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A Spectroscopic Study of Ion Association. Lithium Picrate in 2-Butanone[1]

W. R. Gilkerson* and Angela McCaskill Roberts

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.

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Abstract: The near-UV spectra of solutions of lithium picrate in 2-butanone at 25 °C in the range 340–500 nm have been studied as a function of salt concentration and in the presence of added lithium tetraphenylborate. The spectrum of tetra-*n*-butylammonium picrate has also been observed. The spectra are consistent with two species being present in the lithium picrate solutions, the free ions and ion pairs. The molar absorptivities of free picrate anion are obtained from the spectra of tetra-*n*-butylammonium picrate while those for the lithium picrate ion pair are obtained from the spectra of the latter salt in the presence of swamping quantities of lithium tetraphenylborate. Values of the ion pair association constant K_A(spec) were calculated at each of 13 salt concentrations at five different wavelengths, giving a weighted average value of $K_A = 9440 \pm 480$. This value is significantly larger than the value $K_A(\text{cond}) = 6610 \pm 40$ obtained from conductance measurements reported earlier from this laboratory. These results are compared with recent measurements of K_A(spec) for the systems cesium tetraphenylborate and for silver nitrate, both in acetonitrile. The possible significance of the observations that $K_A(\text{spec}) > K_A(\text{cond})$ for the system lithium picrate in 2-butanone and cesium tetraphenylborate in acetonitrile is discussed.

The association of oppositely charged ions in solution to form ion pairs is a ubiquitous phenomenon,

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

becoming important in water solution in the 0.1–0.01 M concentration range and at even lower concentrations in less polar solvents. The values of the ion pair association constants, K_A, have usually been determined by conductance methods.[2,3] A number of theoretical equations for the electrical conductance of electrolyte solutions have been developed, all based on the Debye–Hückel theory of interionic attraction; among these are the equations of Fuoss and Onsager,[4] of Pitts,[5] of Fuoss and Hsia,[6] linearizations of the latter two by Fernandez-Prini and Prue,[7] of Justice,[8] and most recently Fuoss's 1975 equation[9] followed by his 1977 equation.[10] If it is assumed, as is usual, that the ion pairs do not contribute to the conductance, all of these equations for symmetrical electrolytes may be represented by the forms

$$\Lambda = \gamma[\Lambda_0 - f(\Lambda_0, R, C\gamma)] \qquad (2)$$

$$K_A = (1 - \gamma)/\gamma^2 C y_\pm{}^2 \qquad (3)$$

$$\ln y_\pm{}^2 = -2\varkappa q/(1 + \varkappa R) \qquad (4)$$

where $\varkappa = (16\pi N/1000)^{1/2} q^{1/2} (C\gamma)^{1/2}$ and is the Debye–Hückel characteristic inverse distance, $q = z^2 e^2/2DkT$ and is Bjerrum's characteristic distance, and R is a distance parameter such that the ions of opposite charge within that distance of one another are considered to be paired and are free at distances greater than R.

Several measurements of ion pair association constants using spectroscopic techniques have been reported recently: a laser-Raman determination[11] of K_A for silver nitrate in acetonitrile and a ^{133}Cs NMR study[12] of cesium tetraphenylborate in acetonitrile. The spectroscopic values of K_A are in both instances larger than the conductance values.[11,13-15] If these differences are real, and not artifacts of either the experimental methods or data treatment, then they are contrary to what one might have expected based on conventional wisdom. The spectroscopic differences between free ions and ion pairs are due to perturbations in the electronic energy levels because of interaction between the ions in the ion pairs, presumably at short range. The nonconducting ion pairs not detected by the conductance technique may include solvent-separated ion pairs, $M^+{\cdots}X^-$

$$M^+ + X^- \rightleftarrows M^+{\cdots}X^- \rightleftarrows M^+, X^- \qquad (5)$$

in addition to those contact ion pairs, M^+,X^- in eq 5, detected spectrophotometrically.[2,16] One thus would expect the conductance value K_A(cond) to be greater than the spectrophotometric value K_A(spec). These differences reported between K_A(spec) and K_A(cond) may be real but both of these recent reports dealt with systems in which the value of K_A(cond) obtained depends on the model, i.e., the conductance equation and the R parameter specified.[17-19]

A salt-solvent system, lithium picrate (LiPi) in 2-butanone (dielectric constant = 18.01 at 25 °C), appeared to be an ideal system for a comparison of spectroscopic and conductance ion pair association constants. Recent conductance measurements carried out in this laboratory[20] gave a value of $K_A(\text{cond}) = 6600$ for this salt at 25 °C, large enough to be practically independent of the conductance model used.[17] The near-UV spectrum of the picrate anion has a strong absorption band ($\epsilon \sim 10^4$ cm^{-1} M^{-1}) which is very sensitive to the extent of pairing with alkali-metal cations[21] so that meaningful spectrophotometric measurements could be carried out in the same concentration range as were the conductance measurements. Accordingly we report here a near-UV spectrophotometric study of solutions of lithium picrate in 2-butanone as a function of salt concentration and in the presence of

