Among the possible products are surface uranium hydride and gaseous hydrogen, methane, iodomethane, or hydrogen iodide.

*Acknowledgment.* We are grateful to Dr. C. Politis, Institut für Angewandte Kernphysik I, Kernforschungszentrum, Karlsruhe, for the preparation of the UC sample. J.G.D. expresses gratitude to the Department of Chemistry and to Virginia Tech for granting an educational leave.

**Registry No.** $I_2$, 7553-56-2; $CH_3I$, 74-88-4; UC, 12070-09-6.

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# Ion Association. Comparison of Spectroscopic and Conductance Values of Association Constants

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Molar conductances of potassium, rubidium, and cesium picrate and of cesium tetraphenylborate have been determined in 2-butanone at 25 °C over a concentration range of 0.1–1.6 mmol $L^{-1}$. These $\Lambda,C$ data together with those for lithium and sodium already determined in this laboratory were fitted by using the Lee–Wheaton (LW), the Pitts (P), the Fuoss 78 (F), and the Justice (J) conductance equations to obtain values of ion association constants, $K_A$, and limiting molar conductances. Spectrophotometric absorbance changes were measured for sodium and cesium picrate and remeasured for lithium and tetra-*n*-butylammonium picrate at 380 nm and 25 °C over a concentration range of 0.02–1.4 mmol $L^{-1}$. Values of the cesium-133 NMR chemical shifts of cesium picrate were determined over a concentration range of 0.1–3 mmol $L^{-1}$ while those for cesium tetraphenylborate were determined over a range from 0.25 to 10 mmol $L^{-1}$. We calculated values of ion association constants for the various salts using these spectroscopic data. The values of $K_A$ determined spectroscopically and the values determined conductimetrically are the same within experimental error with one exception; for cesium tetraphenylborate, the NMR value depends on the concentration range of data included in the analysis.

## Introduction

A variety of spectroscopic techniques has been applied to the study of ion–solvent and ion–ion interactions in electrolyte solutions in addition to the application of more classical physicochemical methods.[1] Spectroscopic studies of ion–ion interaction have usually focused on structural aspects, but the increasing sensitivity of modern instruments and their availability (FT NMR spectrometers, for example) has made possible the application of these techniques to concentrations as small as a millimolar or less.

The association of oppositely charged univalent ions in solution to form ion pairs

$$M^+ + X^- \rightleftharpoons M^+\cdots X^- \rightleftharpoons M^+,X^- \qquad (1)$$

where $M^+\cdots X^-$ represents a solvent-separated ion pair and $M^+,X^-$ represents the contact ion pair, becomes important in water when the electrolyte reaches the 0.01–0.1 mol $L^{-1}$ range and at even lower concentrations in less polar solvents. Equilibrium constants for ion association, $K_A$, have usually been determined by conductance methods, but there have been a number of reports of spectroscopic determinations.[2–9] In several instances there have been conductance data available so that comparison of the results of the different physical techniques was made; there was agreement between spectroscopic values and conductance values of the association constant in some cases[2,3,7] and disagreement in others.[5,6,8] There has been some discussion in the literature (see Covington et al.[5]) concerning the significance of any such differences; what has appeared has been in the nature of suggestion or the expression of opinion.

The spectroscopic differences between free ions and ion pairs are due to perturbations of energy levels in either the cation, anion, or both, because of interaction between the ions, presumably at short range. Those ions counted as paired (nonconducting) by the conductance technique may include solvent-separated ion pairs, $M^+\cdots X^-$, in addition to those contact ion pairs, $M^+,X^-$ detected spectroscopically. If there are real differences in values of $K_A$ obtained by using the different physical techniques, then these differences could possibly be exploited to yield further information about the pair formation process, including details of the role the solvent molecules must play in the final step, formation of the contact pair. If the differences in values of $K_A$ that have been determined by the several different techniques are not real but are traceable to some experimental error, then establishment of that fact would mean that one element of controversy could be removed from the use of spectroscopic techniques to probe the state of electrolyte solutions.

A program is under way in this laboratory to compare the values of ion association constants as found by the conductance method with those determined by using spectroscopic techniques under conditions such that both kinds of measurements are carried out over the same range of electrolyte concentration and for which the same expressions for ion activity coefficients are used in treating both kinds of data. This is a report of UV–visible spectrophotometric studies of lithium, sodium, and cesium picrates, cesium-133 NMR chemical shift studies of cesium picrate and cesium tetraphenylborate, and conductance studies of potassium, rubidium, and cesium picrate and of cesium tetraphenylborate, all in 2-butanone solvent at 25 °C. The inclusion of these conductance measurements together with data from a recent study of lithium and sodium picrate[10] furnishes data on a complete series of alkali-metal picrates. We have analyzed these data using four

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(1) See, for example: *Faraday Discuss. Chem. Soc.* **1977**, *No. 64*.

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recently derived conductance equations, and the results are compared.

An earlier report[11] from this laboratory of a UV–visible spectrophotometric study of lithium picrate in 2-butanone yielded a value of $K_A$(UV–vis) some 40% larger than the conductance value, a surprising result. A number of improvements in the experimental approach have been made with the result that the previous value of $K_A$ for lithium picrate is shown to be incorrect. We find agreement, within experimental error, between the spectroscopic and conductance values of $K_A$ for all the salts included in this study, with one possible exception, the NMR value for cesium tetraphenylborate salt.

## Experimental Section

2-Butanone (Fisher Scientific Co., Certified) was purified following the procedure of Hughes,[12] except that the molecular sieves (Davison Type 4A, grade 512) were removed before the second distillation under nitrogen. A third distillation was carried out if found necessary to lower impurity levels. The water content in the final solvent was determined by GC on Poropak Q to be 10–20 ppm, and its specific conductivity was in the range (2–7) $\times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Solvent was recovered by passing the alkali-metal salt solutions through a $1.5 \times 33\ \mathrm{cm}^2$ column packed with alumina (Alcoa, grade F-20).[13]

Lithium and sodium picrates were prepared and purified as before.[10] Potassium and rubidium picrates were prepared by adding 70% ethanolic solutions of the bromide or iodide, respectively, to tetrabutylammonium picrate also in 70% ethanol. Cesium picrate was prepared by the addition of aqueous solutions of cesium chloride to picric acid in 90% ethanol. The salts were recrystallized three or four times from water and dried in vacuo at 132 °C (except for cesium picrate which was dried at room temperature) for 5–7 days. Cesium tetraphenylborate was prepared by the reaction of 5 g of cesium chloride (in 40 mL of acetone plus 12 mL of water) with 10.2 g of sodium tetraphenylborate (Fisher Scientific Co., Certified) dissolved in a similar mixture. The resulting precipitate was recrystallized three times from acetone and water and dried in vacuo for several days (in some cases with heating to 60 °C). Tetra-*n*-butylammonium picrate had been prepared several years earlier by Juliet Hahn of this laboratory by converting the corresponding iodide to the hydroxide with silver oxide and neutralizing the hydroxide with picric acid in 95% ethanol. The crude product was recrystallized eight times from hot ethanol by adding water (1–4 mL), cooling, and drying for 7 days in vacuo over phosphorus pentoxide before the first series of measurements; it was recrystallized four more times and dried 11 days before the second series and dried 3 more days before the last series. Another preparation attempted during this period was contaminated with what was tentatively identified as the triiodide salt (green-black crystals, mp 68–69 °C (lit. mp 70–70.5 °C));[14] this may be one cause of poor reproducibility of spectrophotometric absorbances of those picrates prepared from iodide salts. Tetra-*n*-butylammonium triiodide exhibits a broad strong absorption peak at 365 nm in methylene chloride.[15] Earlier use of iodide salts led to difficulties, but switching to chloride precursors in preparing the alkali-metal salts greatly enhanced the reproducibility of spectroscopic measurements. All salts were stored in the dark, and solutions were protected from possible photolysis[16] by foil wrapping.

