

## Interaction of Li<sup>+</sup> with Phenoxide Ions in Acetonitrile

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The charge transfer bands of a betaine dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate (**1**), and *p*-nitrophenoxide in solutions in acetonitrile are blue shifted in the presence of various concentrations of LiI. The shape of these bands changes with LiI concentration in a manner consistent with the formation of 1:1 complexes between the probes and Li<sup>+</sup>. The  $\pi \rightarrow \pi^*$  region of the betaine spectrum is also altered by addition of LiI, and three isosbestic points appear when spectral intensities are made consistent with the association constant,  $K_{\text{LiB}^+}$ . The spectra are most consistent with values of  $3.3 \times 10^4$  and  $5.5 \times 10^4 \text{ M}^{-1}$  for  $K_{\text{LiP}}$  and  $K_{\text{LiB}^+}$ , respectively. Conductance also supports the formation of a specifically bound lithium *p*-nitrophenoxide.  $K_{\text{LiP}}$  is larger by 3 powers of ten than the formation constant for the lithium iodide ion pair. These results illustrate the advantage of using a broad range of frequencies, spanning a large fraction of a spectroscopic band, in interpreting electronic spectra of solutions, rather than focusing on a small number of frequencies.

### Introduction

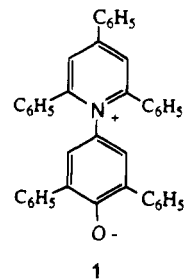
This paper aims to clarify the interaction of Li<sup>+</sup> with phenoxide ions in dipolar aprotic solvents. It also attempts to illustrate the advantage of analyzing a large fraction of the relevant bands in interpreting the electronic spectra of solutions, rather than focusing on a small number of frequencies, as is the usual practice.

The term halochromism was introduced by Baeyer and Villiger<sup>1</sup> in 1902 to describe the spectroscopic changes exhibited by basic chromophoric compounds on acidification. Since then, the term has been used to describe spectral changes that originate from both specific and nonspecific effects. Specific effects occur when the addition of a salt (or acid or base) to a chromophoric substance gives rise to a new absorbing species. Nonspecific effects occur when the added electrolyte gives rise to an electric field which acts as a perturbation on the absorbing species or changes the dielectric constant of the medium. The object of this paper is to determine which type of effect is responsible for the spectroscopic changes that attend the addition of LiI to solutions of solvatochromic phenoxides in acetonitrile.

Kosower<sup>2–4</sup> first reported halochromism for 4-carbomethoxy-1-methylpyridinium iodide. For this probe he observed a concentration dependence of  $\lambda_{\text{max}}$  in solutions in chloroform (0.13 M ethanol) and in methylene chloride. Kosower assigned concentration-dependent *Z* values to these solutions, implying a nonspecific origin for this effect. Davidson and Jencks<sup>5</sup> reported spectral changes in aqueous solutions of the merocyanine dye 1-methyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (MOED) in the presence of salts. All of the spectra exhibit isosbestic behavior, and it was concluded that the spectral changes are due to the appearance of new absorbing species in the presence of the salts. In 1992, Rezende et al.<sup>6</sup> reported that the addition of sodium or lithium salts to pyridinophenoxide dyes in solvents of low to moderate dielectric constant leads to the appearance of a new absorption band. It was suggested that this band is due to the formation of a tight dye–cation pair. However, in dimethyl sulfoxide, a good cation solvator,  $\lambda_{\text{max}}^{-1}$  is a linear function of salt concentration. This was attributed to an electric field effect.

Evidence was presented that the effect was mainly due to the added cations. We<sup>7</sup> found that the charge transfer band of 4-cyano-1-(3,7-dimethyloctyl)pyridinium iodide (Py<sup>+</sup>I<sup>−</sup>) shifts to higher frequency with increasing concentration, in solvents with dielectric constants between 4 and 8. The magnitude of the shift depends on the solvent and is largest in chlorobenzene. A dielectric continuum theory was developed which attributed this shift to the increase in the dielectric constant of the medium brought about by the added ion pairs. In 1993, Rezende et al.<sup>8</sup> reported the effect of salts on the charge transfer band of (*N,N,N',N'*-tetramethylenediaminoacetyl)(acetato)-copper(II) perchlorate. The halochromism of the copper complex was attributed to the transition from a square-planar geometry to the octahedral form. The solvated anion acts as an axially bound ligand. Thus both specific and nonspecific halochromism appear to be fairly well documented.

Reichardt et al.<sup>9</sup> have studied the halochromism of a solvatochromic pyridinium *N*-phenoxide betaine dye, **1**, in acetonitrile–electrolyte solutions, using group I and group II cations.



**1**  
The Betaine Dye

They found that the magnitude of the shift in  $\lambda_{\text{max}}$  depends on the nature of the added cation ( $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$ ). They claimed that the band shape is substantially unchanged by the added salts. The molar shift in frequency is linearly related to the cation charge to mass ratio. Cations which have a strong effect on the frequency also reduce the integrated intensity of the band. They concluded that the betaine dye exhibits “true halochromism”<sup>9</sup> because addition of the salt results in a hypsochromic shift that they believed is not accompanied by a change in the chemical identity

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of the betaine dye. Thus, in our present terminology, they considered that their observations were due to a nonspecific electric field effect rather than to a change in speciation. On the basis of this belief, they assigned  $E_T(30)$  values to salt solutions in acetonitrile.

In the present work, the change in frequency and band shape of the betaine dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate (**1**), is investigated as a function of added salt concentration in acetonitrile solution. An analogous anion, *p*-nitrophenoxide, was also studied, to permit comparison between results based on conductance, which is directly related to free ion concentration, with results based on spectroscopic data, which is directly related to the contact ion pair concentration. The betaine dye is a zwitterion, and conductance cannot be used to measure its association. Both sets of results indicate that the lithium cation forms 1:1 compounds with the spectroscopic probes. We have used the concentration dependence of the band shapes to calculate formation constants for Li<sup>+</sup> with both dyes. The formation constant from conductance is even larger than that calculated from spectra and more than 3 powers of ten larger than a typical ion pair formation constant in acetonitrile.

### Experimental Section

Lithium *p*-nitrophenoxide was prepared by allowing *p*-nitrophenol (Eastman Chemicals) to react with excess lithium hydroxide in aqueous solution. The yellow product was recrystallized from hot water, made basic with lithium hydroxide. The <sup>1</sup>H NMR spectrum of this substance, in acetone solution, was consistent with its assigned structure.

Tetra-*n*-butylammonium *p*-nitrophenoxide was prepared by allowing *p*-nitrophenol to react with excess tetrabutylammonium hydroxide in aqueous solution. The yellow product was recrystallized from hot water, made basic with tetrabutylammonium hydroxide. The melting range was 147.0–148.5 °C. The <sup>1</sup>H NMR spectrum of this substance, in CDCl<sub>3</sub> solution, was consistent with its assigned structure and very similar to the spectrum of the lithium compound apart from the bands due to the aliphatic protons.

The betaine dye, **1**, was purchased from Aldrich and used without further purification.

Anhydrous lithium iodide, 99%, was purchased from Janssen Chimica and used without further purification.

Tetra-*n*-butylammonium iodide (Aldrich) was recrystallized twice from absolute ethanol and dried under vacuum at room temperature.

