The Use of Gas Solubilities for the Determination of Solvation Numbers and to Detect Ion Pairing Involving Alkali Metal Cations

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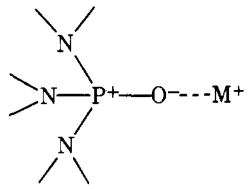
Abstract: A new method has been developed for the determination of solvation numbers for cations in solution. In the absence of ion pairing, a plot of the reciprocal of Henry's constant controlling the solubility of methylacetylene in hexamethylphosphoramide vs. the concentration of added alkali metal perchlorates is linear. The slope of the line obtained from this plot has been algebraically related to the solvation (coordination) number for the cation. For Cs^+, K^+, Na^+, and Li^+ these numbers are 5, 4, 3, and 4, respectively. At higher salt concentrations the Cs, K, and Li salts exhibit curvature in this plot due to the presence of ion pairing. The amount of ion pairing and thus the amount of curvature in this plot follows the order: $Cs^+ > K^+ \simeq Li^+ > Na^+$. This is the same order found for the coordination numbers, and is interpreted to mean that smaller coordination numbers lead to larger cation solvent interactions and thus more negative heats of solution. Indeed the single ion heat of solution in hexamethylphosphoramide was found to be 21.6 kcal/mol more exothermic for Na^+ than for K^+. The ion pairing indicated by the curvature of the Henrys' constant plot between K^+ and ClO_4^- was confirmed via an ESR technique, from which the ion association constant was estimated to be about 0.1. The sodium cation does not readily form ion pairs with paramagnetic organic anions in this solvent, while the other cations studied do, as evidenced by ESR studies.

Since the classic work of Brauman and Blair,[1] it is well understood that solvation energies are just as important in the determination of the thermodynamic stability of anions in solution as are the intramolecular considerations. Since one of the most important phenomena in the determination of solvation energy is ion pairing, both the solvation of the anion and of the cation are of critical importance. Consequently, studies concerning the thermodynamics of solvation, solvation numbers, and the structure of solvation sheaths are most valuable. A vast amount of extremely useful information in this regard has been reported by Parker and co-workers.[2,3] They have provided relative solvation energies for a variety of cations in a wide variety of solvent systems as well as insight to the structures and the electronic interactions involved in solvation sheaths. They have found that the free energy of transfer of K^+ from water to some 14 nonaqueous solvents is exothermic. To hexamethylphosphoramide (HMPA) it is more exothermic than to any of the other 13 solvent systems, which include dimethyl sulfoxide (Me_2SO), dimethylformamide (DMF), propylene carbonate (PC), acetonitrile (ACN), and methanol.[3a] More recently, they report that the ability of commonly used solvents to solvate monovalent cations follows the order HMPA > Me_2SO > DMF ≫ H_2O > ACN > methanol.[2] Further, Aitken and Gilkerson[4] have found that, for several tertiary ammonium cations, the order of increasing affinity of the ligand for the cations is HMPA > Me_2SO > DMF > acetone.

Given the special solvation power of HMPA for cations, it would be of interest to know the number of HMPA molecules that surround an alkali metal cation in solution (solvation number). It is in part our intention here to report on a new method for the determination of solvation numbers for cations in HMPA, which may be extended to other solvent systems. The minimal solvation number for K^+ in HMPA has been estimated to be two.[2] For this solvent the second solvation layer is probably not important, since the very large HMPA molecules prevent the second layer from coming close enough to the cation to interact electrostatically.[2]

The affinity that HMPA has for a particular cation and the structure of the solvation shath determines the amount of ion pairing between the cation and the corresponding anionic species. It has been pointed out that anions are not well solvated by HMPA,[5] thus solvation of the cation is the only important solution effect in controlling ion pairing in this solvent.

