percent.

Another possible source of systematic error in the calculated values of f_{CIP} and K_A is the assumption that f_{CIP} is unchanged by increasing the electrolyte concentration. This assumption is highly suspect because the average probe dipole is expected to become larger as the interaction between the probe and the near-neighbor electrolytes increases. The SSIP has a larger dipole than the CIP, and therefore increasing the electrolyte concentration should favor the SSIP. In terms of eq 7, f_{CIP} is expected to decrease with increasing electrolyte concentration. To put this effect in perspective, it was assumed that the f_{CIP} decreases by 10% over the concentration range studied. That is, in eq 7, f_{CIP} has been replaced with $f_{CIP}(1 - 0.10C_0/C_{0,max})$, where $C_{0,max}$ is highest concentration of the probe studied in a given solvent. We then recalculated K_A and f_{CIP}. These results are also presented in Table 5. The calculation with the new formulation of f_{CIP} appears to reproduce the experimental data equally well and gave somewhat higher values of f_{CIP}. However, our qualitative conclusions would be unchanged.

Figure 7 shows a plot of ΔG (from K_i in eq 1) vs $1/D$ for the formation of SSIP from CIP. The SSIP/CIP ratio is sensitive to the solvent dielectric constant, in accord with the predictions of Weller.[70] The slope of the plot is 0.65. This result can be compared to a value of 0.96 that can be calculated from the data of Arnold et al.[30] These results indicate that the slope is sensitive to either the structure of the probe or the nature of the solvents, or both. Since the size and molecular weight of the probes are similar, it would suggest that the continuum dielectric theory is oversimplified. Also, the uncertainties in the equilibrium constants are large enough to account for some of the difference in the slope. Considering the different systems and methodologies used, we consider the agreement to be very satisfactory.

The present results disagree, by an order of magnitude, with the conclusions of Peters and Li,[31] who studied the picosecond dynamics of the photosolvolysis of diphenylmethyl chloride in acetonitrile. Their reported rate constants give $f_{CIP} \sim 0.04$. The ions involved are different, but the ion pair molecular weights are similar, and electrostatic interaction should not be very structure-specific. We believe that the major source of the disagreement between our results and those of Peters and Li is the use of different working definitions of a CIP. Peters and Li count as CIP only those species that can collapse directly to the neutral molecule without a diffusion step. This is similar to Winstein's definition of a CIP.[2] This requires that the ions not only be in contact but be correctly positioned to form a covalent bond. Our definition of a CIP counts those species that contribute to the intensity of the charge-transfer band. It is calibrated by comparison with the intensity observed in low dielectric constant solvents, where we have assumed that all species present are CIP. This is probably more similar to the conductance definition of a CIP.[40−42,71] It counts as CIP all ion pairs that do not have any solvent between the cation and the anion. As the positive charge on the diphenylmethyl cation is delocalized over the aromatic groups, it is reasonable to believe that chloride ion in contact with the cation is also delocalized over these groups. Such chloride ion is not in a position to collapse to the neutral molecule without a prior diffusion step. Thus, Peters and Li count as SSIP species that we would identify as CIP.

Conclusions

We have evaluated the ion association constant, K_A, for 1-alkyl-4-cyanopyridinium iodides from the variation in the molar intensity of the charge-transfer transition with concentration in a number of solvents. However, in solvents of low dielectric constant the effect of dissociation cannot be distinguished from other effects and/or experimental artifacts. A nonlinear concentration dependence of this intensity shows the presence of a substantial concentration of free ions in solvents of higher permittivity. Tributyl phosphate gives similar evidence of dissociation, but only at lower concentrations. Solvents of higher permittivities also give apparent molar intensities below the average of less polar solvents at high ion pair concentration. This is regarded as evidence for the presence of solvent-separated ion pairs (SSIP). Ion pair association constants, K_A, and fractions of contact ion pairs (CIP) were determined in a number of solvents. The CIP:SSIP concentration ratio is about 2:3 in trimethyl phosphate, 1:1 in acetonitrile, 3:2 in 1-propanol, 7:3 in 2-propanol, 2-butanol, and triethyl phosphate, and 4:1 in tributyl phosphate and is still higher in other solvents. The effect of electrolyte concentration on the ratio of CIP:SSIP, ignored in the determination of the above results, can lead to significant errors in this ratio and will most likely result in ratios that are larger than those given above. We would like to emphasize the qualitative nature of the results.