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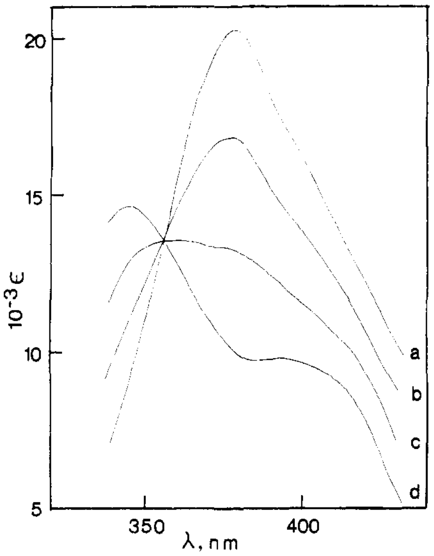

Figure 1. Spectra in 2-butanone at 25 °C. Molar absorptivity, ϵ, in cm^{-1} M^{-1}, vs. wavelength, λ, in nm: (a) 0.176 mM tetra-*n*-butylammonium picrate; (b) 0.114 mM lithium picrate; (c) 1.02 mM lithium picrate; (d) 0.67 mM lithium picrate plus 15.3 mM lithium tetraphenylborate.

added lithium tetraphenylborate.

Experimental Section

The solvent and salts were all prepared and purified as previously reported.[20] Salt solutions were prepared by weight and transferred to stoppered 1-mm path length cells in a nitrogen-filled drybox. The salt concentrations were known within 0.2%. Spectra were recorded from 340 to 500 nm using a Cary 14 spectrophotometer equipped with a thermostated cell compartment maintained at 25.0 ± 0.1 °C. One set of measurements for tetra-*n*-butylammonium picrate were carried out using a Cary 219 spectrophotometer. The experimental uncertainty in the molar absorptivities calculated from the absorbances is estimated to be 2% at the lower concentrations (0.1 mM) and falls to 0.6% for 1 mM picrate salt. The major source of the uncertainty was the measurement of the absorbances.

Results

The spectra of lithium picrate in 2-butanone show large changes in molar absorptivity ϵ as the salt concentration is reduced from 1 to 0.1 mM, Figure 1. In contrast, tetra-*n*-butylammonium picrate exhibits only small changes over the same concentration range; for example, at its maximum at 380 nm, ϵ is 19 800 M^{-1} cm^{-1} at 0.893 mM, 19 950 at 0.691 mM, 20 110 at 0.429 mM, and 20 350 at 0.176 mM. The spectrum of lithium tetraphenylborate (15.3 mM in 2-butanone) is almost indistinguishable from that of the solvent over the wavelength range of interest; the absorbance of the salt solution is 0.01 unit larger than that of the solvent at 340 nm. The molar absorptivity ϵ at 380 nm of 0.548 mM lithium picrate in 2-butanone decreased upon the addition of lithium tetraphenylborate (concentrations in parentheses follow the values of ϵ): 14 400 (none), 10 500 (3.68 mM), 9900 (9.92 mM), 9900 (15.3 mM) M^{-1} cm^{-1}.

These results are all consistent with the increased association of lithium with picrate ion, either as the total concentration of lithium picrate is increased or as the lithium ion concentration is increased by the addition of lithium tetraphenylborate to a solution containing a fixed concentration of the picrate salt. We identify the limiting value of ϵ as the ratio of lithium tetraphenylborate to that of lithium picrate is increased as the molar absorptivity ϵ_p of picrate ion in the lithium picrate ion pair. Assuming that there are only two absorbing species of picrate ion in the solutions (note the isosbestic point at 358 nm in Figure 1), then at any wavelength in this range