Water and the alcohols strongly solvate both the anion (via hydrogen bonding) and the cation (via interaction with the electrons on the oxygen atom).[6] Thus, even though HMPA is a better solvator of cations, there is less ion pairing in water. Like water, HMPA also solvates the cation through the electronegative oxygen atom (structure I). Confirming this is the fact that the P-O stretch is decreased by 15-25 cm^{-1} upon coordination to a monovalent cation.[7]



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From the above it is clear that the size of the cation will effect its solvation, but the nature of this effect is not understood. For instance, in methanol and ACN the order of decreasing ion pairing is $Cs^+ > K^+ > Na^+ > Li^+$.[8] However, in propylene carbonate exactly the opposite order has been recently observed,[9] even though both methanol and PC coordinate the cation through an oxygen atom. This is because methanol is protic and PC is aprotic. In this report we will investigate the effect of ion size upon its solvation in HMPA.

Although it has been shown that ESR is a powerful tool in the investigation of the nature of ion pairing, this technique has been limited to the study of paramagnetic salts. For diamagnetic salts a variety of techniques have been employed for the determination of ion pair association constants. These include NMR,[10] visible spectroscopy,[11] and conductivity.[12] Although conductivity is one of the most versatile, only with difficulty can conductivity be utilized in highly solvating aprotic solvents.[13,14] Consequently, for a series of potassium salts, on which conductivity measurements were carried out in HMPA, only KNO_3 yielded data allowing the calculation of the ion association constant.[13] Here we wish to describe a new technique for the determination of ion association constants for diamagnetic salts utilizing ESR spectroscopy. Thus, this report is fourfold in purpose: (1) to describe the use of gas solubilities in the determination of solvation numbers and in detecting ion pairing, (2) to describe the use of ESR for the determination of ion pair association constants for diamagnetic salts, (3) to

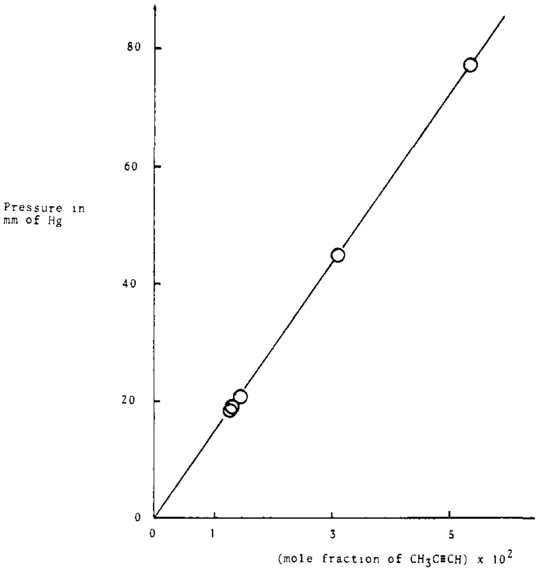


Figure 1. Henry's plot for methylacetylene in HMPA at 25 °C.

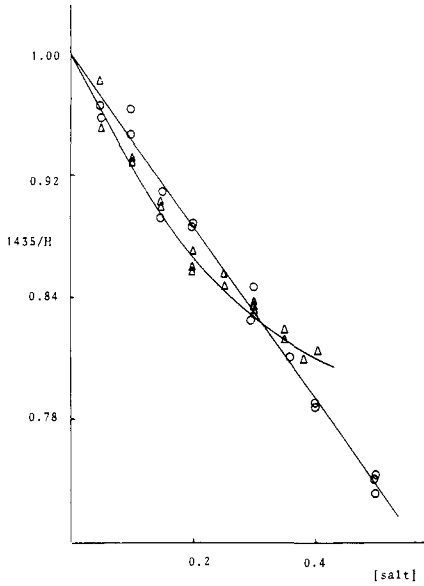


Figure 2. Plots of 1435/H for HMPA solutions of $NaClO_4$ (○) and $LiClO_4$ (▽) vs. the concentration (M) of dissolved salt. The gas is methylacetylene.