Tetra-*n*-heptylammonium iodide, 99%, was purchased from Eastman Kodak and used without further purification.

Acetonitrile (UV grade, double glass distilled) was purchased from Burdick and Jackson and used without further purification. The percent water, determined by Karl Fischer titration, was reported by Burdick and Jackson to be 0.001% ( $4.4 \times 10^{-4}$  M). In previous, similar experiments  $1-4 \times 10^{-3}$  M of adventitious water was found in the solutions from which spectra were obtained.<sup>10</sup> Langhals has found that up to 0.1 M water in acetonitrile has no detectable effect on  $\lambda_{\max}$  for **1** in acetonitrile.<sup>11</sup> We have, therefore, concluded that the amount of water likely to be present would have no effect on our results.

The conductivity measurements were made using an Orion model 180, microprocessor-based conductivity meter (frequency, 4000 Hz). A Jones-type conductance cell was used. A cell constant of  $0.33030 \pm 0.00008 \text{ cm}^{-1}$  was determined using 0.01000 M aqueous potassium chloride solution (purchased from Orion). This cell constant is reasonably consistent with

the geometry of the cell. All measurements were made in a water bath, maintained at  $25.00 \pm 0.05$  °C.

Absorption spectra were obtained with a Milton Roy Spectronic 3000 double-beam diode array spectrophotometer with a diode spacing of 0.38 nm per diode. Cylindrical cells of 0.20, 2.0, 5.0, and 10.0 cm path length were used. All spectra were made with a cell of equal path length and identical design, filled with the same solvent as that used to dissolve the unknown, in the reference beam. In addition, to correct for any inequality in the absorbance of the windows of the reference cell and the unknown cell, very weak absorbances of the unknown cell filled with the solvent were subtracted from the measured spectra before they were used.

All glassware was rinsed with concentrated ammonium hydroxide prior to drying. This was helpful in reducing the scatter in the intensity. All glassware was dried overnight in an oven at 100 °C prior to use.

### Log–Normal Fitting of Spectra

The charge transfer bands of the betaine–salt solutions have a wavelength of maximum absorption,  $\lambda_{\max}$ , between 520 and 630 nm in acetonitrile. The short wavelength tail of the charge transfer band in some cases is overlapped by the long wavelength tail of the  $\pi$  to  $\pi^*$  spectrum. This is also true for the charge transfer transition of the *p*-nitrophenoxide anion, where  $\lambda_{\max}$  ranges from 400 to 432 nm. The band of interest was separated from the rest of the spectrum, and its integrated intensity was estimated, by fitting the measured molar absorptivities,  $\epsilon(\nu)$ , to a log–normal equation in frequency,  $\nu$ , as shown in eq 1,<sup>12,13</sup> from the shortest wavelength still judged to be free

$$\epsilon(\nu) = \frac{\epsilon_0 b}{\nu_0 - a} \exp\left\{-\frac{c^2}{2} - \frac{1}{2c^2} \left[\ln\left(\frac{\nu - a}{b}\right)\right]^2\right\} \quad \text{for } \nu > a \quad (1)$$

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

where

$$\nu \equiv \text{frequency}$$

$$a \equiv \nu_0 - H\left(\frac{Q}{Q^2 - 1}\right)$$

$$c \equiv \frac{\ln(Q)}{\sqrt{2 \ln 2}}$$

$$b \equiv H\left(\frac{Q}{Q^2 - 1}\right) \exp(c^2)$$

$$H \equiv \nu_b - \nu_r$$

$$Q \equiv \frac{\nu_b - \nu_0}{\nu_0 - \nu_r}$$

of interference to a wavelength at which the absorbance is essentially zero. Seven hundred to one thousand  $\epsilon(\nu)$  values, obtained from individual diodes, were fitted. Equation 1 gives  $\epsilon(\nu)$  as a function of four independent parameters:  $\nu_0$ , the frequency of maximum absorption;  $\epsilon_0$ , the molar absorptivity at  $\nu = \nu_0$ ;  $\nu_b$ , the frequency at half the maximum absorption on the blue side (higher energy) of  $\nu_0$ ; and  $\nu_r$ , the frequency at half the maximum absorption on the red side (lower energy) of  $\nu_0$ . These parameters were optimized as described below. The integrated intensity of the band,  $I$ , was estimated using eq 2.

$$I = \epsilon_0 c H \sqrt{2\pi} \left( \frac{\rho}{\rho^2 - 1} \right) \exp\left(\frac{c^2}{2}\right) \quad (2)$$

The four log-normal parameters for the experimental spectra were obtained as follows. First, values of  $\nu_0$  and  $\epsilon_0$  were selected to minimize the variance between experimental  $\epsilon(\nu)$  values and those calculated by the log-normal equation for the 80 data points closest to  $\nu_0$  (spanning 15.2 nm on each side of  $\nu_0$ ). To do this, values of  $\nu_0$ ,  $\epsilon_0$ , and  $\nu_r$  were selected by inspection. Using them, a value of  $\nu_b$  was found by a systematic search of frequencies above  $\nu_0$ . The best value was chosen so as to minimize the variance between experimental and calculated  $\epsilon(\nu)$  values for the 80 data points. Then  $\nu_r$ ,  $\epsilon_0$ , and  $\nu_0$  were successively reevaluated, in the same way, by the same criterion, starting the search, in each case, with the previous value. In each case, while one parameter was optimized, the other three were fixed. This cycle was repeated until successive values of  $\nu_0$  varied by less than  $0.05 \text{ cm}^{-1}$ . Throughout this phase of the search, comparison of the experimental and calculated  $\epsilon(\nu)$  values was limited to the 80 points closest to  $\nu_0$  so as to ensure that the resultant  $\nu_0$  value would not be compromised in order to improve the fit elsewhere. The resulting  $\nu_0$  and  $\epsilon_0$  values were adopted and fixed. The remaining log-normal parameters,  $\nu_b$  and  $\nu_r$ , were optimized by a similar, one-dimensional iterative technique but minimizing the variance for the full set of data: typically 700–1000 data points. The first trial values for this second set of calculations were the final values of  $\nu_b$  and  $\nu_r$  obtained from the first set of calculations. On the blue side of  $\nu_0$ , all data for  $\nu$  greater than half the frequency between  $\nu_0$  and the adjacent higher energy minimum were eliminated from the calculation. The data on the red side of  $\nu_0$  go to 900 nm, the limit of our spectrophotometer. For the *p*-nitrophenoxide charge transfer band,  $\lambda_{\text{max}}$  is between 400 and 432 nm. The charge transfer band does not extend to wavelengths larger than approximately 750 nm. After a reference spectrum was subtracted, the base line was adjusted to average zero between 800 and 900 nm. A typical adjustment was  $\pm 0.002$ . The average difference between the experimental data points and those calculated from eq 1 using the best fit parameters typically ranged from 0.3% to 0.5% of  $\epsilon_0$ .

The betaine spectra have a nonzero absorption at 900 nm. These spectra were not further adjusted after subtracting the reference spectrum. The average difference between a calculated and an experimental data point for the betaine charge transfer spectra ranged from 0.35% to 4.2% of  $\epsilon_0$ . The higher discrepancies for the betaine data occurred at LiI concentrations where the spectra are not accurately described by a single log-normal function. This is in contrast to the *p*-nitrophenoxide charge transfer band, which appears to be accurately described by a single log-normal function over the whole concentration range studied. Nevertheless, for the betaine charge transfer band, a single log-normal function appears to accurately determine  $\nu_0$  and  $\epsilon_0$  and reproduces the trends for the other parameters. Our inability to adjust the base line for betaine spectra may also be a factor in these discrepancies.