$$\epsilon = \gamma\epsilon_i + (1 - \gamma)\epsilon_p \qquad (6)$$

where $\gamma = [Pi^-]/C$, C is the stoichiometric concentration of lithium picrate, and ϵ_i is the molar absorptivity of free picrate anion. The values of ϵ_i were obtained by extrapolation of the values of ϵ for tetra-*n*-butylammonium picrate as outlined below for the data at 380 nm. The ions of this salt are expected to be associated as ion pairs to only a slight degree in this solvent; K_A is 17 M^{-1} at 25 °C for this salt in acetone (dielectric constant = 20.47).[26] Equation 6 can be rearranged to the form $\epsilon = \epsilon_i + (\epsilon_p - \epsilon_i)(1 - \gamma)$. Equation 3 may be rearranged to yield $(1 - \gamma) = K_A C\gamma^2 y_\pm^2$; as $C \rightarrow 0$, the right-hand side becomes $K_A C$, since the product $\gamma^2 y_\pm^2$ approached unity. A plot of ϵ vs. C yields the intercept 20 460 M^{-1} cm^{-1} and the slope is 7.4×10^5 M^{-2} cm^{-1}. If the intercept is taken to be ϵ_i, an estimate of $K_A \simeq 70$ M^{-1} for tetra-*n*-butylammonium picrate is calculated from the values for the intercept, the slope, and the value of ϵ_p obtained above. This value of K_A in 2-butanone is experimentally very uncertain; however, its magnitude serves as a check on the assumption that in dilute solutions in this solvent the quaternary ammonium salt is practically completely dissociated so that the extrapolated value of ϵ_i is indeed that for the free picrate anion.

Table I. Spectrophotometric Values of K_A for Lithium Picrate in 2-Butanone at 25 °C

C, mM	$10^{-3}K_A$[a]	λ, nm	$10^{-3}K_A$[b]	$10^{-3}\sigma$[c]
1.076	11.05	340	10.41	2.25
0.741	9.42		6.89	1.41
0.521	9.41			
0.214	8.54	345	11.57	1.83
0.108	7.33		8.71	1.61
1.271	11.34			
1.025	9.42	370	11.05	3.02
0.706	9.64		11.95	1.77
0.521	9.52			
0.385	9.35	380	9.15	1.36
0.252	8.30		9.51	0.94
0.160	10.01			
0.114	8.49	420	10.08	2.48
			9.05	2.64

[a] At 380 nm. [b] Top values listed are for the first run; the lower value is for the second run. [c] Standard deviation.

Equation 6 can be rearranged to give $\gamma = (\epsilon - \epsilon_p)/(\epsilon_i - \epsilon_p)$. Values of γ were calculated using the values of ϵ_i and ϵ_p determined as outlined above. Inserting these values into eq 2 and 3 (setting $R = q$),[8,17,20] values of K_A have been calculated at each of five salt concentrations in the first run, and at each of eight salt concentrations in the second, at five different wavelengths. These results at 380 nm appear in Table I. At each wavelength, values of K_A at each salt concentration were averaged within a run; these concentration-average values of K_A, together with their associated standard deviations, appear in the last two columns of Table I.

The spectrophotometric values of K_A listed in the second column of Table I are seen to decrease slightly as the salt concentration decreases in the first run, but show no such trend in the second run at 380 nm. No trend in K_A with concentration was noted in either run at the other four wavelengths. The maximum change in ϵ with change in salt concentration occurred at 380 nm; note that the standard deviations in K_A are the least for both runs at this wavelength. The values of K_A averaged over concentrations within a run (column 4 of Table I) show no particular trend with wavelength. A weighted average value of K_A (over the five wavelengths and two runs) was calculated, taking the weight of each value of K_A in the fourth column of Table I to be the inverse of the square of its standard deviation; K_A (weighted average) = 9440 ± 480.

Discussion

The comparison of K_A(spec) with K_A(cond) would ideally be made under the following conditions: (a) the range of electrolyte concentration would be the same in the different experiments and (b) the value of K_A(cond) would *not* depend significantly on the conductance model used to treat the data. This last condition is often not met when the magnitude of K_A is less than 100.

The salt concentrations cover the same range in the present UV-visible spectroscopic study as used in the determination of K_A(cond),[20] while the salt concentration ranges overlapped in the cesium tetraphenylborate–acetonitrile (^{133}Cs NMR vs. conduc-

Table II. Conductance and Spectroscopic Values of K_A at 25 °C

method or model	$CsBPh_4$ in acetonitrile	$AgNO_3$ in acetonitrile	LiPi in 2-butanone
LL[a]			6020 ± 90[m]
FO[b]	2.2 ± 0.5 (min 3.2)[f]	70.3 ± 1.2 (min 3.1)[j]	6140 ± 290 (min 2.6)[n]
FH[c]	19 ± 2 (min 7.8)[g]		
J[d]	17.7 ± 0.2 (q)[h]	83.5 ± 0.4 (*q*)[k]	6610 ± 40 (*q*)[o]
F77[e]	20.7 ± 0.2 (q)[h]	89.6 ± 0.4 (min 11.1)[k]	6710 ± 17 (min 7.4)[p]
spectro-	40 ± 10 (NMR)[i]	84 ± 14 (*l* – *r*)[l]	9440 ± 480 (UV–Vis)[q]