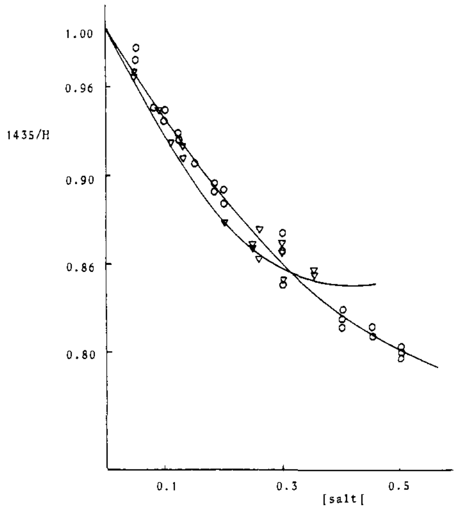


Figure 3. Plots of 1435/H for HMPA solutions of $CsClO_4$ (▽) and $KClO_4$ (○) vs. the concentration (M) of dissolved salt. The gas is methylacetylene.

determine the effect of ion size upon the solvation number and ion pair dissociation constant, and (4) to coordinate these data to gain insight into the nature of cation solvation in HMPA.

Results and Discussion

Gas Solubilities. Henry's constant was determined for methylacetylene (MA) in HMPA in the manner previously described (H = 1435 mmHg at 28 °C).[15] The major factor in controlling the solubility of MA in HMPA is the hydrogen bonding between the acidic proton in MA and the oxygen atom in HMPA.[15] Henry's constant is normally larger (the gas is less soluble) when salt is added to the solvent (salting out effect).[16] In HMPA the same oxygen atom used to coordinate the cation is needed for hydrogen bonding to the MA when this gas is present in solution. Thus, there should be a relationship between Henry's constant and the number of HMPA molecules involved in coordinating the cation.

Henry's constant is given by

$$H = P/X_{\mathrm{MA}} = P([\mathrm{MA}] + [\mathrm{HMPA}])/[\mathrm{MA}] \qquad (1)$$

where P is the pressure of MA at equilibrium, and X_{MA} is the mole fraction of MA. H is determined from the slope of the line taken from a plot of P vs. X_{MA}, Figure 1. If a salt that fully dissociates in HMPA is added, Henry's constant should increase, since some of the HMPA is involved in coordinating the M^+ ions and is not available for hydrogen bonding with the MA. For an experiment carried out with an HMPA sample containing a dissolved salt

$$H/([\mathrm{MA}] + [\mathrm{HMPA}]) = 1435/([\mathrm{MA}] + [\mathrm{HMPA}] - N_c[\mathrm{M}^+]) \qquad (2)$$

where H is Henry's constant measured for the solution, and N_c is the coordination (solvation) number for the cation (M^+). Thus $N_c[M^+]$ is the concentration of HMPA that is made unavailable for hydrogen bonding to MA.

Since the concentration of MA dissolved in the HMPA solution is much smaller than $[M^+]$ and $[M^+] \ll [\mathrm{HMPA}]$

$$H/1435 = [\mathrm{HMPA}]/([\mathrm{HMPA}] - N_c[\mathrm{M}^+]) \qquad (3)$$

and

$$1435/H = 1 - N_c[\mathrm{M}^+]/[\mathrm{HMPA}] \qquad (4)$$

If the salt is fully dissociated, a plot of 1435/H vs. the concentration of added salt should be linear and have a slope of $N_c/[\mathrm{HMPA}]$. However, if some ion pairing is present, curvature will be observed in this plot. For solutions of sodium perchlorate in HMPA such a plot is linear and yields a value of 3.0 for N_c, Figure 2. This is in agreement with the fact that ion pairing could not be observed for this system using conductivity measurements.[13]

The perchlorates of Cs, K, and Li all show curvature (Figures 2 and 3) with the degree of curvature, and thus ion pairing, being $Cs^+ > K^+ \simeq Li^+$. The observed value for N_c can now be taken from the initial slopes. These values are 4 for Li^+ and K^+ and 5 for Cs^+. Theoretically, the ion association constant ($K_a = [M^+, ClO_4^-]/[M^+]^2$) could be obtained from the degree of curvature in these plots, but this would require that the coordination number of the ion pair be known.