With the exception of  $\epsilon_0$ , all the log-normal parameters changed systematically as a function of the lithium cation concentration. At low LiI concentrations the  $\epsilon_0$  values showed scatter consistent with the goodness of fit described above and changed systematically with the LiI concentration, as the other parameters did. However, as the LiI concentration increased, the scatter increased, with discrepancies sometimes exceeding 20% at LiI concentrations  $\approx 10^{-3} \text{ M}$ . As shown in Figures 4 and 9, this scatter partially obscured the systematic trend. For reasons given below, we believe the discrepancies to be

systematically toward lower  $\epsilon_0$  values, rather than equally distributed above and below a most probable value. They occur for both *p*-nitrophenoxide and betaine spectra. In *p*-nitrophenoxide solutions with tetra-*n*-butylammonium iodide (TBAI) as the added salt, the standard deviation is approximately 2% for concentrations of TBAI less than  $1.0 \times 10^{-3} \text{ M}$ . This suggests that the scatter in lithium *p*-nitrophenoxide solutions is impurity related. While acidic impurities in acetonitrile might be a culprit in decreasing  $\epsilon_0$ , adding the base triethylamine at  $1.0 \times 10^{-3} \text{ M}$  resulted in no improvement in the reproducibility of  $\epsilon_0$ . We now believe that small fractions of the  $\Gamma^-$  were adventitiously oxidized to  $\text{I}_3^-$  in handling and that the  $\text{I}_3^-$  reacted with the probes when the mixed solutions were made, giving products which lack the charge transfer band. To overcome this problem, each  $\epsilon$  in these spectra was multiplied by  $\epsilon_{0,\text{calc}}/\epsilon_{0,\text{exp}}$ , where  $\epsilon_{0,\text{calc}}$  is obtained from a theory described below. The values of  $\epsilon_{0,\text{calc}}/\epsilon_{0,\text{exp}}$  ranged from 1.0 to 1.5. The conclusion that the scatter is toward lower  $\epsilon_0$  values is ultimately justified by the good agreement between theoretical and experimental spectra which can be achieved by making this assumption.

### Equilibrium Constants

If the interaction between  $\text{Li}^+$  and *p*-nitrophenoxide or the betaine is a conventional 1:1 association, the equilibrium constant for association between  $\text{Li}^+$  and *p*-nitrophenoxide anion ( $\text{P}^-$ ) can be written as

$$K_{\text{LiP}} = \frac{\gamma_{\text{LiP}}[\text{LiP}]}{\gamma_{\text{Li}^+}[\text{Li}^+]\gamma_{\text{P}^-}[\text{P}^-]} \quad (3)$$

where  $K_{\text{LiP}}$  is the association constant and  $\gamma$ 's are activity coefficients. The total salt concentration,  $S_0$ , and the total phenoxide concentration,  $C_0$ , are given by the mass balance equations.

$$S_0 = [\text{Li}^+] + [\text{LiI}] + [\text{LiP}] \quad (4)$$

$$C_0 = [\text{P}^-] + [\text{LiP}] \quad (5)$$

The association constant for LiI,  $K_{\text{LiI}}$ , is given by eq 6.

$$K_{\text{LiI}} = \frac{\gamma_{\text{LiI}}[\text{LiI}]}{\gamma_{\text{Li}^+}[\text{Li}^+]\gamma_{\text{I}^-}[\text{I}^-]} \quad (6)$$

Substituting eq 6 into eq 4 and rearranging gives eq 7.

$$[\text{Li}^+] = \frac{S_0 - [\text{LiP}]}{1 + \gamma_{\text{Li}^+}\gamma_{\text{I}^-}[\text{I}^-]K_{\text{LiI}}/\gamma_{\text{LiI}}} \quad (7)$$

Substituting eq 7 into eq 3, using eq 5, and solving for the [LiP] concentration gives eq 8.

$$[\text{LiP}] = \frac{1}{2} \left( C_0 + S_0 + \frac{Q}{\gamma_{\text{Li}^+}\gamma_{\text{P}^-}K_{\text{LiP}}/\gamma_{\text{LiP}}} \right) - \sqrt{\left[ \frac{1}{4} \left( C_0 + S_0 + \frac{Q}{\gamma_{\text{Li}^+}\gamma_{\text{P}^-}K_{\text{LiP}}/\gamma_{\text{LiP}}} \right)^2 - C_0 S_0 \right]} \quad (8)$$

where,

$$Q = 1 + \gamma_{\text{Li}^+}\gamma_{\text{I}^-}[\text{I}^-]K_{\text{LiI}}/\gamma_{\text{LiI}}$$

The equilibrium constant for association between  $\text{Li}^+$  and betaine (B) can be written as eq 9.

$$K_{\text{LiB}^+} = \frac{\gamma_{\text{LiB}^+}[\text{LiB}^+]}{\gamma_{\text{Li}^+}[\text{Li}^+]\gamma_{\text{B}^-}[\text{B}^-]} \approx \frac{[\text{LiB}^+]}{[\text{Li}^+][\text{B}^-]} \quad (9)$$

The ratio of activity coefficients,  $\gamma_{\text{LiB}^+}/(\gamma_{\text{Li}^+}\gamma_{\text{B}^-})$ , was approximated as unity because the association produces no change in charge types, and non-Coulombic solute-solute interactions should be similar for reactants and products.<sup>14,15</sup> A treatment similar to that used for the *p*-nitrophenoxide then gives eq 10.

$$[\text{LiB}^+] = \frac{1}{2} \left( C_0 + S_0 + \frac{Q}{K_{\text{LiB}^+}} \right) - \sqrt{\left[ \frac{1}{4} \left( C_0 + S_0 + \frac{Q}{K_{\text{LiB}^+}} \right)^2 - C_0 S_0 \right]} \quad (10)$$

These treatments have neglected the association between tetra-*n*-alkylammonium cation (or LiB<sup>+</sup>) and the anions iodide or phenoxide. The association constant for LiI,  $K_{\text{LiI}}$ , from conductance, is 30 M<sup>-1</sup>. Ignoring the association of LiI would result in an error of less than 0.2% at  $S_0 = 4.0 \times 10^{-5}$  M and an error of less than 5% at  $S_0 = 1.0 \times 10^{-3}$  M. The larger cations would presumably have still smaller association constants.

The activity coefficients in eq 8 and the remaining activity coefficients in eq 10 occur in combinations like  $\gamma_{\text{Li}^+}\gamma_{\text{P}^-}/\gamma_{\text{LiP}}$  or  $\gamma_{\text{Li}^+}\gamma_{\text{I}^-}/\gamma_{\text{LiI}}$ , such that the substances leading to the numerators have the same composition as the substances giving the denominators. The Coulombic contributions to these combinations were approximated by using the Debye-Hückel theory for the activity coefficients of ions,<sup>16-19</sup> with the mean ionic diameter,  $R$ , given by Bjerrum's characteristic distance,<sup>19-21</sup> 7.64 Å in acetonitrile. The non-Coulombic contribution was assumed to cancel, because the non-Coulombic interactions are short ranged and the substances leading to the numerator and the denominator have the same atomic composition.<sup>14,15</sup> Both of these assignments are suspect, and some of their possible consequences are discussed below, in comparing association constants based on conductance with association constants based on spectroscopic measurements.

