CATION-ELECTRON INTERACTIONS IN METAL SOLUTIONS -
FROM SOLVATED ELECTRONS TO ALKALI METAL ANIONS

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Abstract - The solvent has a pronounced effect on the nature of species formed by
solvated electrons and alkali metal cations. Neutral species form, which can be
described as solvent-shared and contact ion-pairs. However, short-range "core"
repulsions characteristic of normal contact pairs are absent so that a continuum
of states with varying atomic character exists depending upon the solvent, the
metal, and the temperature. In addition to cation-electron interactions,
electron-electron interactions occur which stabilize singlet ground states. The
cation can play a major role in this process, retaining its own solvation in a
good donor solvent such as ammonia or forming a genuine alkali metal anion with
two electrons in the outer s orbital in poorer donor solvents. Intermediate states
such as contact triple-ions may also form but there is no direct evidence for
such species.

INTRODUCTION

It is now 113 years since Weyl discovered that the alkali metals dissolve in liquid ammonia
(1). These solutions, blue when dilute and bronze when concentrated, have fascinated
chemists and physicists for years because they form a bridge between electrolytic and metal-
lic behavior. In recent years enough data in a variety of solvents have been accumulated
that it should now be possible to describe, at least in qualitative terms, the effect of the
solvent and the metal on the nature of the species which form. It is interesting to compare
the similarities and differences between solutions of the alkali metals and solutions of
ordinary salts in the same solvents. A major difference between the solvated electron and
a normal solvated anion is that the former has neither a central nucleus nor "core"
electrons. Its attraction to the polarization center which it creates in a polar solvent
is relatively weak, the "charge cloud" is highly polarizable, and the electron is free to
move readily to a region of higher stability. However, the solvation energy of the electron
is important [about 40 kcal mole^{-1} in ammonia(2)], amd must be considered in any description
of electron-cation interactions. Of even greater importance to such interactions is the
solvation energy of the cation. Therefore, while it might be tempting to consider the
formation of an alkali metal atom by simple attachment of e_s^- to M^+, such a neutralization
reaction would require loss of the solvation energy of both e_s^- and M^+ with a gain of just
the electron affinity of M^+.

It is not the aim of this paper to describe the detailed nature of the solvated electron nor
to provide a comprehensive review of the properties of metal solutions. Four international
conferences on the nature of electrons in fluids (under the general name of Colloque Weyl)
have been held(3-6) and two other meetings stressed the overlap between metal solution
studies and radiation chemistry(7-8). The reader is referred to these conference papers for
review material, details of the techniques used, and general references. Rather, I wish to
describe a general scheme (with many features which have been previously suggested) which
considers the species formed by cation-electron and electron-electron interactions at
dilute to moderate concentrations, and the influence of the solvent and the metal on these
interactions.

Because many species are required to explain the diverse behavior of metal solutions and
because of the scarcity of data relevant to some of them, some of the descriptions are
highly speculative. However it is possible to devise a consistent picture of metal solutions
which utilizes concepts which are very familiar to anyone who has studied ionic interactions
in non-aqueous solvents.

SOLVATED ELECTRONS

As late as 15 years ago the solvated electron (e_s^-) had been detected in only about a half-dozen amine and poly-ether solvents. Except for ammonia, methylamine ($MeNH_2$) and ethylene-diamine (EDA) metal solubilities were low and only fragmentary data (usually optical spectra) were available. Then, by using pulse radiolysis techniques(9,10), radiation chemists began to detect e_s^- in a wide range of solvents, including hydroxylic, amine, and ether solvents. Indeed, except for very non-polar solvents and a few solvents which react with the electron before it has time to become solvated, electron solvation is a very general phenomenon in liquids. Of course in many cases, even when the oxidizing species which are also produced can be scavenged, e_s^- reacts rapidly with the solvent so that, in general, only fast detection methods (nanosecond to millisecond) can be used. However, this is long enough to provide us with much information about the properties and reactions of solvated electrons in a wide variety of solvents.

Studies of metastable solutions of alkali metals require non-reactive solvents and, with the exception of hexamethyl phosphoric triamide (HMPA), have been limited to amine and ether solvents. A major difficulty - low solubility caused by low cation solvation energies - was eliminated in 1970 when we showed (11) that cation complexing agents of the crown ether class greatly enhanced alkali metal solubilities. Since then, both crown (12) and cryptand (13) cation complexing agents have been used by us(14-21) in metal solution studies.