It has been previously observed that anions in HMPA act as hydrogen bond acceptors, but the affinity of these anions for the proton donor is much less than that of the HMPA.[15,16] Also the small interaction between the anion and the HMPA is through the "back" part of the molecule and does not involve the oxygen atom. This type of anion solvation has been proposed by Tomoi and co-workers to account for the presence of a solvent separated ion pair between Mg^{2+} and the cyclopen-

Table I. Observed Coupling Constant of the 2,6-Di-*tert*-butylbenzoquinone Anion Radical in HMPA at 25 °C with Added KNO_3[a]

$[KNO_3]_{total}$, M	$[K^+_{free}]$, M	$\bar{A}$, G
0	0	2.346
0.0143	0.0108	2.312
0.0191	0.0129	2.309
0.0246	0.0151	2.306
0.0452	0.0220	2.291
0.0532	0.0242	2.279
0.0637	0.0270	2.270
		2.05

[a] Only a representative set of data is shown.

tadienyl anion separated by a molecule of HMPA.[17] All of this coupled with the fact that the solvation of anions in HMPA is very weak,[5] indicates that no correction to the solvation numbers found is necessary due to the effect of the anion. Thus the coordination numbers for Cs^+, K^+, Na^+, and Li^+ are 5, 4, 3, and 4, respectively.

The order of decreasing coordination number is the same as the order of decreasing ion pairing ($Cs^+ > K^+ \simeq Li^+ > Na^+$). This suggests that ions with smaller solvation numbers hold the HMPA molecules in tighter to the charged center, and it is consequently more difficult to disrupt these stronger Coulombic forces to form ion pairs. Indeed, Na^+ forms ion pairs much less readily than does K^+ in HMPA.[18,19]

Ion Association Constants for Diamagnetic Salts by ESR. The reduction of 2,6-di-*tert*-butylbenzoquinone in HMPA by potassium metal results in the formation of the free anion radical, which exhibits an ESR signal consisting of a triplet due to two equivalent protons with a coupling constant of 2.346 ± 0.005 G.[20] Successive additions of potassium nitrate to this solution result in a gradual decrease in the observed coupling constant. This decrease is due to the formation of the ion pair (β), which is in rapid equilibrium with the free ion (α), eq 5.[20,21]

$$\beta \rightleftarrows \alpha + K^+ \qquad (5)$$

The observed coupling constant and g value ($\bar{A}$ and $\bar{g}$, respectively) have been previously shown to be weighted averages between those for the free ion (A^0 and g^0) and those for the ion pair (A' and g').[20-22] When the weighted average expression is combined with the expression for the thermodynamic equilibrium constant for eq 5, $K_{diss} = [\alpha][K^+_{free}]/[\beta]$, leads to the following expressions.[22,23]

$$1/(\bar{A} - A^0) = K_{diss}/[K^+_{free}](A' - A^0) + (A' - A^0)^{-1} \qquad (6)$$

and

$$1/\Delta\bar{g} = K_{diss}/\Delta g'[K^+_{free}] + 1/\Delta g' \qquad (7)$$

where $\Delta\bar{g}$ and $\Delta g'$ represent the difference in the observed g value and the g value for the ion pair, respectively, with that for the free ion.[23] Both of these expressions yield the same value for K_{diss} ($K_{diss} = 0.076$).[22]