The equilibrium constants,  $K_{\text{LiP}}$  and  $K_{\text{LiB}^+}$ , were determined using a one-dimensional iteration scheme specifically adapted to deal with the intensity problem described above, as follows. A trial value of  $K$  was chosen, at the high end of the reasonable range. Trial values of  $\nu_0$ ,  $\nu_b$ ,  $\nu_r$ , and  $\epsilon_0$  for the unassociated species were taken from the spectra of solutions with Li<sup>+</sup> concentration below  $2 \times 10^{-6}$  M. For the associated species, solutions with concentrations of Li<sup>+</sup> above  $2 \times 10^{-3}$  M were used to obtain these parameters. Using  $K$ , the concentration of associated and unassociated species was calculated at each Li<sup>+</sup> concentration using eq 8 or 10. Using the spectroscopic parameters and the species concentrations, the contributions to the spectrum by the associated and unassociated species were calculated. Adding these together, an  $\epsilon_{\text{calc}}$  was obtained at each diode frequency, including  $\nu_0$ . If  $\epsilon_{0,\text{exp}}$  was smaller than  $\epsilon_{0,\text{calc}}$ , each  $\epsilon_{\text{exp}}$  in the spectrum was multiplied by  $\epsilon_{0,\text{calc}}/\epsilon_{0,\text{exp}}$ , to obtain an adjusted experimental spectrum. If  $\epsilon_{0,\text{exp}}$  was equal to or greater than  $\epsilon_{0,\text{calc}}$ , no adjustment was made. This is justified by the explanation of the scatter given above, which would diminish but not increase the spectral intensity. The variance was then calculated by eq 11, where the  $\epsilon_{\text{exp}}(\nu)$  values are

$$\sigma^2 = \frac{\sum (\epsilon_{\text{calc}}(\nu) - \epsilon_{\text{exp}}(\nu))^2}{n - 1} \quad (11)$$

actually the adjusted values in some cases. The number of

TABLE 1: Summary of the Conductance Results

compound	$K_A$ (M <sup>-1</sup> )	$\Lambda_0$ (S cm <sup>2</sup> mol <sup>-1</sup> ) <sup>a</sup>	$\eta\Lambda_0^{a,b}$ (cP S cm <sup>2</sup> mol <sup>-1</sup> )
TBAP	31.2 ± 3.8	150.5	51.6
LiI	30.4 ± 4.1	172.9	59.2
TBAI	15.1 ± 0.1 <sup>c</sup>	164.2 <sup>c</sup>	56.3
LiP	3.59 × 10 <sup>5</sup> ± 1.2 × 10 <sup>5</sup>	279.0	95.6
	1.07 × 10 <sup>5</sup> ± 3.9 × 10 <sup>4</sup> <sup>d</sup>	159.3 <sup>e</sup>	54.6

<sup>a</sup> S = siemens = ohms<sup>-1</sup>, <sup>b</sup>  $\eta = 0.3426$  cP for acetonitrile. <sup>c</sup> Papadopoulos and Ritzoulis<sup>29</sup> obtained values of 19 M<sup>-1</sup> and 164.2 S cm<sup>2</sup> mol<sup>-1</sup> for  $K_A$  and  $\Lambda_0$ , respectively, using the Lee and Wheaton conductance equation implemented by the program of Pethybridge.<sup>43</sup> <sup>d</sup> Recommended value. <sup>e</sup> Calculated from  $\Lambda_0$  of TBAP, LiI, and TBAI. See text for an explanation.

frequency values used in the calculation is  $n$ . It is in the range 700–1000 for each spectrum in both sets of data.

This calculation was repeated, using successively lower values of  $K$  and keeping all the spectroscopic parameters constant, until the variance was minimized. Then the spectroscopic parameters of the unassociated and associated species were optimized in the same way, one at a time. This process was repeated, cyclically, until further repetition changed no parameter by more than 0.01%. (This is an exaggerated requirement for convergence, but it was easier for us to impose an exaggerated convergence requirement than to find another way to guard against correlated errors.) We know of no way to be certain that the optimum found is the global optimum and not merely a local optimum, but the excellent agreement between calculated and observed spectroscopic parameters and spectra shown in Figures 1–10 gives confidence that global optima have been found.

Typical values of  $\sigma/\epsilon_0$  for spectra of solutions with Li<sup>+</sup> concentrations close to the equivalence point are ~0.006. Since concentrations are proportional to  $\epsilon$  values, it is reasonable to assume that this is the uncertainty in the concentrations of the associated and unassociated species. Propagating error in the usual way,<sup>22</sup> we conclude that the association constants are uncertain by ~10%. In this estimate, it was assumed that the [Li<sup>+</sup>] and the activity coefficient ratios were known exactly. This estimate does not, of course, take any account of unforeseen systematic errors.

## Conductance Results

Conductance results for lithium iodide and tetrabutylammonium *p*-nitrophenoxide were analyzed using the Lee and Wheaton conductance equations,<sup>16-18,23</sup> which lead to optimum values of the limiting equivalent conductance,  $\Lambda_0$ , and the association constant,  $K_A$ . The Lee and Wheaton equations are based on the same model as the Fuoss 1978 conductance equations.<sup>23</sup> It takes account of ion pairing, viscosity, and the ion atmosphere effect. The Lee and Wheaton equations give conductance as a function of salt concentration, limiting equivalent conductance, the formation constant for nonconducting ion pairs, and the physical properties of the solvent. The program for optimizing  $\Lambda_0$  and  $K_A$  was kindly provided to us by Prof. William Gilkerson and has been described previously.<sup>19,20</sup> This program was used with minor modifications. Table 2 shows the effectiveness of this calculation in an uncomplicated case.

For the lithium *p*-nitrophenoxide, the limiting equivalent conductance,  $\Lambda_0$ , obtained from the Lee and Wheaton conductance equations, is unreasonably large (279 S cm<sup>2</sup> mol<sup>-1</sup>, Table 1). We attribute this difficulty to the large value of  $K_{\text{LiP}}$ , which

**TABLE 2: Conductance Values of Tetra-*n*-butylammonium-*p*-nitrophenoxide in Acetonitrile<sup>a</sup>**

$c_0 \times 10^4$ (M)	$\Lambda_{\text{obs}}$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_{\text{calc}}^b$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\gamma_{\pm}^2$ <sup>c</sup>	$K_A^d$ (M <sup>-1</sup> )
9.129	139.0	138.3	0.82	23.4
13.28	136.2	135.6	0.79	26.6
18.26	134.6	132.9	0.77	20.9
28.44	129.3	128.4	0.73	27.3
34.23	127.6	126.3	0.71	26.2
47.39	118.5	122.2	0.68	44.6
57.05	119.7	119.7	0.66	31.3

<sup>a</sup> This is a representative set of points from a much larger body of data. <sup>b</sup> Calculated using the Lee and Wheaton conductance equation with  $\Lambda_0 = 150.5$  and  $K_A = 31.2$  M<sup>-1</sup>. <sup>c</sup> Calculated using the Debye-Hückel equation with Bjerrum's distance, which is 7.64 Å for acetonitrile, as the mean ionic diameter. <sup>d</sup> Calculated using the Lee and Wheaton conductance equation with 150.5 as  $\Lambda_0$ .