Reactions of e_s^-

Just as the solvated proton is the strongest Brönsted acid in any solvent (thermodynamically speaking), so the solvated electron is the strongest reducing agent. Any stronger reducing agent would tend to transfer its electron(s) to the solvent. Similarly, any solute species with a larger electron affinity than the solvent will tend to react with e_s^- to form a species of lower (thermodynamic) reducing power than e_s^-. As we shall see, even alkali cations and alkali metal atoms can be reduced under certain circumstances.

Of course the presence of easily reducible substances, such as oxygen, acids, alcohols (including water), aromatic compounds, etc. must be avoided if stable metal solutions are to be prepared and studied. Having often seen many hours of preparative work lost by solution decomposition, I am constantly reminded of the thermodynamic instability of metal solutions. Fortunately, in clean systems with solvents which have been pre-treated with good reducing agents, alkali metal solutions have high enough stabilities to permit one to make quantitative, reproducible measurements. However, contamination by decomposition remains the most serious deterrent to reliable studies of these systems. In many cases, the decomposition seems to be auto-catalytic such that the onset of decomposition brings on a rapid and complete decomposition of the solution. In general, the problems are worse in ethers than in amines and solutions of sodium are generally much more stable than are those of the other alkali metals. There is a great need for systematic studies of solution decomposition processes in amines and ethers.

Solubility considerations

As we shall see, saturated metal solutions contain a number of different species. This complicates any attempt to calculate metal solubilities since the actual solubility will always be higher than that calculated on the basis of only M^+ and e_s^-. Nevertheless, it was possible to describe the solubility trends for solutions in ethylenediamine (14) by examining only the two equilibria

$$M(s) \; \rightleftharpoons \; M^+ + e_s^- \tag{1}$$

$$M^+ + e_s^- \; \rightleftharpoons \; M^+ \cdot e_s^- \tag{2}$$

The extended Debye-Hückel expression was used together with ion-pair association constants from conductivities to correct for effects of non-ideality and ion-pairing. The measured solubilities (22) and spectra (23) of potassium were used to establish the value of ΔG_s^0 for this metal. Then it was assumed that the differences in solvation free energies of the cations are the same as in ammonia (24). As a result, the solubilities of the other metals were calculated and the general trends were shown to be in agreement with experiment. In particular, the observation that sodium is least soluble and lithium most soluble was readily explained. These trends in solubility; Li > Cs > Rb > K > Na, are qualitatively observed in other solvents as well although quantitative solubility data are scarce.

In order to assess the effect of solvent on the solubility we would need either the solvation free energies or the free energy of transfer of M^+ from ammonia or EDA to the solvent in question. Although such estimates have been made for some solvents and ions (25,26) they are not available for the solvents considered here. However, it is clear that the drastic decrease in metal solubility as the solvent donicity decreases is largely caused by the decrease in the free energy of solvation of the cation. In fact, were it not for the formation of the other species described in this paper, the solubilities

would be even lower than they are.

SPECIES OF STOICHIOMETRY M

The importance of ion-pairing in non-aqueous solvents has been apparent for some time (27). In order to explain conductivities, optical spectra, esr and nmr spectra, etc. of salt solutions it is necessary to consider ion pairs of different types such as contact pairs, solvent-shared pairs and solvent separated pairs. In order to describe conductance behavior, sometimes all pairs with center-to-center distances smaller than the Bjerrum distance are considered to be paired. However since the Bjerrum distance is very large in media of low dielectric constant, it hardly seems appropriate to consider such "ion-pairs" as distinct species. Since perturbations of the optical and/or magnetic properties of one ion by its counter-ion die out rapidly with distance, we will include as distinct species only contact and solvent-shared ion-pairs. Changes in the properties caused by longer-range interactions will be treated as perturbations of the properties of the separated ions.

EPR studies
Because the solvated electron has an unpaired spin which can interact with the alkali metal nucleus, when the electron and the cation are close together, the resulting EPR pattern can provide useful and sometimes very detailed information about the nature of the neutral species, M. When M lives long enough, the EPR signal is a multiplet of $2I + 1$ lines, in which I is the nuclear spin of the alkali metal. The separation of the lines, the hyperfine splitting, is a direct measure of the average contact density of the electron at the nucleus. When this splitting is expressed as a percentage of that of the free gaseous atom, it gives the "percent atomic character" of M. We will refer to the species which yield hyperfine patterns as "monomers".