The conductance bridge and oil-filled thermostat (25.00 ± 0.001 °C) have already been described.[10] A Jones type conductance cell having a cell constant of 1.8381 $\mathrm{cm}^{-1}$ (determined by the method of Lind et al.)[17] was used. The cell was rinsed with solvent or solution three times before filling. Resistances of solutions (accurate to 3 ppm) were measured at 0.5, 1, and 2 kHz; the extrapolation to infinite frequency was omitted in all of those cases where the change in resistance was less than 0.01%, the value at 1 kHz then being listed in Table I. Solutions were prepared by weight, and all transfers were carried out in a nitrogen-filled drybox. Concentrations of solutions (accurate to 0.05%) were calculated by taking the solution density to be the same as that of the solvent. The pertinent physical constants of 2-butanone at 25 °C are dielectric constant 18.01, density 0.7996 g $\mathrm{mL}^{-1}$, and viscosity 0.3774 cP.[18]

**TABLE I: Molar Conductances in 2-Butanone at 25 °C**

| $10^4C$/mol $\mathrm{L}^{-1}$ | $\Lambda/\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$ | $10^4C$/mol $\mathrm{L}^{-1}$ | $\Lambda/\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$ |
|---|---|---|---|
| KPi | | $CsBPh_4$ | |
| 12.993 | 81.13 | 16.015 | 88.30 |
| 9.1204 | 87.90 | 8.518 | 94.49 |
| 6.3933 | 94.43 | 5.092 | 98.72 |
| 5.1183 | 98.30 | 4.302 | 100.06 |
| 3.9314 | 102.63 | 2.093 | 104.27 |
| 3.8773 | 102.63 | | |
| 1.5868 | 114.81 | CsPi | |
| | | 7.942 | 99.03 |
| RbPi | | 5.059 | 106.19 |
| 7.4097 | 95.96 | 2.862 | 113.88 |
| 4.9803 | 102.51 | 1.296 | 121.47 |
| 4.0433 | 105.55 | 14.75 | 87.91 |
| 3.4322 | 108.04 | 10.37 | 94.18 |
| 0.8515 | 122.35 | 5.794 | 103.88 |
| | | 1.637 | 119.39 |

Spectrophotometric measurements were carried out using a Cary 14 spectrophotometer equipped with a thermostated cell compartment maintained at 25.0 ± 0.1 °C. Most measurements were made using a dilution pipet (Teflon stopcocks), mixing flask, Teflon diaphragm circulating pump, and silica flow cells (0.1- and 0.5-cm light paths, Hellma Cells, Inc.) all connected with Bev-a-line IV tubing under a positive pressure of dry nitrogen. The dilution pipet and mixing flask were filled in the drybox. Several measurements were carried out at low concentrations of lithium picrate using cylindrical 2- and 5-cm path length cells. All absorbance measurements used in equilibrium calculations were made at a fixed wavelength of 380 nm (the wavelength of maximum change for the picrates), were between 0.5 and 1.4 in magnitude, and were read directly from the slide-wire pointer.

Cesium-133 NMR measurements were carried out at 26.25 MHz on a Bruker WP-200 spectrometer using a 10- and 15-mm probe. The magnetic field was locked on the 2-butanone solvent methyl singlet proton signal. The temperature at the probe was maintained at 25 ± 0.5 °C. Downfield shifts are assigned positive values. Reference to cesium-133 chloride at infinite dilution in water was established with aqueous cesium chloride as an external standard with the field locked on the water proton signal. Proton NMR spectra of aqueous 1.0 M cesium chloride and of 2-butanone each with a coaxial capillary containing $Me_4Si$ as an external reference were obtained on a Varian EM-360 spectrometer. The difference in the methyl singlet and the water proton shifts yielded a lock signal correction of 3.23 ppm. The cesium-133 NMR shifts of aqueous cesium chloride solutions used as external standards (Table III) were referenced to infinite dilution at 25 °C by using the results of Richards.[19] The bulk susceptibility correction (2-butanone vs. water) is +0.88 for the WP-200 experiments.[20] Experimental uncertainties in the chemical shifts are estimated to be less than 0.04 ppm.

## Results

The molar conductances, Λ, of potassium, rubidium, and cesium picrates in the concentration range of 0.1–1.6 mmol $\mathrm{L}^{-1}$ are listed

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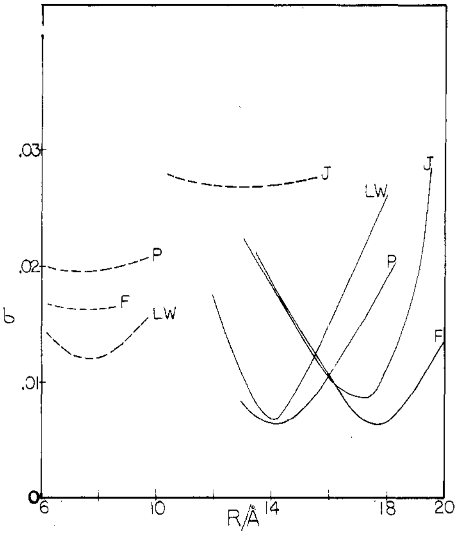

**Figure 1.** Standard deviations σ plotted as a function of the distance parameter *R* for the fit of the conductances in 2-butanone at 25 °C of lithium picrate (dashed lines) and of cesium picrate (solid lines, first set) to eq 2–4 using the Lee–Wheaton (LW), the Fuoss 1978 (F), the Pitts (P), and the Justice (J) conductance functions.

in Table I. Values of molar absorptivity, ϵ, calculated from the absorbance changes, $\Delta A$, at 380 nm and 25 °C for lithium, sodium, cesium, and tetra-*n*-butylammonium picrates at salt concentrations ranging from 0.02 to 1.4 mmol L$^{-1}$ are listed in Table III. The cesium-133 NMR chemical shifts of cesium picrate and cesium tetraphenylborate are also listed in Table III as a function of salt concentration.

The changes in all three observables, molar conductance, molar absorptivity, and chemical shift for the alkali-metal salts, are taken to be related to changes in the fraction, γ, of ions remaining unassociated:

$$\Lambda = \gamma\Lambda^{\circ\prime} \tag{2}$$

$$\epsilon = \gamma\epsilon_I + (1-\gamma)\epsilon_p \tag{3}$$

$$\delta = \gamma\delta_I + (1-\gamma)\delta_p \tag{4}$$

where $\Lambda^{\circ\prime} = \Lambda^\circ - f(\Lambda^\circ,R,\gamma C)$. Here $\Lambda^\circ$ is the limiting equivalent conductance and $f(\Lambda^\circ,R,\gamma C)$ is the correction term for ion atmosphere effects. $\epsilon_I$ is the molar absorptivity of completely dissociated salt, $\epsilon_p$ is that for the ion pairs, and $\delta_I$ and $\delta_p$ are the corresponding values of the cesium-133 chemical shift. The data were fitted to these equations together with eq 5 and 6 by using procedures described below.

$$K_A = (1-\gamma)/Cy_\pm{}^2\gamma^2 \tag{5}$$

$$\ln y_\pm{}^2 = -2\kappa q/(1+\kappa R) \tag{6}$$

Here $\kappa = (16\pi Nq/1000)^{1/2}(C\gamma)^{1/2}$, the Debye–Hückel characteristic inverse distance, $q = z^2e^2/(2DkT)$, Bjerrum's distance, and *R* is the separation distance beyond which ions are considered to be unassociated. γ was assumed (as a working hypothesis) to be different for each of the kinds of experiments represented by eq 2–4 above.