**TABLE 3: Conductance Values of Lithium *p*-Nitrophenoxide in Acetonitrile<sup>a</sup>**

$c_0 \times 10^4$ (M)	$\Lambda_{\text{obs}}$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\Lambda_{\text{calc}}^b$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\gamma_{\pm}^2$ <sup>c</sup>	$K_A \times 10^4$ <sup>d</sup> (M <sup>-1</sup> )
1.226	39.65	38.58	0.96	10.0
4.582	20.76	21.41	0.95	11.4
9.809	13.68	15.01	0.93	12.9
18.33	11.24	11.15	0.92	10.5
32.08	9.87	8.53	0.91	7.90
73.57	8.77	5.71	0.89	4.46
122.6	8.53	4.45	0.88	2.87

<sup>a</sup> This is a representative set of points from a much larger body of data. <sup>b</sup> Calculated using the Lee and Wheaton conductance equation with 159.3 as  $\Lambda_0$  and  $K_A = 1.07 \times 10^5$  M<sup>-1</sup>. <sup>c</sup> Calculated using the Debye-Hückel equation with Bjerrum's distance, which is 7.64 Å for acetonitrile, as the mean ionic diameter. <sup>d</sup> Calculated using the Lee and Wheaton conductance equation with 159.3 as  $\Lambda_0$ .

**TABLE 4: Spectroscopic Parameters and Equilibrium Constant for the Association between Lithium and *p*-Nitrophenoxide**

	lithium <i>p</i> -nitrophenoxide	free <i>p</i> -nitrophenoxide
$\nu_0$ (cm <sup>-1</sup> )	$2.4660 \times 10^4$ (405.5 nm)	$2.3185 \times 10^4$ (431.3 nm)
$\epsilon_0$ (M <sup>-1</sup> cm <sup>-1</sup> )	$2.220 \times 10^4$	$3.147 \times 10^4$
$\rho$	1.536	1.404
$H$ (cm <sup>-1</sup> )	$3.246 \times 10^3$	$2.745 \times 10^3$
$I$ (M <sup>-1</sup> cm <sup>-2</sup> )	$7.953 \times 10^7$	$9.401 \times 10^7$
$K_{\text{LiF}}$ (M <sup>-1</sup> )	$(3.34 \times 10^4) \pm (1.5 \times 10^4)$	
$\sigma/\epsilon_0$	$4.80 \times 10^{-5}$	

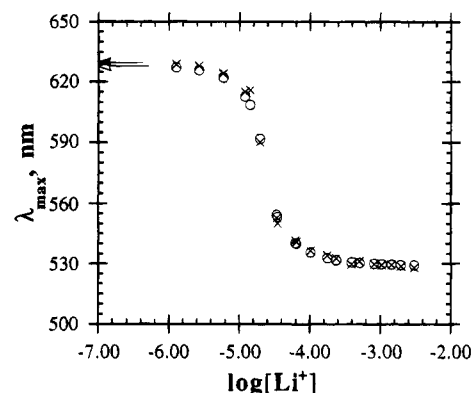
makes the conductance too small for accurate measurements in a range of concentrations where most of the ions are unassociated. A limiting equivalent conductance was calculated for lithium *p*-nitrophenoxide in acetonitrile from the limiting equivalent conductances of lithium iodide, tetra-*n*-butylammonium iodide, and tetra-*n*-butylammonium *p*-nitrophenoxide, given in Table 1.<sup>24</sup> None of these is strongly associated in the concentration range of the measurements. The calculated limiting equivalent conductance is 159.3. Using this value for  $\Lambda_0$ ,  $K_A$  was calculated for each experimental conductance using the Lee and Wheaton conductance equation. The results are presented in Table 3.  $K_A$  is approximately constant up to  $2 \times 10^{-3}$  M lithium *p*-nitrophenoxide concentration, with an average value of  $1.1 \times 10^5$  M<sup>-1</sup>.

### Spectroscopic Results

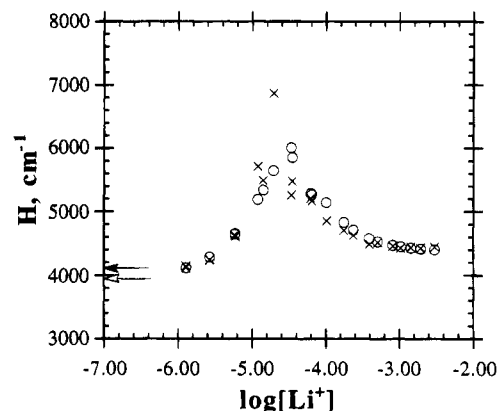
The best results of fitting the spectroscopic data to an equilibrium between an associated species and an unassociated species are presented in Tables 4 and 5. The integrated intensity of the charge transfer band is  $I$ . Plots of the log-normal parameters as a function of  $\log[\text{Li}^+]$  for both the experimental

**TABLE 5: Spectroscopic Parameters and Equilibrium Constant for the Association between Lithium and Betaine**

	lithium betaine	free betaine
$\nu_0$ (cm <sup>-1</sup> )	$1.890 \times 10^4$ (529.1 nm)	$1.5912 \times 10^4$ (628.5 nm)
$\epsilon_0$ (M <sup>-1</sup> cm <sup>-1</sup> )	$3.137 \times 10^3$	$4.910 \times 10^3$
$\rho$	1.197	1.227
$H$ (cm <sup>-1</sup> )	$4.378 \times 10^3$	$3.964 \times 10^3$
$I$ (M <sup>-1</sup> cm <sup>-2</sup> )	$1.472 \times 10^7$	$2.089 \times 10^7$
$K_{\text{LiB}^+}$ (M <sup>-1</sup> )	$(5.47 \times 10^4) \pm (3.0 \times 10^3)$	
$\sigma/\epsilon_0$	$1.44 \times 10^{-5}$	

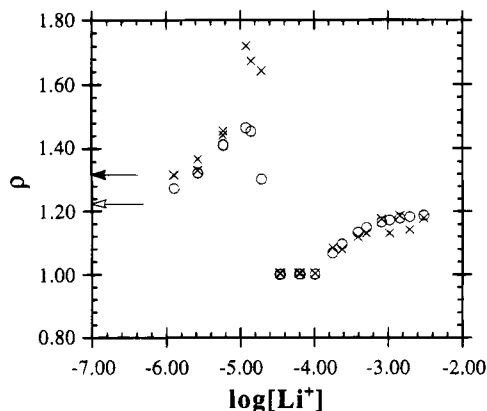


**Figure 1.**  $\log[\text{Li}^+]$  versus  $\lambda_{\text{max}}$  for betaine-LiI solutions. The  $[\text{Li}^+]$  is calculated from eqs 9 and 10 with  $K_{\text{LiB}^+} = 5.47 \times 10^4$  M<sup>-1</sup> and  $K_{\text{LiI}} = 30.4$  M<sup>-1</sup>.  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.