When processes such as

$$M \underset{\leftarrow}{\rightarrow} M^+ + e^- \tag{3}$$

$$(e_s^-)^* + M \underset{\leftarrow}{\rightarrow} M^* + e_s^- \tag{4}$$

become rapid compared to the reciprocal of the hyperfine splitting, only a single line is observed. This represents an exchange-averaged signal and degrades the information about the nature of M. On the other hand, with slow exchange one can observe simultaneously the hyperfine pattern of the monomer and the single line of e_s^-.

The striking effect of the solvent and metal on the EPR pattern is illustrated in Fig. 1 for solutions of K, Rb and Cs in $MeNH_2$, $EtNH_2$, and n-propylamine respectively(32). With
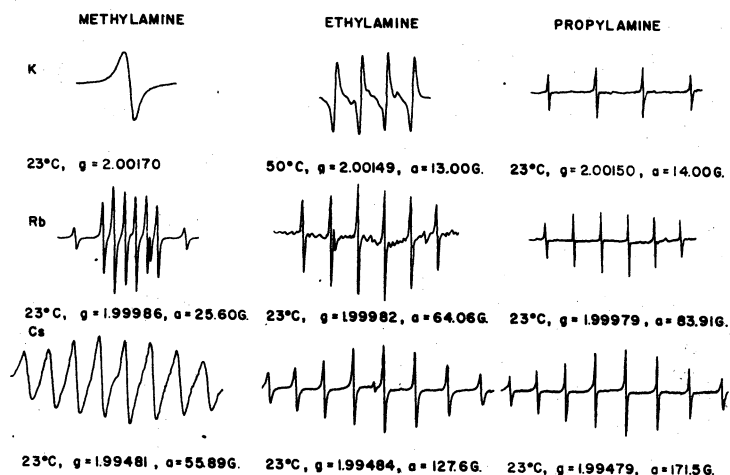

Fig. 1. Some EPR spectra of K, Rb and Cs in three solvents (32). Note the change in scale from pattern to pattern as indicated by the hyperfine splittings given.

ammonia as the solvent, only a single narrow line is observed: rapid exchange and low contact densities at the metal nucleus cause collapse of any potential hyperfine pattern. In this case, alkali metal nmr studies (28) provide some information since interaction of the nucleus with a solvated electron produces a paramagnetic shift of the metal nmr signal. If the concentration of M can be separately determined, for example from conductivities, then the atomic character of M can be calculated from the magnitude of the shift. It has

been estimated (29) for example that the ion-pair $Na^+ \cdot e_s^-$ in ammonia has about 0.5% atomic character.

With K in $EtNH_2$ at appropriate concentrations, the exchange processes are slow enough to permit observation of the two four-line patterns of ^{39}K and ^{41}K monomers in addition to the central single line of e_s^-. It should be noted that the central line need not arise only from isolated solvated electrons, but can also include contributions from "loose" ion-pairs which exchange rapidly with M^+ and e_s^-.

The percent atomic character of the monomer in all solvents increases markedly with temperature. For example, in ethylamine as solvent, the separation of the four lines increases with temperature (30) to give a change from 4% atomic character at -50° to 30% at 100°. In solvent mixtures, the atomic character changes smoothly as a function of concentration. In ethylamine-ammonia mixtures at 25°, the atomic character changes from 12% in pure ethylamine to 3% at 0.15 mole fraction NH_3 (31).

The shape and position of the EPR pattern also tell us something about the nature of the monomer. As shown in Fig. 2 for the case of Cs in $EtNH_2$ (32), the linewidths of the
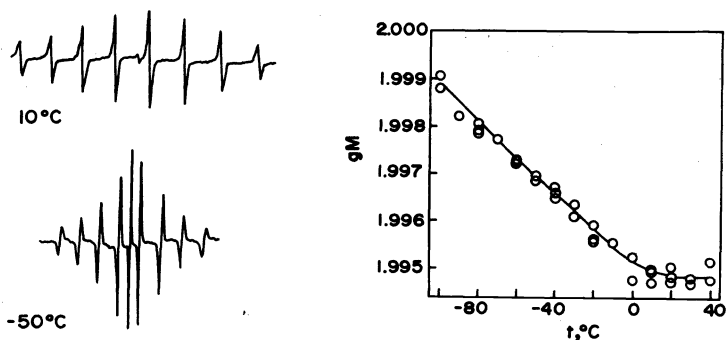