*Conductance.* The sets of $\Lambda,C$ data listed in Table I together with those for lithium and sodium picrate[10] were fitted to eq 2, 5, and 6 by using the Lee–Wheaton (LW) conductance equation,[21] the Fuoss 1978 (F) conductance equation,[22] the Pitts equation (P),[23] and the Justice equation (J)[24,25] to calculate the function $f(\Lambda^\circ,R,\gamma C)$ in eq 2. We have followed Pethybridge and Taba[26] in treating all ion pairs as nonconducting in applying the Fuoss 1978 equation and have used their expansions of the $C_1$–$C_5$ functions of Lee and Wheaton and also the *S* and *T* functions of Pitts. Computer programs were written for each of the con-

**TABLE II: Conductance Parameters of Alkali-Metal Salts**

| eq | $K_A$/L mol$^{-1}$ | $\Lambda^\circ/\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $R_M$/Å | $10^2\sigma$ |
|---|---|---|---|---|
| | | LiPi | | |
| LW | 6765 ± 13 | 131.43 ± 0.08 | 7.8 | 1.2 |
| P | 6646 ± 21 | 130.85 ± 0.13 | 7.1 | 2.0 |
| F | 6688 ± 17 | 131.00 ± 0.11 | 7.4 | 1.6 |
| J | 6557 ± 26 | 130.17 ± 0.17 | 13.0 | 2.5 |
| | | NaPi | | |
| LW | 2348 ± 1 | 131.38 ± 0.10 | 8.6 | 0.4 |
| P | 2318 ± 4 | 131.19 ± 0.04 | 7.8 | 1.8 |
| F | 2334 ± 3 | 131.24 ± 0.03 | 8.2 | 1.2 |
| J | 2379 ± 4 | 131.04 ± 0.04 | 13.0 | 1.8 |
| | | KPi | | |
| LW | 879 ± 6 | 132.71 ± 0.14 | 16.4 | 8.3 |
| P | 905 ± 6 | 132.72 ± 0.14 | 17.3 | 8.3 |
| F | 923 ± 6 | 132.79 ± 0.15 | 19.5 | 8.4 |
| J | 922 ± 6 | 132.66 ± 0.14 | 18.3 | 8.2 |
| | | RbPi | | |
| LW | 705 ± 4 | 133.19 ± 0.10 | 15.6 | 6.6 |
| P | 723 ± 4 | 133.17 ± 0.10 | 15.6 | 6.6 |
| F | 744 [illegible] 4 | 133.16 ± 0.10 | 19.5 | 6.6 |
| J | 754 ± 4 | 133.11 ± 0.10 | 20.7 | 6.7 |
| | | CsPi | | |
| LW | 594 ± 1 | 135.12 ± 0.02 | 14.1 | 0.7 |
| P | 606 ± 1 | 135.07 ± 0.02 | 14.1 | 0.6 |
| F | 628 ± 1 | 135.09 ± 0.02 | 17.3 | 0.6 |
| J | 621 ± 1 | 135.07 ± 0.02 | 17.3 | 0.9 |
| LW | 584 ± 2 | 134.42 ± 0.08 | 15.6 | 4.6 |
| P | 603 ± 2 | 134.42 ± 0.08 | 15.9 | 4.4 |
| F | 623 ± 2 | 134.48 ± 0.07 | 19.4 | 4.5 |
| J | 613 ± 3 | 134.48 ± 0.08 | 17.3 | 5.1 |
| | | CsBPH$_4$ | | |
| LW | 170 ± 2 | 114.02 ± 0.08 | 13.0 | 6.2 |
| P | 169 ± 2 | 113..0 ± 0.07 | 12.4 | 6.0 |
| F | 200 ± 2 | 113.95 ± 0.07 | 16.4 | 6.1 |
| J | 181 ± 2 | 113.99 ± 0.08 | 14.8 | 6.4 |

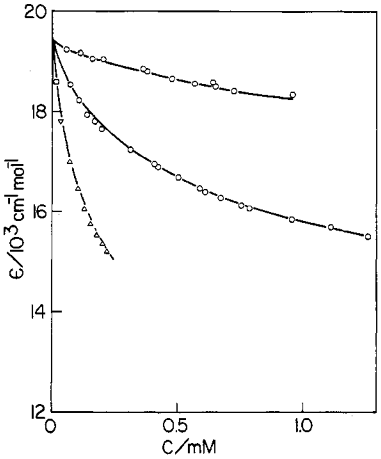

**Figure 2.** Molar absorptivities ϵ for lithium picrate (lower curve), sodium picrate (middle curve), and cesium picrate (upper curve) are plotted as a function of salt concentration *C* in 2-butanone at 25 °C. The solid lines are calculated from the parameters listed in Table V.

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**TABLE III: Molar Absorptivities and Cesium-133 Chemical Shifts for Salts in 2-Butanone at 25 °C**

| $C$/mmol $L^{-1}$ | $\epsilon$/$cm^{-1}$ L $mol^{-1}$ | $C$/mmol $L^{-1}$ | $\epsilon$/$cm^{-1}$ L $mol^{-1}$ |
|---|---|---|---|
| LiPi | | CsPi | |
| 0.01754 | 18.59[a] | 0.0571 | 19.26[d] |
| 0.03734 | 17.82[b] | 0.1095 | 19.18 |
| 0.07257 | 16.98[c] | 0.1578 | 19.10 |
| 0.1036 | 16.47 | 0.2024 | 19.07 |
| 0.1317 | 16.04 | 0.3633 | 18.86 |
| 0.1573 | 15.75 | 0.6429 | 18.59 |
| 0.1808 | 15.53 | 0.9593 | 18.36 |
| 0.2024 | 15.36 | 0.3790 | 18.81 |
| 0.2222 | 15.21 | 0.4791 | 18.68 |
| | | 0.5693 | 18.57 |
| NaPi | | 0.6510 | 18.51 |
| 0.07274 | 18.56[c] | 0.7253 | 18.41 |
| 0.1064 | 18.23 | | |
| 0.1384 | 17.95 | $Bu_4NPi$ | |
| 0.1690 | 17.80 | 0.4327 | 19.34 |
| 0.1981 | 17.64 | 0.6142 | 19.27 |
| 0.3162 | 17.24[d] | 0.9244 | 19.24 |
| 0.4122 | 16.96 | 0.6023 | 19.34 |
| 0.5041 | 16.70 | 0.7174 | 19.29 |
| 0.5921 | 16.47 | 0.3508 | 19.33 |
| 0.6764 | 16.29 | 0.4374 | 19.34 |
| 0.7573 | 16.13 | 0.5135 | 19.28 |
| 0.4214 | 16.90 | 0.5808 | 19.27 |
| 0.6118 | 16.41 | 0.6408 | 19.26 |
| 0.7904 | 16.09 | 0.6946 | 19.26 |
| 0.9582 | 15.83 | | |
| 1.116 | 15.69 | | |
| 1.265 | 15.49 | | |
| 1.406 | 15.40 | | |
| $C$/mmol $L^{-1}$ | $-\delta$/ppm | $C$/mmol $L^{-1}$ | $-\delta$/ppm |
| CsPi | | $CsBPh_4$ | |
| 2.889 | 19.60[e] | 10.134 | 40.37[e] |
| 2.076 | 19.75 | 8.237 | 38.48 |
| 1.543 | 20.00 | 6.861 | 36.97 |
| 1.500 | 20.03 | 5.653 | 35.45 |
| 0.6347 | 20.77 | 5.169 | 34.84 |
| 0.1080 | 21.49 | 3.719 | 32.74 |
| | | 1.534 | 28.81[f] |
| | | 1.100 | 27.56 |
| | | 0.4709 | 25.24 |
| | | 0.2520 | 24.24 |

[a] 5-cm cylindrical cell. [b] 2-cm cylindrical cell. [c] 5-mm flow cell. Includes all values below this entry unless otherwise noted. [d] 1-mm flow cell. Includes all values below. [e] The cesium-133 NMR shift of 0.94 M CsCl in water referenced to infinite dilution at 25 °C is 9.40 ppm. [f] The cesium-133 NMR shift of 1.0 M CsCl in water referenced to infinite dilution at 25 °C is 10.15 ppm.