[a] Onsager limiting law, ref 2. [b] Fuoss–Onsager equation, ref 4. [c] Fuoss–Hsia equation, ref 6. [d] Justice's method, ref 8 and 22. [e] Fuoss's 1977 equation, ref 10. [f] Reference 14. Number in parentheses is value of R (Å) used in conductance model, while min indicates that R was varied in the data fitting process. [g] Reference 15. [h] This work, using conductance data from ref 14. q = 7.79 Å in acetonitrile at 25 °C. [i] Reference 12. Method in parentheses. [j] Reference 13. [k] This work, using conductance data from ref 13. [l] Reference 11. Method indicated in parentheses. [m] This work, using conductance data of ref 20. [n] Reference 23. [o] Reference 20. q = 15.56 Å in 2-butanone at 25 °C. [p] This work, using conductance data from ref 20. [q] This work.

tance) studies[13,14] and in the silver nitrate–acetonitrile (laser-Raman vs. conductance) studies.[11,12]

The values of K_A calculated from conductance data, Table II, show a pronounced dependence on the conductance model in the cases of both cesium tetraphenylborate and silver nitrate for the earlier models (LL and FO) but the values calculated using the more recent models agree within 10%. The values of K_A(cond) listed in Table II for lithium picrate in 2-butanone are the same within 10% even using the earlier conductance models in the calculations. The difference between K_A(spec) and K_A(cond) for this latter salt–solvent system could be due to impurities in the salt and/or solvent. This possibility appears unlikely in the present case for two reasons: first, the salt samples used in the two runs (Table I) were from different preparations (from lithium carbonate and picric acid), each being recrystallized four times from acetone–benzene (1:2 v/v), and second, values of K_A(cond) calculated from the conductance measurements reported from this laboratory (K_A = 6610 ± 40) and those reported from another laboratory[23] (K_A = 6140 ± 290) are in satisfactory agreement.[27] The 50% increase in K_A(spec) over K_A(cond) in this case then appears to be real, and not an artifact of either the method of data treatment or of the salt concentration used. The 100% increase in K_A(spec) over K_A(cond) (recent models) for cesium tetraphenylborate in acetonitrile is probably real but there exists an element of uncertainty because K_A is so small. In the case of silver nitrate in acetonitrile, the values of K_A(cond) calculated using the three models listed in Table II are seen to bracket the value of K_A(spec) so that there does not appear to be any real difference in the values determined using these two different experimental techniques. K_A(spec) for silver nitrate is based on differences in one of the vibrational frequencies of the nitrate ion in the ion pairs and in the free anion. Janz and Müller assume that the ion-pair species detected spectroscopically is the contact ion pair and conclude from the agreement between K_A(spec) and K_A(cond) that solvent-separated ion pairing makes no significant contribution in this system at the concentrations involved. We concur with their conclusion.

Given that the difference between K_A(spec) and K_A(cond) is real in the case of lithium picrate in 2-butanone (and possibly for cesium tetraphenylborate in acetonitrile), why should K_A(spec) be *larger* than K_A(cond)? As pointed out in the introduction, an explanation was at hand if the reverse had been observed. It may be that the electrical field of the approaching lithium cation perturbs the electronic energy levels of the picrate anion at distances significantly greater than the contact distance, so that the UV–visible spectra indicate a greater fraction of the ions as paired than does the conductance technique. Another possible explanation is that ion pairs in contact or near the contact distance may contribute significantly to the conductance. Fuoss has recently[24,25] introduced a new model for the effect of the external electric field on those anions and cations within a distance R of one another, eq 5; those ions in contact (at $r = a$, the distance of closest approach, represented by M^+, X^- in eq 5) act as dipoles, rotating in the electric field but experiencing no change in center-to-center distance and so do not contribute to the transport of charge, while the remaining pairs, denoted by $M^+ \cdots X^-$ in eq 5, simultaneously within the distance R but separated from one another by at least one solvent molecule, do contribute to the conductance but *not* to the long-range forces affecting ions at distances greater than R (i.e., the ion atmosphere). Applying this model to the conductance data for lithium picrate in 2-butanone[20] and setting $R = q$, one obtains K_A = 7250 ± 30, with the fraction of ions in contact, $\alpha = 0.990$. This value of K_A is closer to the value of K_A(spec) than those obtained using other recent models but it is increased only by some 10%. It may well be that those ion pairs in contact contribute to the net charge transport in some way.

We offer no explanation for the fact that silver nitrate shows no difference between K_A(spec) and K_A(cond). Since only two of the three systems for which information is available show the same trend with respect to the difference between K_A(spec) and K_A(cond), more experiments involving salt–solvent systems where K_A is of the order of 1000 or greater need to be carried out to determine how widespread such differences might be and how the nature of salt and solvent might affect such differences.

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