Fig. 2.   Variation of the EPR spectrum of Cs in $EtNH_2$ with temperature and the temperature dependence of the g-value (32).

components of the hyperfine pattern depend upon the nuclear spin quantum number. Also shown in Fig. 2 is the variation of g-value with temperature. As the electron density at the nucleus increases, the g-value decreases. Both the linewidth pattern and the g-value change indicate the presence of considerable spin-orbit coupling. The simplest interpretation of these results is the introduction of spin-orbit coupling by a non-spherically symmetric structure. The change in g-value with temperature would then result from a stronger electron-cation interaction at higher temperatures with correspondingly greater spin-orbit coupling. However, the linewidth variation could also result from a distribution of species of slightly different contact densities (33) or from very rapid exchange among different types of monomers (32,34).

Optical spectra of monomers

The EPR intensities show that the monomer is generally a minor species in metal solutions at equilibrium. Therefore it has not been possible to determine its optical spectrum by static methods. Pulse radiolysis (35,36) and flash photolysis (37-39) techniques can lead to transient concentrations of M (by the reaction of e_s^- with M^+) high enough to detect optically. The correlation of the solvent dependence of the shift of the optical absorption and the percent atomic character of the monomer as obtained by EPR studies is striking. In the good donor solvents NH_3 and EDA, the optical spectrum of e_s^- is practically unaffected by interaction with M^+ and the electron density at the metal nucleus is also small. However, in the poorer solvent THF, the shift of the absorption band is large and metal-dependent. These effects are summarized in Table 1 for the case of potassium in four solvents. It seems likely that the transient species produced by radiolysis or photolysis is the same as that studied with metal solutions by EPR methods.

TABLE 1. Solvent dependence of the shift of the optical band and the percent atomic character for the potassium monomer at 25°.

Solvent	$(\bar{\nu}_M - \bar{\nu}_{e_s^-})$[36] (cm^{-1})	% atomic character[29,30]
NH_3	0 to -600	0.5
$MeNH_2$	~0	3^a
$EtNH_2$	+1600	12
THF	+3600	36

^{a}Estimated from the values for Rb and Cs in $MeNH_2$

The role of ion-pair formation

A simple view of the nature of M which is consistent with all of the solvent, metal, and temperature effects described above considers the formation of solvent-shared and contact ion-pairs between e_s^- and M^+. In the solvent-shared ion-pair the nature of the metal is secondary, the electron density at the metal nucleus is small and the optical spectrum of e_s^- is only slightly perturbed by the presence of M^+. Such ion-pairs are the predominant form of M in strongly coordinating solvents such as NH_3 and EDA. Solutions of lithium also tend to yield solvent-shared rather than contact ion-pairs. An interesting verification of this is found for the case of Li in $EtNH_2$. The EPR spectrum shows (40,41) that e_s^- interacts with four equivalent nitrogen nuclei to give a nine-line hyperfine pattern at low temperatures in addition to the singlet of e_s^-. However, the contact density of e_s^- at the lithium nucleus is very small (41). A straightforward explanation of these results is that the four amine molecules on the species $Li(EtNH_2)_4^+$ interact strongly with e_s^- because they are shared between Li^+ and e_s^-. Rotation of the solvated Li^+ or rapid movement of e_s^- around it would make all four nitrogen atoms equivalent on the EPR time scale. Because the rates of dissociation of both the solvent-shared ion-pair and the ethylamine molecules bound to Li^+ are slow, a nine-line nitrogen hyperfine pattern results. Presumably, other solvent molecules around e_s^- exchange rapidly. At higher temperatures and for the other alkali metals the rate of dissociation of the amine molecules from the solvated cation is too rapid to give hyperfine splitting by nitrogen.