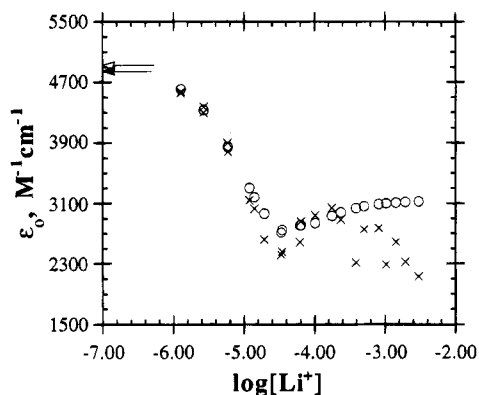


**Figure 2.**  $\log[\text{Li}^+]$  versus  $H$ , the log-normal parameter for the full width-half height, for betaine-LiI solutions. The  $[\text{Li}^+]$  is calculated from eqs 9 and 10 with  $K_{\text{LiB}^+} = 5.47 \times 10^4$  M<sup>-1</sup> and  $K_{\text{LiI}} = 30.4$  M<sup>-1</sup>.  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.

spectra and the calculated spectra of the betaine-LiI solutions are shown in Figures 1-4. The agreement between calculated and experimental values for  $\lambda_{\text{max}}$ ,  $H$ , and  $\rho$  is excellent. For all the experimental parameters, there is either an inflection point or a discontinuity at  $\log[\text{Li}^+] \approx -4.5$ , as there is in the calculated spectra. This identifies the  $[\text{Li}^+]$  at which the concentrations of betaine and its lithium derivatives are equal. The adjusted experimental spectra are shown with the calculated spectra at several different LiI concentrations in Figure 5. The calculation is able to accurately reproduce the experimental band shapes even in the concentration range where the ratio of the associated species to the unassociated species is near unity. We would expect that the agreement between the calculated and



**Figure 3.**  $\log [\text{Li}^+]$  versus  $\rho$ , the log-normal skewness parameter, for betaine-LiI solutions. The  $[\text{Li}^+]$  is calculated from eqs 9 and 10 with  $K_{\text{LiB}^+} = 5.47 \times 10^4 \text{ M}^{-1}$  and  $K_{\text{LiI}} = 30.4 \text{ M}^{-1}$ .  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.

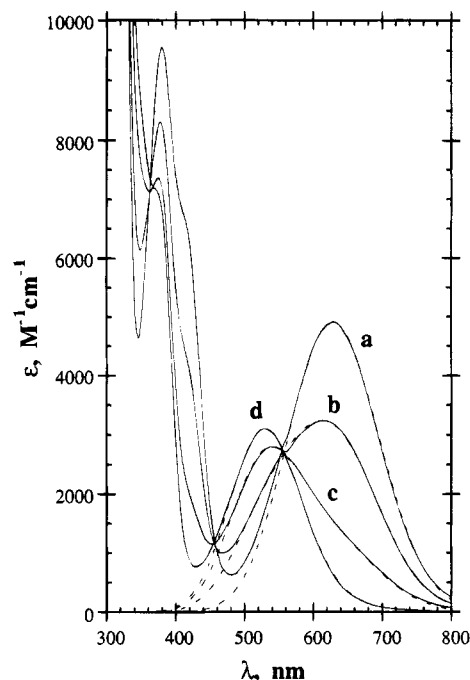


**Figure 4.**  $\log [\text{Li}^+]$  versus  $\epsilon_0$ , for betaine-LiI solutions. The  $[\text{Li}^+]$  is calculated from eqs 9 and 10 with  $K_{\text{LiB}^+} = 5.47 \times 10^4 \text{ M}^{-1}$  and  $K_{\text{LiI}} = 30.4 \text{ M}^{-1}$ .  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration *without* adjustment.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.

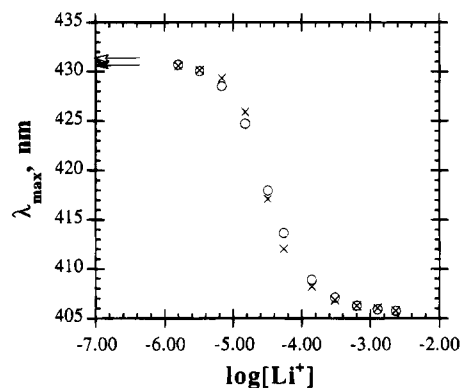
the experimental spectra would be most sensitive to errors in  $K_{\text{LiB}^+}$  in this region. The isosbestic points provide strong support for the intensity adjustment procedure, as well as the formulation of the equilibrium.

Plots of the log-normal parameters for both the experimental spectra and the calculated spectra for the *p*-nitrophenoxide-LiI solutions are shown in Figures 6–9. The agreement between calculated and experimental values for  $\lambda_{\text{max}}$ ,  $H$ , and  $\rho$  is reasonable but not as good as the corresponding betaine-LiI agreement. The region where there is either an inflection point or a discontinuity varies from  $\log [\text{Li}^+] \approx -4.2$  to  $\log [\text{Li}^+] \approx -4.5$ . The adjusted experimental spectra are shown with the calculated spectrum at several different LiI concentrations in Figure 10. As with the betaine-LiI spectra, there is good agreement between the adjusted experimental charge transfer spectra and the calculated charge transfer spectra.

We have also studied the effects of tetra-*n*-alkylammonium iodide salts on the betaine charge transfer band. Within the limits of experimental error,  $\nu_0$ ,  $\rho$  and  $H$ , do not change. Both the tetra-*n*-butylammonium iodide (TBAI) and the tetra-*n*-heptylammonium iodide (THAI) solutions show a systematic decrease in the molar absorptivity,  $\epsilon_0$ , reaching a factor of 2 at  $\sim 3 \times 10^{-3} \text{ M}$  THAI. In the presence of THAI,  $\epsilon_0$  is

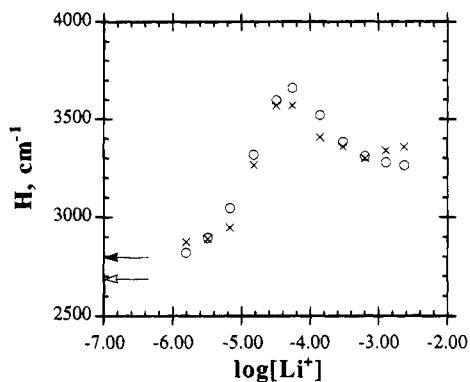


**Figure 5.** Betaine-LiI charge transfer spectra. This is a selection from a much larger available group of spectra. The betaine concentration is between  $4.4$  and  $4.8 \times 10^{-4} \text{ M}$  in all cases: (a) no added LiI; (b) lithium iodide concentration,  $S_0$ , is  $3.096 \times 10^{-5} \text{ M}$ ,  $[\text{Li}^+] = 1.194 \times 10^{-5} \text{ M}$ ; (c)  $S_0$  is  $9.691 \times 10^{-5} \text{ M}$ ,  $[\text{Li}^+] = 6.200 \times 10^{-5} \text{ M}$ ; (d)  $S_0$  is  $8.846 \times 10^{-4} \text{ M}$ ,  $[\text{Li}^+] = 8.181 \times 10^{-4} \text{ M}$ . For each set of spectra, the solid line is the experimental data, adjusted as described in the text. The dashed line is the spectrum calculated by summing the absorbances of betaine and Li-betaine at the concentrations given by the equilibrium expressions eqs 9 and 10 with  $K_{\text{LiB}^+} = 5.47 \times 10^4 \text{ M}^{-1}$  and  $K_{\text{LiI}} = 30.4 \text{ M}^{-1}$ . The factors  $\epsilon_{0,\text{cal}}/\epsilon_{0,\text{exp}}$  used for the adjustment were (a) 1.01, (b) 1.05, (c) 1.09, and (d) 1.35. The weak inflections in several of the spectra at  $\sim 555 \text{ nm}$  are due to an instrumental artifact.