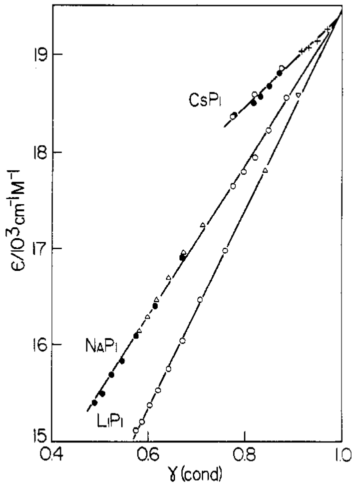

**Figure 3.** Molar absorptivities $\epsilon$ plotted as a function of the fraction $\gamma$ (of salt that is not ion paired) for lithium picrate, sodium picrate, and cesium picrate in 2-butanone at 25 °C. The molar concentrations of the salts are in the 0.1–1 mmol $L^{-1}$ range. The conductance values of ion association constants, $K_A$, were used to calculate values of $\gamma$ as outlined in the text.

ductance equations by using a nonlinear least-squares procedure (GAUSS) minimizing $S^2 = \sum[\Lambda - \Lambda(\text{calcd})]^2$, yielding values of $K_A$ and $\Lambda°$ for a given value of the distance parameter $R$. Calculations for each data set were repeated, incrementing $R$ from 4 to 30 Å. Plots of the standard deviation, $\sigma$ vs. $R$, appear in Figure 1 for lithium and cesium picrate. Values of $\Lambda°$, $K$, and $R$ at the minimum in $\sigma$ are listed in Table II.

*UV–Visible Spectra.* The molar absorptivities of tetra-*n*-butylammonium picrate are some 5% lower than those previously reported[11] and show a smaller decrease with increasing molar salt concentration $C$; a least-squares fit yields the equation $\epsilon = 19400 \pm 40 - (1.7 \pm 0.6) \times 10^5 C$, with a standard deviation in $\epsilon$ of 30 $cm^{-1}$ L $mol^{-1}$. The molar absorptivities of lithium, sodium, and cesium picrate are shown in Figure 2, plotted vs. salt concentration, $C$.

It is assumed that only two absorbing species, free and paired picrate anion, are present in the alkali-metal picrate solutions.[27] These data were treated by least-squares procedures using two different approaches: the first using $K_A$ and $\epsilon_p$ as fitting parameters at a series of fixed values of $\epsilon_I$ and the second using conductance values of $K_A$ with $\epsilon_I$ and $\epsilon_p$ as fitting parameters. In the first approach the sets of data were fitted using a variant of eq 3

$$\Delta A = dc[\epsilon_p + (\epsilon_I - \epsilon_p)\gamma] \qquad (7)$$

together with eq 5 and 6 in a nonlinear least-squares program (GAUSS) minimizing $S^2 = \sum[\Delta A - \Delta A(\text{calcd})]^2$ and yielding values of $K_A$ and $\epsilon_p$ for fixed values of $\epsilon_I$ and $R$. Here $d$ is the cell path length. The values of $\epsilon_I$ were incremented over the range from approximately 19 200 to 20 000 $cm^{-1}$ L $mol^{-1}$. Initially all calculations were carried out with $R$ set equal to Bjerrum's $q$. Equation 7, explicit in $\Delta A$ rather than the more usual form (eq 3), was chosen since the experimental uncertainties in $\Delta A$ were constant over the range used ($0.5 < \Delta A < 1.4$) while those in $\epsilon$ would vary inversely with the salt concentration; the statistical weight of each observation was accordingly set equal to 1.0. The lithium picrate data gave $\sigma = 0.00038$ at $\delta_I = 18900$ $cm^{-1}$ L $mol^{-1}$, showed a shallow minimum of $\sigma = 0.00020$ at $\delta_I = 19650$ $cm^{-1}$ L $mol^{-1}$, and rose to $\sigma = 0.00026$ at $\delta_I = 20000$ $cm^{-1}$ L $mol^{-1}$. The sodium picrate data showed no minimum in $\sigma$, the latter quantity ranging from 0.0052 at $\delta_I = 19300$ $cm^{-1}$ L $mol^{-1}$ to 0.0045 at $\delta_I = 20000$ $cm^{-1}$ L $mol^{-1}$. The cesium picrate data gave $\sigma = 0.0042$ at $\delta_I = 19300$ $cm^{-1}$ L $mol^{-1}$, decreasing to 0.0025 at $\delta_I = 19400$ $cm^{-1}$ L $mol^{-1}$ and then showing a very shallow minimum of $\sigma = 0.0023$ at $\epsilon_I = 19700$ $cm^{-1}$ L $mol^{-1}$. The fitting parameters for these salts at $\epsilon_I = 19400$ $cm^{-1}$ L $mol^{-1}$ and at the minimum in $\sigma$ (lithium and cesium picrate) are listed in Table V. These calculations were repeated for lithium picrate with $R$ = 12.45 and 7.24 Å, for sodium picrate with $R$ = 12.96 and 8.64 Å, and for cesium picrate with $R$ = 9.96 and 7.78 Å. The minima in $\sigma$ for lithium and cesium picrates did not shift, and values of $K_A$ decreased by less than 2% for lithium and sodium picrate and by 10% for cesium picrate at the smaller $R$ values.

The second approach to treatment of the UV–visible spectroscopic data is based on the fact that the observed changes in $\epsilon$ for cesium picrate in the accessible concentration range are relatively small, leading to a large uncertainty in the value of $K_A$; the principal usefulness of these data then lies in the determination of $\epsilon_I$ for picrate anion. The cations of the picrate salts used here make a negligible contribution to the observed absorbance at 380 nm. One value of $\epsilon_I$ is given by the intercept (as concentration goes to zero) of the molar absorptivity of tetra-*n*-butylammonium picrate (noted above). Another is obtained from the cesium picrate data; we calculated values of $\gamma$ for this salt using the conductance value of $K_A$ and setting $R = q$ in eq 6. According to eq 3, $\epsilon$ should be linear in $\gamma$ with an intercept of $\epsilon_p$ at $\gamma = 0$ and $\epsilon_I$ at $\gamma = 1$. The results of these calculations are shown in Figure 3. Included

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[27] An isosbestic point occurs in the sodium picrate spectra at 360 nm, similar to that observed in lithium picrate solutions (see Figure 1 of ref 11).