The contact ion-pair between e_s^- and M^+ is the "monomer" referred to earlier. Because e_s^- has no inner core electrons and no central nucleus, the contact ion-pair need not have a fixed distance between charge centers as is the case for ordinary contact ion-pairs. Instead, the atomic character can vary with solvent and temperature towards the non-ionic limit of a dissolved atom. With this picture it is natural to expect a lower ionic character and greater atomic character as the solvating ability of the solvent decreases. This is in accord with both the solvent and temperature dependence of the EPR spectra and with the solvent dependence of the optical spectra. An alternative explanation considers a rapid equilibrium between solvent-shared and contact ion-pairs with the proportions of each depending upon the solvent and the temperature. The main problem with this view is the extremely rapid exchange required. For example, with K in ethylamine the average lifetime of the contact ion-pair would have to be shorter than 10^{-9} sec. (31). Also, since separate signals can be seen for M and for e_s^-, the exchange between contact pairs and solvent-shared pairs would have to be faster than that between solvent-shared pairs and the dissociated ions. It seems more reasonable for the converse to be true - formation and break-up of contact pairs being slower than for solvent-shared pairs. If this is true, then the variation of properties with solvent and temperature implies a continuum of states of the contact ion pair as proposed above. The concept of a contact pair also introduces axial symmetry which can explain the variation of linewidth with hyperfine component and the variation of the g-value with temperature.

Catterall (33) has observed complicated EPR patterns in rapidly frozen metal-HMPA solutions which require the presence of a number of different monomeric species each with characteristic hyperfine splittings. This might imply the presence of a distribution of monomer types in the liquid solution as well, but it could also result from the presence of a variety of trapping sites in the solid.

DIAMAGNETIC ELECTRON-CATION CLUSTERS

Solvated electrons, ion-pairs and monomers are all paramagnetic species with an electron spin of 1/2. As the concentration of metal solutions is increased, spin-pairing occurs and diamagnetic states become very important. For example, at a concentration of 0.01 molar K in NH_3 at -33° half the spins are paired (42). Spin-pairing becomes even more predominant

at lower temperatures. Direct calorimetric measurements (43) with sodium solutions in NH_3 also indicate exothermic spin-pairing. In amines and ethers spin-pairing can occur through the formation of alkali metal anions as described later. There are few data which bear on the question of whether diamagnetic species other than alkali metal anions are also formed in amines and ethers. However, the generally weak intensity of the EPR singlet, *even in solutions which show a large infrared optical absorption of e_s^-* (31) indicates that spin-pairing is also favored in these solvents in addition to that which occurs through the formation of "genuine" anions. Therefore, what we say about spin-pairing in metal-ammonia solutions probably also applies to other solvents although this has not been verified by quantitative experiments.

Diamagnetic species in metal-ammonia solutions

One of the most puzzling features (44) of metal solutions in ammonia is the slight effect which spin-pairing has on solution properties other than the magnetic behavior. The optical spectrum shifts only slightly and, although the intensity of the shifted band correlates well with the extent of spin-pairing (45-47), the spectrum is independent of the metal used and its shape remains nearly independent of concentration. This suggests that the spin-pairing process perturbs the solvated electron spectrum but does not fundamentally change the nature of the absorption. Similarly, the large volume expansion which accompanies solvated electron formation is not perturbed by the spin-pairing process. Electrochemical properties (44) are also relatively insensitive to spin-pairing. Yet pairing <u>does</u> occur and the narrowness of the EPR abosrption shows that dissociation of the paired state is relatively slow ($\tau \gtrsim 10^{-6}$ sec) (44).

The nature of the electron-electron interaction is not well understood at this time. Calculations of the stability of two electrons in a single polarization center (the dielectron) (48-51) indicate that it might be marginally stable compared with two separate solvated electrons although the latest calculation (48) indicates that it is probably not stable. A recent calculation (52) of the interaction energy of a pair of solvated electrons as a function of their separation distance indicates that the lowest singlet state is energetically more stable than the lowest triplet state by the order of kT at distances as large as 10.5 Å. This view of the interaction permits the formation of a stable pair of solvated electrons without destroying their essential characteristics. Presumably, the presence of a cation would further stabilize the spin-paired state. Because the pairing interaction in ammonia seems to introduce relatively small perturbations in the properties of the system rather than the large changes expected for a radically different species, the simplest model of the spin-paired species is that of a triple-ion, stabilized not only by the usual electrostatic forces, but also by substantial electron-electron interactions. In a good solvent such as ammonia, we would expect this to be a solvent-shared triple-ion. Note that it is not necessary to restrict the geometry to a linear collection of three ions. Indeed, electron-electron interactions might tend to form a bent aggregate.

It is intriguing to speculate about the nature of triple-ions in poorer solvents. Perhaps one could form contact triple-ions. There is no evidence on this point, however. Rather, a new species, the spherically symmetric alkali metal anion, becomes the predominant species in metal solutions in "poor" solvents.