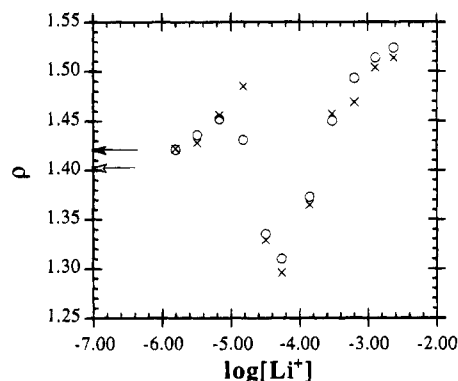


**Figure 6.**  $\log [\text{Li}^+]$  versus  $\lambda_{\text{max}}$  for *p*-nitrophenoxide-LiI solutions. The  $[\text{Li}^+]$  is calculated from eqs 7 and 8 with  $K_{\text{LiP}} = 3.34 \times 10^4 \text{ M}^{-1}$  and  $K_{\text{LiI}} = 30.4 \text{ M}^{-1}$ .  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.

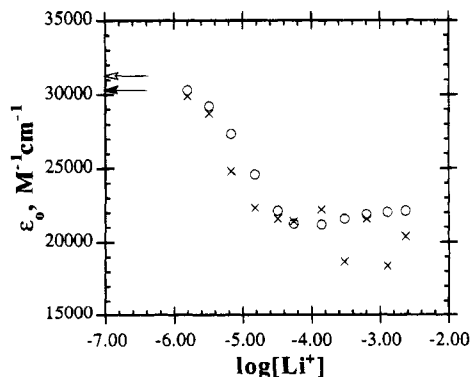
systematically somewhat higher at higher betaine concentrations, suggesting an impurity explanation for the decrease in  $\epsilon_0$ . Addition of triethylamine to an otherwise complete cell containing a mixed solution of the betaine and THAI also causes an increase in  $\epsilon_0$ , suggesting that an acidic impurity may be partly responsible. In neither case does  $\epsilon_0$  recover to the expected value. Another reason for loss of optical intensity may be adventitious oxidation of  $\text{I}^-$  to  $\text{I}_3^-$ , followed by reaction of  $\text{I}_3^-$  with the betaine to give a product lacking the charge transfer band, as described above.



**Figure 7.**  $\log [Li^+]$  versus  $H$ , the log-normal full width-half height parameter, for *p*-nitrophenoxide-LiI solutions. The  $[Li^+]$  is calculated from eqs 7 and 8 with  $K_{LiP} = 3.34 \times 10^4 M^{-1}$  and  $K_{LiI} = 30.4 M^{-1}$ .  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.

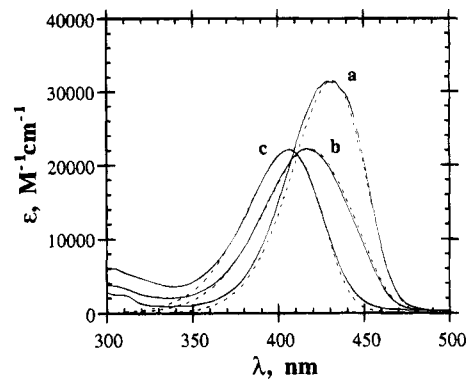


**Figure 8.**  $\log [Li^+]$  versus  $\rho$ , the log-normal skewness parameter, for *p*-nitrophenoxide-LiI solutions. The  $[Li^+]$  is calculated from eqs 7 and 8 with  $K_{LiP} = 3.34 \times 10^4 M^{-1}$  and  $K_{LiI} = 30.4 M^{-1}$ .  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.



**Figure 9.**  $\log [Li^+]$  versus  $\epsilon_0$  for *p*-nitrophenoxide-LiI solutions. The  $[Li^+]$  is calculated from eqs 7 and 8 with  $K_{LiP} = 3.34 \times 10^4 M^{-1}$  and  $K_{LiI} = 30.4 M^{-1}$ .  $\times$  symbols are from the log-normal best fit of the experimental spectra at each concentration without adjustment.  $\circ$  symbols are from the log-normal best fit of the calculated spectra. The filled arrow indicates the infinite dilution experimental value. The open arrow indicates the infinite dilution calculated value.

The adjustment of  $\epsilon_0$  does not alter  $\nu_0$ ,  $\rho$ , or  $H$ , so the agreement of the calculated and observed values of these parameters, shown in Figures 1–4 and 6–9, does not depend on the adjustment. In effect, our programs use the shape of



**Figure 10.** *p*-Nitrophenoxide-LiI charge transfer spectra. This is a selection from a much larger available group of spectra. In all cases the tetra-*n*-butylammonium *p*-nitrophenoxide concentration is  $3.661 \times 10^{-5} M$ : (a) no added LiI; (b) lithium iodide concentration,  $S_0$ , is  $5.110 \times 10^{-5} M$ ,  $[Li^+] = 3.208 \times 10^{-5} M$ ; (c)  $S_0$  is  $1.363 \times 10^{-3} M$ ,  $[Li^+] = 1.275 \times 10^{-3} M$ . For each set of spectra, the solid line is the experimental data, adjusted as described in the text. The dashed line is the spectrum calculated by summing the absorbances of *p*-nitrophenoxide and Li-*p*-nitrophenoxide at the concentrations given by the equilibrium expressions eqs 7 and 8, with  $K_{LiP} = 3.34 \times 10^4 M^{-1}$  and  $K_{LiI} = 38.9 M^{-1}$ . The factors  $\epsilon_{0,calc}/\epsilon_{0,exp}$  used for the adjustment were (a) 1.04, (b) 1.03, and (c) 1.20.

the bands to evaluate  $K_{LiP}$  and  $K_{LiB^+}$  and then use the association constants to evaluate the factor by which the  $\epsilon(\nu)$  values are adjusted. Figures 5 and 10 demonstrate the success of these procedures. Without considering the whole array of  $\epsilon(\nu)$  values, it would not have been evident that only two-chromophore equilibria were involved or possible to evaluate association constants accurately.

The results determined from conductance data are summarized in Table 1. The average discrepancy between  $\Lambda_{obs}$  and  $\Lambda_{calc}$  from the conductance data of LiI in acetonitrile is 0.6%.  $K_{LiI} = 30 \pm 4 M^{-1}$ . The mean ionic diameter,  $R$ , is badly determined by the results. The values of  $R$  that will give  $K_{LiI}$  values between 26 and  $34 M^{-1}$  range from 2.6 to 15 Å.  $K_A$  and  $\Lambda_0$  are not strongly dependent on  $R$ .<sup>21,25</sup> Therefore,  $R$  was fixed at Bjerrum's distance<sup>21</sup> (7.6 Å for acetonitrile). Other parameters used are  $\eta = 0.3426 \text{ cP}^{26}$  and  $D = 36.70$ .<sup>27</sup>

## Discussion

All spectroscopic results for both betaine and *p*-nitrophenoxide in the presence of LiI are consistent with the formation of well defined lithium phenoxide compounds. For *p*-nitrophenoxide this is confirmed by the conductance measurements, although the association constant determined by conductance is larger than that determined spectrophotometrically. Moreover, the lithium phenoxide association constant is 3 powers of ten larger than the LiI association constant, while the latter is similar to other ion pair formation constants in acetonitrile.<sup>26,28–30</sup> Thus the compound formed by lithium ion and phenoxide appears to have some covalent character. The formation constant for lithium betaine is similar to that for lithium *p*-nitrophenoxide. It is reasonable to suppose that its bonding is similar and that it, too, has covalent character.