**TABLE IV: Effect of Maximum Concentration in Fitting Chemical Shift Data for Cesium Tetraphenylborate**

| no. of points | $C_{max}$/mmol $L^{-1}$ | $-\delta_I$ | $\sigma$ | $K_A$/L $mol^{-1}$ |
|---|---|---|---|---|
| 10 | 10.1 | 23.1 | 0.167 | 90 ± 8 |
| 9 | 8.2 | 23.0 | 0.153 | 106 ± 9 |
| 8 | 6.9 | 22.8 | 0.134 | 137 ± 11 |
| 7 | 5.6 | 22.68 | 0.096 | 166 ± 10 |
| 6 | 5.2 | 22.64 | 0.091 | 178 ± 11 |
| 5 | 3.7 | 22.50 | 0.040 | 225 ± 8 |

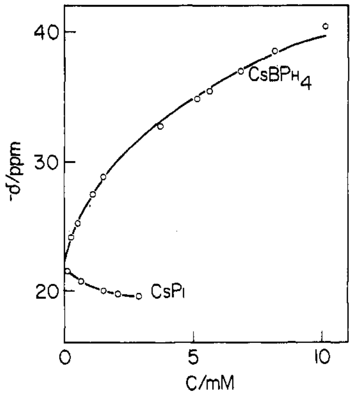

**Figure 4.** Cesium-133 NMR chemical shifts for cesium picrate and cesium tetraphenylborate in 2-butanone at 25 °C. Solid lines are calculated from parameters listed in Table V.

in this figure are results for sodium picrate (with $K_A$ = 2350 L $mol^{-1}$) and lithium picrate (with $K_A$ = 6670 L $mol^{-1}$). A linear least-squares treatment of each of these sets of data yielded the following values of $\epsilon_I$: cesium picrate, 19 400 ± 260, sodium picrate, 19 320 ± 120, and lithium picrate, 19 490 ± 100, all with units $cm^{-1}$ L $mol^{-1}$. The best value of $\epsilon_I$ is then taken to be the weighted average of the cesium and tetrabutylammonium picrate values, 19 400 ± 56 $cm^{-1}$ L $mol^{-1}$.

*Cesium-133 NMR.* Values of the chemical shifts of both cesium picrate and tetraphenylborate are listed in Table III and are plotted in Figure 4 as a function of salt concentration. The upper limit of salt concentration for the picrate was determined by the limited solubility of this salt and its slow rate of dissolution in 2-butanone. The observed chemical shifts are taken to be the weighted average on a mole fraction scale of that of the free cation, $\delta_I$, and that of the paired cation, $\delta_p$.

$$\delta = \delta_p + (\delta_I - \delta_p)\gamma \tag{8}$$

The chemical shift data were fitted to eq 5, 6, and 8 in a nonlinear least-squares program minimizing $S^2 = \sum(\delta - \delta(\text{calcd}))^2$ using $\delta_p$ and $K_A$ as fitting variables for fixed values of $\delta_I$ and $R$(set equal to Bjerrum's $q$ initially). The value of $\sigma$ for the cesium picrate data is 0.126 at $\delta_I = -21.5$ ppm with $K_A$ = 271 L $mol^{-1}$, is a minimum of 0.062 at $\delta_I = -21.85$ ppm with $K_A$ = 730 ± 150 L $mol^{-1}$, and rises to 0.123 at $\delta_I = -22.3$ ppm with $K_A$ = 2200 L $mol^{-1}$. If the fraction of salt dissociated is the same in the conductance and NMR experiments, then a plot of $\delta$ vs. $\gamma$(cond) should be linear (eq 8; see Figure 5). A linear least-squares fit of these data yields an intercept at $\gamma = 1.0$ of $\delta_I = -21.80 \pm 0.07$ ppm, with a standard deviation of 0.064, almost the same as the parameters of the fit using eq 5, 6, and 8 above.

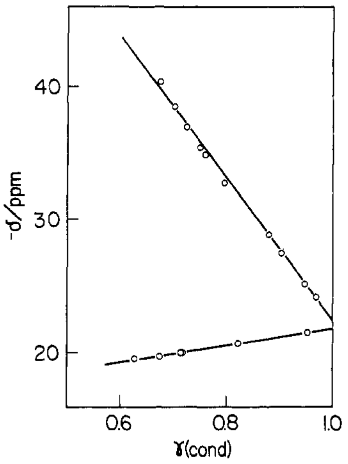

**Figure 5.** Cesium-133 NMR chemical shifts $\delta$ plotted as a function of the fraction $\gamma$ of salt not associated into ion pairs for cesium picrate (lower line) and for cesium tetraphenylborate (upper line) in 2-butanone at 25 °C. The conductance values of the ion association constants $K_A$ were used to calculate the values of $\gamma$.

**TABLE V: Spectroscopic Values of Ion Association Constants**

| salt | $K_A$/L $mol^{-1}$ | $\epsilon_I$ or $\delta_I$[a] | $\epsilon_p$ or $\delta_p$[a] | $10^3\sigma$[b] |
|---|---|---|---|---|
| | | UV–Visible | | |
| LiPi | 7900 ± 250 | 19650 | 9600 ± 130 | 0.20 |
| | 6500 ± 250 | 19400 | 9100 ± 200 | 0.24 |
| NaPi | 1970 ± 190 | 19400 | 11000 ± 300 | 5.1 |
| CsPi | 770 ± 280 | 19400 | 15300 ± 950 | 2.4 |
| | | $^{133}$Cs NMR | | |
| CsPi | 730 ± 150 | −21.84 | −16.13 ± 0.59 | 62 |
| $CsBPh_4$ | 90 ± 8 | −23.1 | −103.8 ± 4.9 | 167 |
| | 225 ± 8[c] | −22.50 | −71.0 ± 2.5 | 40 |

[a] Units for UV–visible values are $cm^{-1}$ L $mol^{-1}$ while the NMR values are in ppm. [b] Standard deviation in the absorbance values (UV–vis) and in the chemical shifts (NMR, in ppm). [c] Upper limit in salt concentration 3.7 mmol $L^{-1}$. See Table IV.

**TABLE VI: Average Values of Conductance Parameters in 2-Butanone at 25 °C**

| salt | $\Lambda°/\Omega^{-1}$ $cm^2$ $mol^{-1}$ | $K_A$/L $mol^{-1}$ | $\lambda_+°/\Omega^{-1}$ $cm^2$ $mol^{-1}$ | $h_{+-}/kT$ |
|---|---|---|---|---|
| LiPi | 130.86 | 6670 ± 80 | 60.3 | 1.53 |
| NaPi | 131.21 | 2350 ± 30 | 60.6 | 1.01 |
| KPi | 132.72 | 910 ± 6 | 62.1 | 0.90 |
| RbPi | 133.16 | 730 ± 4 | 62.6 | 0.84 |
| CsPi | 135.09 | 612 ± 14 | 64.5 | 0.65 |
| $CsBPh_4$ | 113.96 | 180 ± 15 | 64.5 | 0.21 |

The data for cesium tetraphenylborate, when fitted to eq 5, 6, and 8, yield a value of $\sigma$ = 0.232 at $\delta_I = -22.6$ ppm with $K_A$ = 124 L $mol^{-1}$ and a minimum in $\sigma$ of 0.167 at $\delta_I = -23.1$ ppm with $K_A$ = 90 ± 8 L $mol^{-1}$; $\sigma$ then rises to 0.219 at $\delta_I = -23.5$ ppm with $K_A$ = 66 ± 9 L $mol^{-1}$. The best-fit value of $\delta_I$ is 1.25 ppm more negative than that for the picrate salt; they are expected to be the same at infinite dilution where specific anion effects should be absent. A plot of the observed values of $\delta$ for the tetraphenylborate vs. the values of $\gamma$(cond) calculated using the conductance value of $K_A$ also appears in Figure 5; note that the chemical shifts for this salt show upward curvature as the salt concentration increases (and thus $\gamma$ decreases). These chemical shifts were fitted to eq 5, 6, and 8, successively reducing the upper concentration limit of data included in the fitting procedure; the parameters so obtained are shown in Table IV. Note that as the upper salt concentration limit is reduced from 10 to 3.7 mmol $L^{-1}$, the value of $\delta_I$ reduces to −22.50 ppm while $K_A$ increases to 225 L $mol^{-1}$, 22% larger than the conductance value. A linear least-squares fit of the tetraphenylborate chemical shifts to eq 8 using $\gamma$(cond) yields $\delta_I = -22.30 \pm 0.24$ ppm with $\sigma$ = 0.35.