Knowing that, the ion association constant for KNO_3 is 59 ± 8 in HMPA ($[K^+,NO_3^-]/[K^+_{free}][NO_3^-]$),[13] the free potassium ion concentration can be calculated for any amount of KNO_3 that is added to the anion radical solution. A plot of the reciprocal of the potassium ion concentration free of ion pairing vs. $1/(\bar{A} - A^0)$ should be linear and have a slope of $K_{diss}/(A' - A^0)$ and an intercept of $1/(A' - A^0)$. Treated in this manner our data did yield a straight line, Table I, Figure 4. The concentration of potassium ion free of ion pairing used in Figure 4 and Table I is not exactly equal to that calculated from the amount of KNO_3 added and K_a for this salt, since a small correction has been added to account for the potassium ion concentration resulting from the alkali metal used to reduce the neutral molecule to form the anion radical. This correction was omitted in a preliminary communication of this work.[23]

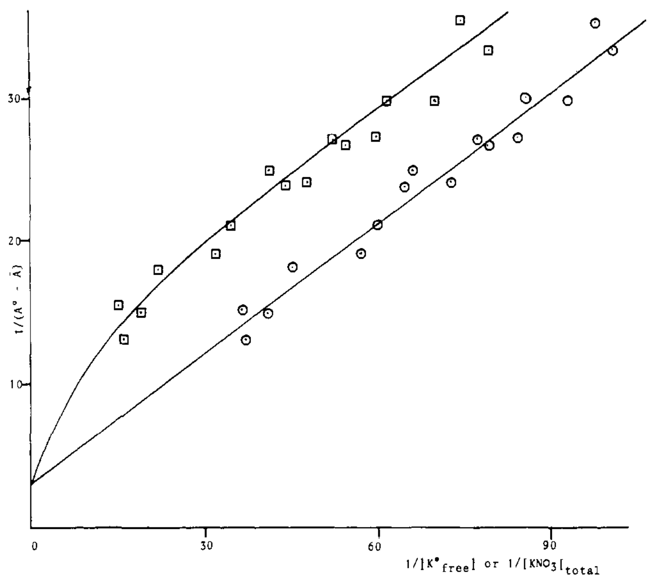


Figure 4. Plots of $1/(A^0 - \bar{A})$ vs. the reciprocal of the total concentration of added KNO_3 (□) and vs. the concentration of K^+_{free} calculated from a K_a of 59 (⊙).

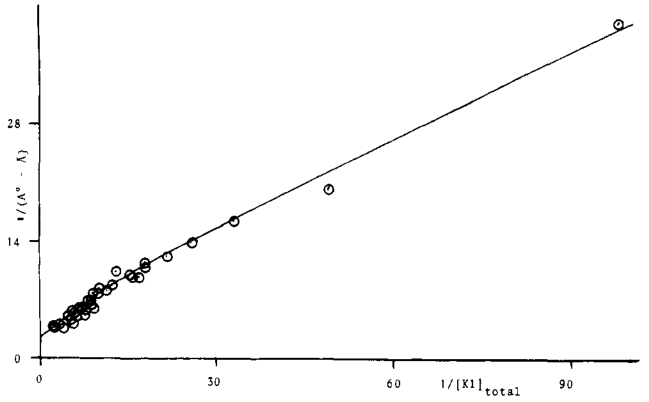


Figure 5. Plot of $1/(A^0 - \bar{A})$ vs. the reciprocal of the concentration (M) of added KI to the 2,6-di-*tert*-butylbenzoquinone anion radical in HMPA. Note the curvature in this plot. If $1/(A^0 - \bar{A})$ is plotted against $1/[K^+_{free}]$ a straight line is obtained if $[K^+_{free}]$ is calculated from a K_a of 1.1.