These results are in agreement with the experimental work of Arnold and co-workers.[30] They are also in general agreement with the theoretical work of Hynes and co-workers[23] and that of Madusoodanan and Tembe.[25] Their calculations indicate that in these solvents the CIP will be significantly more abundant than SSIP.

Acknowledgment. This work was supported by the National Science Foundation through Grant No. NSF/CHE-9208746 to the University of Minnesota. We would like to thank Professor William Gilkerson for kindly providing us with his computer program to calculate results using the Lee and Wheaton conductance equation and for helpful discussions.

References and Notes

(1) Bjerrum, N. K. *Dan. Vidensk. Selsk.* **1926**, *7*, No. 9.
(2) Winstein, J.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169.
(3) Sadek, H.; Fuoss, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 5905.
(4) Bentley, T. W.; Schleyer, P. V. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.
(5) Raber, D. J.; Harris, J. M.; Schleyer, P. V. R. *Ions and Ion Pairs in Organic Reactions*; Wiley: New York, 1974; Vol. 2, Chapter 3.
(6) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161.
(7) Richard, J. P. *Advances in Carbocation Chemistry*; JAI Press, Inc.: Greenwich, CT, 1989; Vol. 1.
(8) Bagchi, S.; Pal, M. *J. Chem. Soc., Perkin Trans. 1* **1985**, *81*, 2323.
(9) Smid, J. *Ions and Ion pairs in Organic Reactions*; Wiley: New York, 1972; Vol. 1, Chapter 2.
(10) Fuoss, R. M.; Accascina, F. *Electrolytic Conductance*; Interscience: New York, 1959.
(11) Grunwald, E.; Kohinoor Begum, M. *J. Am. Chem. Soc.* **1990**, *112*, 5104.
(12) Nicolas, M.; Reich, R. *J. Phys. Chem.* **1981**, *85*, 2843.
(13) O'Brian, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633.
(14) Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1966**, *88*, 307.
(15) Szwarc, M. *Acc. Chem. Res* **1969**, *2*, 82.
(16) Grunwald, E. *Anal. Chem.* **1954**, *26*, 1696.
(17) Hemmes, P.; Costanzo, J. N.; Jordan, F. *J. Phys. Chem.* **1978**, *82*, 387.
(18) Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307.
(19) Peters, K. S.; Simon, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 6542.
(20) Hilininski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepic, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071.
(21) Ciccotti, G.; Ferrario, M.; Hynes, J. T.; Kapral, R. *J. Chim. Phys.* **1988**, *85*, 925.
(22) Ciccotti, G.; Ferrario, M.; Hynes, J. T.; Kapral, R. *Chem. Phys.* **1989**, *129*, 241.
(23) Ciccotti, G.; Ferrario, M.; Hynes, J. T.; Kapral, R. *J. Chem. Phys.* **1990**, *93*, 7137.
(24) Ciccotti, G.; Ferrario, M.; Hynes, J. T.; Kapral, R. *J. Chem. Phys.* **1990**, *93*, 7137.
(25) Madhusoodanan, M.; Tembe, B. L. *J. Phys. Chem.* **1994**, *98*, 7090.
(26) Reichardt, C. *Solvents and Solvent Effects in Organic Chemisty*, 2nd ed.; VCH Publishers: New York, 1994.
(27) Horng, M. L.; Gardecki, J. A.; Papazan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311, and refs 98 and 99 cited within.
(28) Bockman, T. M.; Chang, H. R.; Drickamer, H. G.; Kochi, J. *J. Phys. Chem.* **1990**, *94*, 8483.
(29) Bockman, T. M.; Kochi, J. *J. Am. Chem. Soc.* **1989**, *111*, 4669.
(30) Arnold, B. R.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 5482.
(31) Peters, K. S.; Li, B. *J. Phys. Chem.* **1994**, *98*, 401.
(32) Binder, D. A.; Mead, C. A.; Kreevoy, M. M. *Croat. Chem. Acta* **1992**, *65*, 763.
(33) Morgan, C. R.; Ketley, A. D. *J. Rad. Curing* **1980**, *7*, 10.
(34) Binder, D. A. Ionic Interactions in Solvents of Weak and Intermediate Polarity. Ph.D. Thesis, University of Minnesota, 1994.
(35) Binder, D. A.; Kreevoy, M. M. *J. Phys. Chem.* **1994**, *98*, 10008.