The fitting parameters at the minima in $\sigma$ are listed together with their standard deviations for both cesium picrate and cesium tetraphenylborate in Table V. These calculations were repeated for cesium picrate (taking $R$ = 14 Å), yielding $K_A$ = 720 L $mol^{-1}$ and no shift in the minimum, and for cesium tetraphenylborate (taking $R$ = 12 Å), yielding $K$ = 68 L $mol^{-1}$ and no shift in the minimum.

## Discussion

The ion association constants calculated from conductance data by using the four different conductance equations (Table II) are almost the same for a given salt; averages of the four values for each salt are listed in Table VI. The relative standard deviations

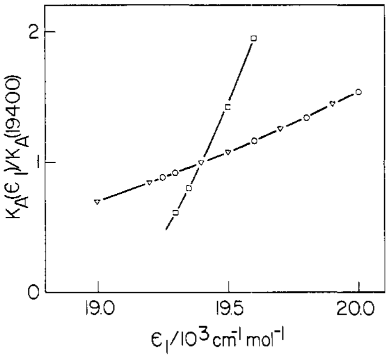

**Figure 6.** The ratios of $K_A(\epsilon_I)/K_A(\epsilon_I{=}19400)$ plotted as a function of the value of $\epsilon_I$ at which $K_A(\epsilon_I)$ was calculated for lithium picrate (○), sodium picrate (▽), and cesium picrate (□) in 2-butanone at 25 °C.

of these values are 1.2% for lithium picrate, 1.3% for sodium picrate, 2.3% for cesium picrate, and 8% for cesium tetraphenylborate. Values calculated by using the more recent theoretical models seem to be in excellent agreement. See below for further discussion of the conductance results.

There are several factors responsible for the greater uncertainty in the spectroscopic values of ion association constants when compared with that of the conductance values, the greater precision with which the latter measurements can be made, and the presence of an additional fitting parameter in the spectroscopic equations, the molar absorptivity (or chemical shift) of the ion pair. The uncertainties in the spectroscopic values of $K_A$ can be greatly reduced if the value of $\epsilon_I$ (or $\delta_I$) can be determined independently. The average value of $\epsilon_I$ for picrate ion calculated from the UV-visible absorbance data of tetra-*n*-butylammonium picrate and of cesium picrate (see Results section above) is 19 400 cm$^{-1}$ L mol$^{-1}$ with a standard deviation of ±56 cm$^{-1}$ L mol$^{-1}$. The value of 20 000 cm$^{-1}$ L mol$^{-1}$ reported earlier[11] is in error, probably due to contamination of the salt by triiodide (see Experimental Section). The UV–visible spectroscopic values of $K_A$ for lithium picrate, sodium picrate, and cesium picrate calculated with this average value of $\epsilon_I$ are taken to be the best values. If the value of the uncertainty in $\epsilon_I$ is conservatively set at ±100 cm$^{-1}$ L mol$^{-1}$, then the uncertainties in the values of $K_A$(spec) calculated with this value can be estimated from a graph of the ratio $K_A(\epsilon_I)/K_A(\epsilon_I = 19400)$ vs. $\epsilon_I$ (Figure 6). The uncertainties are ±8% for lithium picrate and sodium picrate and ±40% for cesium picrate. These are almost the same as those calculated in fitting the data to eq 5, 6, and 7 (Table V).

The uncertainty in the value of $K_A$(NMR) for cesium picrate is somewhat less than but of the same order of magnitude as that based on the UV–visible data; in both cases the large uncertainty is due to the relatively small changes in the observable over the concentration range studied. It is felt that the extrapolation of the picrate shifts to infinite dilution (Figure 5) establishes the best value for $\delta_I$, the free cesium-133 ion shift. The tetraphenylborate chemical shifts present at least two puzzles: the intercept as $\gamma \rightarrow 1.0$ does not coincide with that for the picrate data, and the shifts show marked curvature when plotted vs. $\gamma$(cond) (Figure 5). If the intercept at 23.1 ppm is correct for the tetraphenylborate salt, then the apparent value of $K_A$ (NMR) of 90 L mol$^{-1}$ is only half the conductance value. It has already been noted (see Results) that as the upper limit of the tetraphenylborate concentration used in the data treatment is reduced to the same range as that of the picrate data, the value of $K_A$(NMR) of the former approaches the conductance value. There may be some mechanism operating in addition to ion-pair formation that yields more negative chemical shifts as the concentration of cesium tetraphenylborate is increased. Such a possibility has been suggested[8b] to account for the concentration dependency of the cesium-133 chemical shifts of several salts in other solvents. Clearly, more work should be done on the concentration dependence of cesium-133 NMR chemical shifts of salts in medium dielectric solvents.

Comparison of the ion-pair association constants $K_A$ derived from the different experimental techniques (Tables V and VI) shows them to be the same within experimental uncertainty with the possible exception of the NMR result for cesium tetraphenylborate. The UV–visible value of $K_A$ for lithium picrate calculated from the present data, 6500 ± 250 L mol$^{-1}$, is the same within experimental uncertainty as the average of the conductance values, 6670 ± 80 L mol$^{-1}$. The much higher value of $K_A$(UV-vis) reported earlier[11] is in error, primarily due to incorrect values of $\epsilon_I$ and $\epsilon_p$. The latter parameter was determined by adding lithium tetraphenylborate to solutions of lithium picrate to force ion-pair formation by mass action. It is now clear[28,29] that such a procedure can be in error due to ion atmosphere effects. The value of $\epsilon_I$ for the completely dissociated salt had been determined from extrapolation of the molar absorptivities of tetrabutylammonium picrate solutions to infinite dilution. The molar absorbances of the earlier quaternary salt solutions were some 5% higher than those found presently; these differences are believed to be due to improved salt purity, exclusion of light, and improved solution preparation techniques.

In a solution in which ion association occurs (eq 1), the observed molar absorptivity (or chemical shift) at a given stoichiometric salt concentration $C$ and wavelength may be written in terms of the contribution due to free ions (of molar absorptivity $\epsilon_I$), solvent separated ion pairs (molar absorptivity $\epsilon_{sp}$), and contact ion pairs (molar absorptivity $\epsilon_{cp}$) as

$$\epsilon = \epsilon_I[X^-]/C + \epsilon_{sp}[M^+\cdots X^-]/C + \epsilon_{cp}[M^+,X^-]/C \qquad (9)$$

The variation of $\epsilon$ with salt concentration $C$ can be expressed in terms of the fraction of salt that is dissociated or free, $\gamma = [M^+]/C$, and the fraction of ion pairs that are in contact, $\alpha$, from $K_S = [M^+,X^-]/[M^+\cdots X^-] = \alpha/(1 - \alpha)$, $[M^+,X^-]/C = \alpha(1 - \gamma)$, and $[M^+\cdots X^-]/C = (1 - \alpha)(1 - \gamma)$. Equation 9 becomes

$$\epsilon = \epsilon_I\gamma + \epsilon_{sp}(1 - \alpha)(1 - \gamma) + \epsilon_{cp}\alpha(1 - \gamma) \qquad (10)$$

As the concentration of salt goes to zero in dilute solutions, the free-ion fraction $\gamma \rightarrow 1.0$ so that the observed value of $\epsilon$ becomes $\epsilon = \epsilon_I$, that due to free ions alone. We shall assume, following Khazaeli, Popov, and Dye[8b] that the equilibrium between the two kinds of ion pairs is independent of salt concentration. When the salt concentration is increased, the fraction present as free ions diminishes until in the limit as the salt concentration becomes large enough, $\epsilon$ approaches the value $\epsilon_{sp}[M^+\cdots X^-]/C + \epsilon_{cp}[M^+,X^-]/C$, or in terms of $\alpha$, the apparent molar absorptivity due to ion pairs is given by $\epsilon_p' = \epsilon_{sp}(1 - \alpha) + \epsilon_{cp}\alpha$. It is seen that, regardless of the value of $\epsilon_{sp}$, whether the solvent-separated pair spectroscopically resembles the contact pair or the free ions, a value of $\epsilon_p'$ would be obtained by any extrapolation procedure which contains a contribution due to each kind of ion pair. This analysis shows that, in a spectroscopic experiment in which the absorbance (or chemical shift) is measured as a function of salt concentration, the changes in molar absorptivity will be related solely to the shift in the relative concentrations of free ions and ion pairs (solvent separated and contact) provided the relative activities of the two kinds of ion pairs do not change.