If $1/[KNO_3]_{total}$ is plotted against $1/(A^0 - \bar{A})$ instead of $1/[K^+_{free}]$, considerable curvature is noted (Figure 5) due to the fact that the concentration of K^+,NO_3^- increases at the expense of K^+_{free} as the total salt concentration is increased. The slope and intercept of the straight line in Figure 5 are 0.303 and 3.156, respectively. If a potassium salt (KX) with an unknown K_a is now added to a solution of the 2,6,-di-*tert*-butylbenzoquinone free anion radical, a linear plot with a slope and intercept of 0.303 and 3.156 will be obtained only if $1/[K^+_{free}]$ is calculated from the correct value for K_a. Thus, for KX a series of plots of $1/(A^0 - \bar{A})$ vs. $1/[K^+_{free}]$ can be constructed using trial values of K_a to calculate $[K^+_{free}]$. The best slope (M) and intercept (I) can then be determined from each of these plots, and those comparing most closely to 0.303 and 3.156 come from the best value of K_a. The deviation from these numbers (δ) is expressed by

$$\delta = \sqrt{[(I - 3.156)/3.156]^2 + [(M - 0.303)/0.303]^2} \qquad (8)$$

The K_a yielding the smallest δ was taken as the best value.

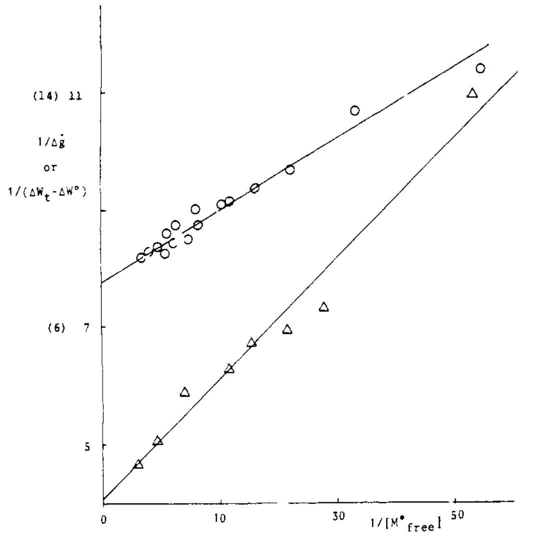


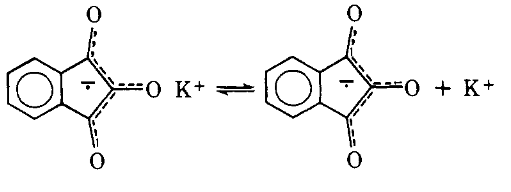
Figure 6. Plots of $1/(\Delta W_t - \Delta W^0)$ vs. the reciprocal of the Cs^+ free concentration (M) (△), and of $1/\Delta \bar{g}$ vs. the reciprocal of the K^+ free concentration (○). The values given in parentheses represent $1/\Delta \bar{g}$ for the potassium system.

Brusset and co-workers[24] have concluded, from a curve of conductivity vs. concentration, that KI is not fully dissociated in HMPA. However, they were not able to obtain K_a, as it is too small to be evaluated by conductivity data. Addition of KI to the free anion radical of 2,6-di-*tert*-butylbenzoquinone in HMPA results in the expected decrease in $\bar{A}$. A plot of $1/(A^0 - \bar{A})$ vs. $1/[K^+_{free}]$ yields the best line (Figure 5) for $K_a = 1.1$ ($\delta = 0.098$). This value for K_a is smaller than that estimated in the preliminary communication,[23] but it is obtained from many more experimental points (32) and the treatment of the data has been improved.

Based upon conductivity data, $KClO_4$ appears to be fully dissociated in HMPA.[13] In contrast to this, we observed curvature in the plot of Henry's constant vs. salt concentration indicating that ion pairing is present (Figure 3). Application of the ESR technique (35 experimental points) yields a value of 0.12 for K_a ($\delta = 0.11$) of $KClO_4$ in HMPA. This small value for K_a would not be observed by conductivity studies, but ion pairing is detected by both the gas solubility and the ESR techniques described here. It must be noted that the problem of activity coefficients is not accounted for, and this could lead to error in the actual values for K_a. We can estimate an error of about 50% in these K_a's.