The formation of a new bond will lead to different wave functions for both the ground and excited states. The ground state energy and the ground state–excited state overlap integral will change. A priori, the intensity of the charge transfer band may show either an increase or a decrease with formation of the new bond and could be either blue shifted or red shifted. However, it seems intuitively likely that formation of a bond with a positively charged partner, at the phenolic oxygen, will increase the energy required to shift an electron from the

phenolic oxygen to another part of the molecule, and it may reduce the donor–acceptor overlap integral. *p*-Nitrophenol, which has a substantially covalent O–H bond in the place of the anionic oxygen, shows a substantially blue-shifted charge transfer band with a substantially diminished intensity.<sup>31</sup> We thus expect a blue shift and a decrease in intensity to accompany the formation of partially covalent Li–O bonds to *p*-nitrophenoxide and the betaine. This is exactly what is observed.

Bond formation at the phenoxide oxygen is also suggested by the spectra shown in Figure 5. These spectra show that not only the charge transfer band but also the  $\pi \rightarrow \pi^*$  bands of the betaine are strongly perturbed in the presence of Li<sup>+</sup>. This would be expected for bond formation but not for an electric field effect. Moreover, these spectra show three isosbestic points. The two at longer wavelength are nearly exact. The one at  $\sim 360$  nm is somewhat dispersed, probably due to the difficulties with intensities that were experienced, but seems to be real. Isosbestic points are a hallmark of two-component mixtures.

The spectrophotometric  $K_{\text{LiP}}$  ( $3.3 \times 10^4 \text{ M}^{-1}$ ) is lower than the conductance  $K_{\text{LiP}}$  ( $1.1 \times 10^5 \text{ M}^{-1}$ ). There are several differences between the two systems that could account for these discrepancies. The solutions for spectrophotometric analysis contained low concentrations of the phenoxide anion with increasing concentrations of lithium iodide. The solutions used for conductance measurements had a one to one mole ratio of lithium cations to *p*-nitrophenoxide anions.  $K_{\text{LiP}}$  is much larger than  $K_{\text{LiI}}$ . At a given total lithium ion concentration, the ionic strength of the spectrophotometric solution was larger than that for the conductance solution. We have tried to take into account the differing ionic strengths using Debye–Hückel activity coefficients. However, our approximation of the non-Coulombic part of the activity coefficient ratio by unity is suspect. While the disagreement is probably too large to be explained only in terms of activity coefficients, errors in activity coefficients could be significant.<sup>19,32–35</sup> With increasing concentration of both the lithium cation and the phenoxide anion, the system may become prone to higher aggregation, particularly the formation of tetramers.<sup>36</sup> With increasing lithium concentration, the experimental spectra broaden and then narrow when the fraction of the associated species becomes greater than approximately 0.50. However, above  $[\text{Li}^+] \approx 1.0 \times 10^{-3} \text{ M}$ ,  $H$  begins to increase again (see Figure 7). We have dealt with this difficulty by truncating the calculation for determining  $K_{\text{LiP}}$  at  $[\text{LiI}] = 1.0 \times 10^{-3} \text{ M}$ . If higher aggregation is responsible for this effect, it is likely that it begins for concentrations less than  $1.0 \times 10^{-3} \text{ M}$ . This aggregation will increase the apparent  $K_{\text{LiP}}$  and is more likely to be important in the solutions used to measure conductance (where the total phenoxide concentration equals the total lithium concentration). Error may also be introduced into the spectrophotometric determination of  $K_{\text{LiP}}$  by the implicit assumption that the salt concentration does not alter the intrinsic spectroscopic properties of the absorbing species.

There are comparisons in the literature between association constants,  $K_A$ , determined from spectrophotometric data and those from conductance data. In some cases, the agreement is good. Gilkerson<sup>19–21</sup> determined  $K_A$  values for group I picrates and tetraphenyl borates 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. Jordan et al.<sup>37</sup> measured  $K_A$  values for 1-methylpyridinium iodide in 95% ethanol spectrophotometrically and conductometrically. Although the spectrophotometric  $K_A$  was wavelength dependent, the discrepancy with the conductance value in no case exceeded 20%. In other cases, where the spectro-

scopic  $K_A$  has been determined by NMR, there is disagreement by at least a factor of 2 between the spectroscopic and conductance values.<sup>19,38–40</sup> Gilkerson and Kendrick<sup>19</sup> have attributed such differences to one or more of the following: experimental errors; use of different expressions for activity coefficients in evaluating  $K_A$  from the different sets of data; and use of different concentration ranges for different experiments. In any event, the discrepancy between the two values of  $K_{\text{LiP}}$  does not jeopardize the conclusion that the changes in the betaine and *p*-nitrophenoxide spectra on addition of Li<sup>+</sup> are due to compound formation.  $K_{\text{LiP}}$  from conductance is even larger than  $K_{\text{LiP}}$  from spectroscopic measurements.

At higher lithium concentrations,  $H$  does not significantly increase for the betaine–LiI solution, although there may be some upward drift (Figure 2). This suggests that higher order aggregation is not as significant for the betaine–LiI solutions as for the *p*-nitrophenoxide–LiI solutions. This is consistent with the results of Jackman and DeBrosse,<sup>36</sup> who found that ortho substituents were effective in controlling the size of lithium phenoxide aggregates.

In contrast, our observation of the 1-alkyl-4-cyanopyridinium iodide system<sup>7,41</sup> does not indicate the formation of a new bond, although ion pair dimers may be involved. In solvents with dielectric constant between 4 and 8, the charge transfer band of 4-cyano-1-(3,7-dimethyloctyl)pyridinium iodide (Py<sup>+</sup>I<sup>−</sup>) shifts to higher frequency with increasing concentration.<sup>7</sup> The intensity of the charge transfer band also increases gradually with increasing salt concentration.<sup>7</sup> The change in intensity of a charge transfer band, in the presence of an electric field, can be explained by considering the electric field effects on the ground and excited state polarizabilities.<sup>42</sup> These results are consistent with an electric field effect which might be associated with ion pair dimerization.

## Conclusion

We conclude that the halochromism reported by Reichardt and co-workers<sup>9</sup> for **1** in the presence of a variety of metallic salts is the result of compound formation, with the magnitude of the limiting shifts reflecting the degree of covalency in the metal–oxygen bond. This would be consistent with the reported correlation between the magnitude of this shift and the ionic radius of the metal.<sup>9</sup> It would be consistent with the failure of quaternary ammonium salts to show a similar effect. The assignment of  $E_T(30)$  values<sup>9</sup> to solutions of LiI or other metal salts in acetonitrile is probably inappropriate because the spectroscopic shifts on which they are based are due to the formation of specific bonds and do not reflect generalized medium effects.

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