If it can be taken then that spectroscopic and conductance methods for measuring ion-pair formation constants should yield the same result, those cases in the literature where different values have been reported using different techniques may have one or more of the following explanations: some undetermined source of error exists (this was the case for lithium picrate[11]), different expressions for activity coefficients were used in evaluating $K_A$ from the different sets of data,[4] or perhaps the different kinds of techniques were applied in different concentration ranges so that the ratios of the two kinds of ion pairs are different because of changes in solvent activity.[5]

Several conductance studies[30] and a number of UV spectrophotometric studies[2-4,29,31] of copper sulfate in water have yielded

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different values for the ion association constant at 25 °C. Acevedo et al. fitted their recent conductance results[30b] using eq 2 (LW equation) 5, and 6 and obtained $K_\mathrm{A} = 260$ L mol$^{-1}$ at $R = 9.6$ Å. Prue and co-workers[2] measured the absorbance of copper sulfate in water alone as a function of salt concentration and using eq 3, 5, and 6 reported that a range of the parameters $\Delta\epsilon$, $K_\mathrm{A}$, and $R$ could be used to fit their data: $K_\mathrm{A} = 130$ L mol$^{-1}$ at $R = 4.3$ Å to $K_\mathrm{A} = 250$ L mol$^{-1}$ at $R = 10$ Å to $K_\mathrm{A} = 290$ L mol$^{-1}$ at $R = 14$ Å. The more recent studies have all been carried out at constant ionic strength and have utilized a variety of expressions for the activity coefficient of copper sulfate in such mixtures to obtain values of $K_\mathrm{A}$. Matheson[3] considered that the ionic strength principle might fail to apply to his solutions and showed how his results could be in agreement with those of Prue.[2] The agreement between Prue's $K_\mathrm{A}$ at 10 Å and the conductance value at 9.6 Å is very good. The sensitivity of $K_\mathrm{A}$(spec) to the value of $R$ used in eq 6 for the activity coefficient is symptomatic of the difficulty of fitting data when the association constant is relatively small. We find that the effect of changes in $R$ on $K_\mathrm{A}$(calcd) for the picrates increases as the association constant decreases (see Results).

The following illustrates the possibility of using extrathermodynamic measurements to obtain thermodynamic information: the fraction $\alpha$ of 0.024 99 M aqueous copper sulfate present as free unpaired ions at 25 °C is calculated to be 0.5203 if one uses Prue's UV absorbance data ($R = 10$ Å)[2]; this combined with Acevedo's conductance value of $K_\mathrm{A} = 262$ L mol$^{-1}$ ($R = 9.6$ Å)[30b] yields $y_\pm{}^2 = 0.2706$ ($= (1-\alpha)/C\alpha^2K_\mathrm{A}$), and thus the stoichiometric activity coefficient $\gamma_\mathrm{i} = \alpha y_\pm = 0.2706$. This is to be compared with $\gamma_\mathrm{i} = 0.2715$ calculated with Miller's values[32] for the coefficients in Pitzer's equation fitting experimental values of $\gamma_\mathrm{i}$ to the concentration.

An example of differences in values of $K_\mathrm{A}$ from studies using different techniques in widely different concentration ranges is furnished by the report of Covington, Freeman, and Lilley[5] of an NMR and Raman spectroscopic investigation of trifluoro- and trichloroacetic acids in water. These workers, studying solutions of trifluoroacetic acid in the concentration range of 0.7–13 mol L$^{-1}$, reported the acidity constant of this moderately strong acid to be almost 5 times larger than values obtained using other techniques.[33,34] A recent reinvestigation of trifluoroacetic acid[35] using cryoscopic and conductance methods in the 0.02–0.2 M concentration range yielded results in agreement with the earlier nonspectroscopic studies;[33,34] Milne and Parker pointed out that the uncertainty in activity coefficients in the more concentrated solutions used in the spectroscopic studies could be responsible for the differences. Covington and co-workers had suggested[5] that the spectroscopic techniques they employed measured the equilibrium between unionized acid and free ions as well as ion pairs, thus giving a larger numerical value than the other methods.

Khazaeli, Popov, and Dye[8b] reported a study of cesium iodide and cesium tetraphenylborate in methylamine solvent, comparing the ion association of the iodide using both cesium-133 NMR and conductance methods. The value of $K_\mathrm{A}$(cond) obtained depended greatly on which conductance equation (limiting law, Pitts,[23] Fuoss–Hsia,[36] or Justice[25]) was used to analyze the data. We have repeated these calculations for salt concentrations between 0.5 and 0.09 mmol L$^{-1}$ (omitting higher concentration data because of triple-ion formation and the lowest salt concentration because of the large deviation of its conductance value) using five data points in all and find $K_\mathrm{A} = 20\,400$ (LW), 20 600 (P), 20 700 (F), and 20 700 (J), all with units L mol$^{-1}$ and an uncertainty of ±2100; $\sigma$ was 0.41 in each case. It is admittedly difficult to extrapolate the NMR data to sufficiently low concentrations to determine $\delta_\mathrm{I}$ in these systems, so that it is not surprising that the NMR value of $K_\mathrm{A}$ is not equal to the conductance value, and we agree with the authors that triple-ion formation could well be important at the higher salt concentrations in this relatively low dielectric solvent.

Hinton and Metz[9] investigated thallium nitrate ion association in liquid ammonia at several temperatures using thallium-205 NMR chemical shifts. The value of $K_\mathrm{A}$(NMR) that they obtain by extrapolating their values down to −33.4 °C is less than the conductance value ($K_\mathrm{A}$(cond) = 476 L mol$^{-1}$)[37] by a factor of 2. However, this difference is within the experimental uncertainty of the NMR value at the lowest temperature (0 °C) employed in this study, so that the difference is probably not real.

The earlier report from this laboratory[11] cited two instances in the literature in which it appeared that $K_\mathrm{A}$(spec) is greater than $K_\mathrm{A}$(cond): silver nitrate[38] and cesium tetraphenylborate[8a] in acetonitrile. A reanalysis of the conductance data for both of these systems has been carried out using the Lee and Wheaton conductance equation. The silver nitrate data[39] yield $K_\mathrm{A} = 84.6 \pm 0.4$ L mol$^{-1}$ for one set and $82.94 \pm 0.03$ L mol$^{-1}$ for the other, both equal to the Raman spectroscopic value of $85 \pm 14$ L mol$^{-1}$, so the disagreement no longer exists for this system. The cesium tetraphenylborate conductance data[40] yield an association constant of $19.11 \pm 0.04$ L mol$^{-1}$ for one set and $20.23 \pm 0.05$ M$^{-1}$ for the second set, unchanged from an earlier analysis;[41] in this case the NMR value of $K_\mathrm{A}$ of $40 \pm 10$ L mol$^{-1}$ remains larger than the conductance value.