The ESR technique described here has been applied to the potassium ion only, due to the fact that conductivity data are scarce for other ions. However, there is no reason why, with future measurements, this technique could not be expanded to include other cations and other solvent systems. The only system studied here for which there is no ion association is $NaClO_4$ in HMPA, Figure 2. It was also concluded from conductivity studies that this salt is free from ion association in HMPA.[13]

Ion Pair Dissociation Constants for Paramagnetic Salts. The addition of cesium, potassium, or lithium perchlorate to the free anion radical of ninhydrin in HMPA results in the formation of the ion pair, which is in rapid equilibrium with the free ion (eq 9). For the case where M^+ represents the potassium ion the equilibrium constant has already been determined by the use of time averaged total line widths (the distance between the first and last ESR line is substituted into eq 6 in place of A).[25] The ESR coupling constants (0.93, 2 H's, and 1.18 G, 2 H's, for the free ion) vary with the addition of salt, but the total line width (ΔW_t) changes more dramatically. A plot of $1/[K^+_{free}]$ vs. $1/(\Delta W_t - \Delta W_t^0)$ yields a straight line and an ion pair dissociation constant of $K_{diss} = 0.014$.[25]


(9)

The addition of KI to this anion radical in HMPA also results in a decrease in the observed g value. This allows a confirmation of K_{diss} by the use of g values and eq 7. The data shown in Figure 6 yield a value of 0.018 ± 0.002 for K_{diss} at 25 °C. The addition of $CsClO_4$ also results in an increase in the total line width and g value. The ion pair dissociation constant for the cesium salt of ninhydrin radical anion is 0.025 ± 0.007, Figure 6. No change in either the total line width or g value was observed upon the addition of $NaClO_4$ up to 0.5 M. This can only mean that K_{diss} for the sodium salt is too large to measure (greater than 50). The addition of $LiClO_4$ to the anion radical solution does not cause enough change in ΔW_t for the determination of K_{diss}. However, the g value is more sensitive to ion pairing, and the use of eq 7 yields a value for K_{diss} of ca. 40.

Conclusions

All of the data taken for Na^+ in HMPA indicates that this ion does not readily associate with monovalent cations in HMPA. The potassium cation, on the other hand, shows curvature in the plot of gas solubility vs. the $KClO_4$ concentration indicating the presence of ion pairing. This was confirmed utilizing the ESR technique, and K_a was found to be about 0.1. Further K^+ readily associates with the ninhydrin anion radical ($K_{diss} = 0.016$), while the K_{diss} for the sodium salt is immeasurably large. The somewhat surprising result is that the coordination number for the sodium cation (3) is actually smaller than that for the potassium ion (4). This must mean that the smaller coordination number for the Na^+ ion in HMPA allows the formation of a stronger interaction between the cation and the HMPA molecules (structure I). This stronger interaction results in the formation of a smaller tighter solvation sheath and consequently a more negative heat of solution for the sodium cation.

The relative single ion heats of solution for the sodium and potassium cations can be found from the known heats of reaction and heats of solution of the sodium and potassium salts of cyclooctatetraene in HMPA.[26,27] The enthalpy of reaction of gas phase sodium ions, two gas phase electrons, and cyclooctatetraene (COT) to form the sodium COT salt in HMPA and the enthalpy of solution of the COT dianion can be combined to give the single ion heat of solution of the sodium cation.

$$2Na^+_{(gas)} + 2e^-_{(gas)} + COT_{(gas)} \rightarrow 2Na^+_{(soln)} + COT^{2-}_{(soln)} \qquad \Delta H^0 = -355.4 \text{ kcal/mol}$$

$$COT^{2-}_{(soln)} \rightarrow COT_{(gas)} + 2e^-_{(gas)} \qquad \Delta H^\circ = 125.1 \text{ kcal/mol}$$

Summing these two equations and dividing by two yields and enthalpy of solution for the Na^+ ion of −115.2 kcal/mol.