(36) Siano, D. B.; Metzler, D. E. *J. Chem. Phys.* **1969**, *51*, 1856.
(37) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1952**, *74*, 69.
(38) Ross, S. D.; Bassin, M.; Finkelstein, M.; Leach, W. A. *J. Am. Chem. Soc.* **1954**, *76*, 69.
(39) Kosower, E. M.; Burbach, J. C. *J. Am. Chem. Soc.* **1956**, *78*, 5838.
(40) Lee, W. H.; Wheaton, R. J. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 743.
(41) Lee, W. H.; Wheaton, R. J. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1456.
(42) Lee, W. H.; Wheaton, R. J. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1128.
(43) Gilkerson, W. R.; Kendrick, K. L. *J. Phys. Chem.* **1984**, *88*, 5352.
(44) Kendrick, K. L.; Gilkerson, W. R. *J. Solut. Chem.* **1986**, *15*, 253.
(45) Davis, K. M. C. *Molecular Association*; Academic Press: New York, 1975; Vol. 1, Chapter 3.
(46) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; John Wiley and Sons: New York, 1962.
(47) Mulliken, R. S. *J. Chem. Phys.* **1939**, *7*, 14.
(48) Demtröder, W. *Laser Spectroscopy: Basic Concepts and Instrumentation*; Springer-Verlag: New York, 1982.
(49) Ritchie, C. D. *Physical Organic Chemistry: The Fundamental Concepts*, 2nd ed.; Marcel Dekker, Inc: New York, 1990.
(50) With a dielectric constant of 7 an ion pair formation constant of 10^7 M^{-1} can be estimated using the equation $\log K_A = 43/D + 0.91$. The linear relationship between $\log K_A$ and $1/D$ was estabilished by Hemmes et al.,[17] and the coefficients were determined by fitting the data from Table 5.
(51) Kjaer, A. M.; Ulstrup, J. *J. Am. Chem. Soc.* **1987**, *109*, 1934.
(52) Ooshika, Y. J. *Phys. Soc. Jpn.* **1954**, *9*, 594.
(53) Lippert, E. *Z. Naturforsch.* **1955**, *A10*, 541.
(54) McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562.
(55) Mataga, N.; Kubota, T. In *Molecular Interactions & Electronic Spectra*; Mercel Dekker: New York, 1970; p 371.
(56) Amos, A. T.; Burrows, B. *Adv. Quantum Chem.* **1973**, *7*, 289.
(57) Liptay, W. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1974; Vol. 1, p 129.
(58) Horng, M. L.; Gardecki, J. A.; Papazan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
(59) Mackay, R. A.; Poziomek, E. J. *J. Am. Chem. Soc.* **1970**, *92*, 2432.
(60) Acevedo, V. H.; deMoran, J. A.; Sales, L. A. *Can. J. Chem.* **1983**, *61*, 267.
(61) Matheson, R. A. *J. Phys. Chem.* **1965**, *69*, 1537.
(62) Milne, J. B.; Parker, T. J. *J. Solut. Chem.* **1981**, *10*, 479.
(63) Davies, W. G.; Otter, R. J.; Prue, J. E. *Discuss. Faraday Soc* **1957**, *24*, 103.
(64) Feng-Chun, H.; Gilkerson, W. R. *J. Solut. Chem.* **1983**, *12*, 161.
(65) Covington, A. K.; Freeman, J. G.; Lilley, T. H. *J. Phys. Chem.* **1970**, *74*, 3773.
(66) Delsigore, M.; Maaser, H. E.; Petrucci, S. *J. Phys. Chem.* **1984**, *88*, 2405.
(67) Khalzaeli, S.; Popov, A. I.; Dye, J. L. *J. Phys. Chem.* **1982**, *86*, 4238.
(68) Fuoss, R. M. *J. Am. Chem. Soc.* **1935**, *57*, 388.
(69) Kamlet, M. J.; Abboud, J. L.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
(70) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *133*, 93.
(71) Fuoss, R. M. *J. Phys. Chem.* **1978**, *82*, 2427.
(72) Maryott, A. A.; Smith, E. R. *Table of Dielectric Constants of Pure Liquids*; U.S. Government Printing Office: Washington, DC, 1951.
(73) Gibson, J. Sovent Extraction and Liquid Membrane. Properties of Trioctyl Phosphate. M.A. Thesis, University of Minnesota, 1982.
(74) Bollinger, J. C.; Yvernault, G.; Ynernault, T. *J. Solut. Chem.* **1978**, *7*, 317.
(75) Flick, E. W. *Industrial Solvents Handbook*; Noyes Data Corp.: Park Ridge, NJ, 1991.
(76) Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807.