*Conductance Results.* A comparison of the goodness of fit of these data to the several conductance equations shows that the sharpest minimum in $\sigma$ vs. $R$ was obtained with the Lee–Wheaton equation for both lithium and sodium picrates, while the curves are remarkably similar for all four of the equations with the remaining salts (Figure 1). The values of $R$ at the minima in $\sigma$ and $R_\mathrm{m}$ are almost the same for lithium and sodium picrate ($0.5q$) when the LW, P, and F equations are used and almost doubled ($0.8q$) when the J equation is used. The value of $R_\mathrm{m}$ for potassium picrate found from the LW equation is almost twice that for sodium picrate; the values found from the P, J, and F equations are successively incremented by 1 Å in that order. For rubidium and cesium picrates, the values of $R_\mathrm{m}$ are equal if one uses the LW and P equations and are larger by 3–4 Å if one uses both the F and J equations. The values of $R_\mathrm{m}$ for cesium tetraphenylborate increase by almost 1 Å if one uses the conductance equations in the order P, LW, J, and F. The average values of $R_\mathrm{m}$ for the salts are as follows: potassium picrate, $1.0q$; rubidium picrate, $1.1q$; cesium picrate, $1.05q$, and cesium tetraphenylborate, $0.9q$. Finding the largest value of $R_\mathrm{m}$ at rubidium picrate in this series of salts is reminiscent of the maxima in cation–crown ether complexation constants[42,43] and may be due to a similar balancing of competing processes, ion–solvent, ion pair–solvent, and solvent–solvent interactions. The limiting molar conductances are nearly independent of the conductance equation used (Table II). The averages of the values of $\Lambda°$ calculated for each salt are listed in Table VI. The values of cationic conductance, $\lambda_+°$, are calculated (and appear in Table VI) by assuming that the transference number of the cation in tetra-*n*-butylammonium tetraphenylborate is 0.519 in 2-butanone, the same as that estimated for methanol solvent,[44] and by using the value of $\Lambda° = 102.84$ for this salt in 2-butanone reported by Hughes.[12] The increases here with increasing cation size are similar to those found by Evans and co-workers in acetone[45] and are the reverse of the order found

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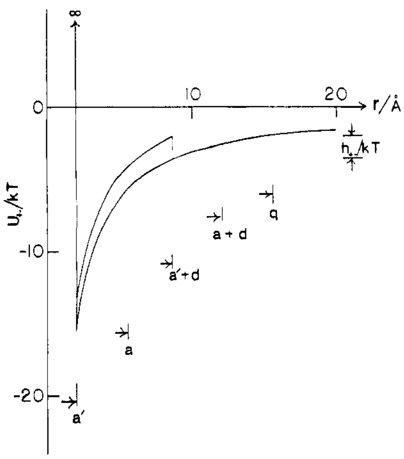

**Figure 7.** A plot of the potential energy function, $U_{+-}/kT$, for the interaction of a singly charged cation and anion in 2-butanone at 25 °C as a function of the interionic distance $r$ where the potential energy function is the sum of the Coulombic term $2q/r$ and the Gurney term, the square mound potential $h_+/kT$ (= 1.53 for lithium picrate). $a$ (= 5.53 Å) is the sum of the ionic radii for cesium tetraphenylborate, $a'$ (= 2.01 Å) is that for lithium picrate, $d$ (= 6.60 Å) is the mean molecular diameter of 2-butanone, and $q$ (= 15.6 Å) is Bjerrum's distance.

in 2-propanol.[46] These variations could be due either to relaxation of solvent dipoles about the moving ions[47] or to specific solvent effects; the smaller mobility for lithium cation in 2-butanone can be due to stronger interaction of this cation with surrounding solvent molecules (see below).

The extent of ion association decreases strongly as cation size increases for the picrates in 2-butanone (Table II). Bjerrum's theory[48] of ion association, based on purely Coulombic interaction between oppositely charged ions, yields

$$K_A(b) = (4\pi N/1000)\int_a^q r^2\,dr\,\exp(2q/r) \qquad (11)$$

where $b = 2q/a$ and $a$ is the distance of closest approach. Taking $a$ to be the sum of the ionic radii,[49] the values of $K_A(b)$ calculated from eq 11 are larger than the observed values, ranging from 30 000 L mol$^{-1}$ for lithium picrate to 210 L mol$^{-1}$ for cesium tetraphenylborate. Justice and Justice[50] have proposed a modification of Bjerrum's theory of ion association based on the square mound potential model of Rasaiah and Friedman.[51] A square mound potential of fixed extent and variable magnitude is used to represent the effects of the discrete nature of ion–solvent interaction in the ion association process. The potential energy of interaction of the two ions becomes $U_{+-} = U_{+-}^* - z^2e^2/(Dr)$, where $U_{+-}^*$ is $+\infty$ for $r \le a$, $U_{+-}^* = h_{+-}$ for $a < r < a + d$ (where $d$ is the average solvent molecular diameter), and $U_{+-}^* = 0$ for $r > a + d$. Now

$$K_A(\text{obsd}) = (4\pi N/1000) \times \left[\exp(-h_{+-}/kT)\int_a^{a+d}\exp(2q/r)r^2\,dr + \int_{a+d}^{q}\exp(2q/r)r^2\,dr\right] \qquad (12)$$

The value of $d$ is set by Friedman at twice the mean molecular radius of the solvent molecules, $d = 2(3M/(4\pi N\rho))^{1/3}$, where $M$ is the molar mass and $\rho$ is the density. Thus

$$\exp(h_{+-}/kT) = [K_A(\text{obsd}) - K_A(b')]/[K_A(b) - K_A(b')] \qquad (13)$$

with $b' = 2q/(a + d)$. The values of $h_{+-}/kT$ calculated with the LW values of $K_A$(obsd) for the picrates and the tetraphenylborate salt are listed in Table VI. Positive values of $h_{+-}/kT$ indicate that specific solvent effects favor free ions over the ion pair. A plot of the potential function $U_{+-}/kT$ vs. $r$ for 1:1 salts in 2-butanone at 25 °C is shown in Figure 7. The distance a represents $r_+ + r_-$ for cesium tetraphenylborate, $a'$ is that sum for lithium picrate, $d$(= 6.60 Å) is the average diameter of a solvent molecule, and $q$ is Bjerrum's distance (15.6 Å). The lower smooth curve decreasing as $r$ decreases represents the Coulomb contribution $(2q/r)$ to the potential function, while the upper curve terminating at $a' + d$ includes the contribution due to the square mound potential $h_{+-}/kT$ (= 1.53) for lithium picrate. The addition of $h_{+-}/kT$ (= 0.21) for cesium tetraphenylborate would be detectable with difficulty at the scale used in Figure 7. For the picrates, $h_{+-}/kT$ decreases as the cation radius increases and decreases when the tetraphenylborate anion replaces picrate with cesium; these changes are reasonable since specific ion–solvent interaction should decrease as the ion size increases. The same trend noted here with the alkali-metal picrates has been observed in the alkali-metal halides in water.[50]

## Conclusions

Spectroscopic methods yield the same extent of ion-pair formation as do other physical methods provided that the same concentration ranges are covered using the different techniques and that the same expressions are used for the actiivity coefficients. Spectroscopic methods can be exploited with some confidence as another tool in studies of electrolyte systems. Such studies of a spectroscopically active species as one component of a mixed electrolyte system are under way in this laboratory.

All four conductance equations, the Lee–Wheaton, the Fuoss 78, the Pitts, and the Justice equations, fit the conductance data presented equally well, and the first two have been found to fit data equally well in 2-propanol solvent. The ion pairs of all the salts involved in this study are primarily contact pairs, based upon Bjerrum's theory; solvent-separated pairs would require a distance of closest approach, $a + d$, that would yield calculated values of $K_A(b')$ which are too small (that calculated for lithium picrate is 106 L mol$^{-1}$, for example).

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**Registry No.** KPi, 573-83-1; RbPi, 23296-29-9; CsPi, 3638-61-7; $CsBPh_4$, 3087-82-9; NaPi, 3324-58-1; LiPi, 18390-55-1; $Bu_4NPi$, 914-45-4; cesium, 7440-46-2.

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