The single ion heat of solution of the potassium cation in HMPA is −93.6 kcal/mol (this single ion heat of solution is not absolutely valid as it is based upon an extra thermodynamic assumption called the TATB assumption).[2] The value for the heat of solution of the potassium ion was used to obtain the heat of solution of COT^{2-}, and error in this number is incorporated into the heat of solution obtained for the sodium ion. Thus it is absolutely valid to say that the heat of solution of Na^+ is more exothermic by 21.6 kcal/mol than the heat of solution of K^+. This difference is apparently sufficient to prevent ion association of sodium salts, while those of potassium can readily form ion pairs.

The trend of increasing solvation number with increasing heat of solution (as evidenced through more ion pairing with ClO_4^-) follows for the series $Cs^+ > K^+ \simeq Li^+ > Na^+$ with solvation numbers of 5, 4, 4, and 3, respectively. In agreement with this trend Na^+ does not form ion pairs with the ninhydrin anion radical. The lithium ion, however, does not follow this trend, and has a K_{diss} that is much too large when the anion radical of ninhydrin serves as the anion. This may be explained in part by the fact that the Li^+ ion does not have p orbitals available for possible interaction with the conjugated π system of the aromatic anion radical.

From the use of a cation sensitive electrode Nakamura has found that the sodium ion is trisolvated by HMPA when HMPA is added to an ACN solution of sodium perchlorate.[28] These results are in perfect agreement with our results. However, from the addition of HMPA to a lithium perchlorate solution in ACN he could only obtain the lithium cation disolvated by HMPA. This was attributed to the steric effect in the reactions between large HMPA molecules around the small lithium cation.[28] Our results are not in accord with this, but their data might be better explained by the existence of a strong competition for the third and fourth coordination sights between the ACN and HMPA in their system. For the sodium ion HMPA dominates the third site, since it has a stronger affinity for the HMPA than does lithium.

Experimental Section

All of the organic compounds used were purchased from Aldrich Chemical Co. The inorganic salts were purchased from Alfa Inorganics and were stored in a vacuum oven for 48 h at 100 °C prior to use. The method of reduction of neutral molecules to form anion radical and the purification of the HMPA has been previously described.[29]

The g values were measured on a Varian E-9 ESR spectrometer using the dual cavity technique.[30] All values for g were obtained by placing a sample of the free ion in one of the two cavities and a sample containing a known quantity of salt in the other.

The determinations of the gas solubilities and Henry's constants were carried out with the use of a vacuum system connected with a Toepler pump fitted with a gas buret in the same manner as previously described.[15] The methylacetylene was also treated and stored as described previously.[15]

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The Simplest Metallocene: Cyclopentadienyllithium

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Abstract: Calculations were carried out on cyclopentadienyllithium with minimum and double ζ basis sets. The potential curve of the Li over the cyclopentadienyl ring was mapped out with the result that the Li is most stable above the middle of the ring. Geometry optimization of both the cyclopentadienyl ring and the most stable cyclopentadienyllithium complex was carried out and the effect of complexation noted. Optimal scale factors were determined with the minimum basis set. The two basis sets were compared with a view toward establishing the reliability of the minimum basis set for work with larger metallocenes. Using the double ζ basis set, it was determined that the hydrogens do not lie in the plane of the C_5 ring.

The area of metallocene chemistry has proven to be a very fertile one; elucidation of the structure of the metallocenes has occupied the efforts of both experimentalists[1,2] and theoreticians.[3] Ferrocene is the most prominent of the metallocenes and indeed its chemistry and structure have been intensively investigated. The nature of its bonding is most often explained as an interaction between the e_{1g} HOMO orbitals of the cyclopentadienyl ligands and the e_{1g} (d_{xz}, d_{yz}) orbitals of the