ALKALI METAL ANIONS

Following the suggestion in 1969 by Matalon, Golden and Ottolenghi (53) that the metal-dependent optical band in metal-amine and metal-ether solutions originates from an alkali metal anion, a number of experiments verified that the stoichiometry of the species responsible for this band is indeed M⁻. (See ref. 21 for a summary of this evidence.) It should be noted that a major stumbling-block to progress in the identification of the species present was removed by Hurley, Tuttle and Golden (54) in 1968 when they showed that earlier confusion about the presence or absence of certain optical bands was caused by sodium contamination from the borosilicate glass used for solution preparation.

Although the presence of "genuine" alkali metal anions with two electrons in the outer <u>s</u> orbital was suggested (53) because of the metal, solvent and temperature dependence of the optical bands it was not possible on the basis of optical, electrochemical and magnetic data to rule out other candidates such as triple-ions or ion-pairs between the cation and the dielectron. For example comparison of the solvent and temperature dependence of the optical bands with the charge-transfer-to-solvent (c.t.s.) transitions of I⁻ and the predicted effect of anion radius were used (53) as evidence for the presence of spherically symmetric anions. However, the band of e_s^- behaves in a similar fashion to the c.t.s. transitions of halide ions and it is now known (36) that the position of the optical absorption of the electron-cation pair can depend strongly upon the metal. Nevertheless, the route to the isolation of well-defined salts of the alkali metal anions began with the suggestions made by Matalon, Golden and Ottolenghi (53). The term "alkali metal anion" will refer in the balance of this paper to the spherically symmetric species with two-

electrons in the outer $\underline{s}$ orbital.

Proof of the existence of alkali metal anions
In 1974 we isolated (17,18) and characterized a crystalline salt of the sodium anion. The salt contains no solvent and consists of alternate layers of cryptated sodium cations and sodium anions in a hexagonal closest-packing arrangement. Polycrystalline films of similar appearance have been prepared (21) with all of the other alkali metals except lithium. In some cases, crown ethers can be used instead of cryptands, but stability of the solid requires the presence of solvent vapor. This is presumably because axial solvation of the cations is required when crown ethers are used. The preparation of solid salts of M⁻ proves that this ion can exist without solvent so that, at least in the solid, triple-ions are ruled out.

Also in 1974 we determined (3) the ^{23}Na nmr spectra of Na⁻ in two solvents. This has now been extended (2) to other solvents, to solutions containing crown ethers, and to Rb⁻ and Cs⁻. The absence of a solvent paramagnetic shift (compared with the gaseous anion) shows that the solvent cannot interact strongly with the $\underline{p}$ electrons of the alkali metal as it does in the case of solvated cations. In addition, the narrowness of the lines suggests that M⁻ is large and spherically symmetric. These results leave no doubt that M⁻ in solution in these solvents is indeed the alkali metal anion.

Thermodynamic arguments can be made (21) which rationalize the stability of salts of the alkali anions. Particularly intriguing is the prediction from such calculations that salts of Li⁻ should also be stable. This anion has not yet been found, either in solution or in a solid salt.

EFFECT OF SOLVENT AND METAL ON THE STABILITY OF VARIOUS SPECIES

The distribution of species in a metal solution will depend upon the balance among various interactions as follows:

1. The cation solvation free energy
Solvents of higher donicity tend to favor solvated cations. The solvation energy of the cation decreases from Li⁺ to Cs⁺. A higher dielectric constant favors cation solvation. Replacement of the first solvation layer by a cryptand or crown ether complexing agent can stabilize the cation tremendously, especially in "poor" solvents.

2. Solvation free energy of the electron
The same factors which favor cation solvation also tend to favor electron solvation. Another factor is the so-called V_0 term which represents the energy of the electron in the quasi-free state in the liquid compared with its energy in vacuo (55,56).

3. Coulombic interaction between ions.
This well-known interaction increases as the dielectric constant decreases. Formation of ion-pairs, particularly contact pairs also depends upon the short-range ion-solvent interactions.

4. Electron-affinity of M⁺
This is, of course, just the ionization potential of the atom and it decreases regularly from Li to Cs. Presumably it is this tendency to capture an electron which increases the contact density of the electron at the metal nucleus in the monomer species when cation and electron solvation energies decrease.

5. Electron-affinity of M.
It is well-known that the electron affinities of the gaseous alkali atoms are positive; that is, electron-attachment is favored. This plays a major role in the stabilization of alkali metal anions. The electron affinity decreases slightly from Li to Cs.

6. Solvation free energy of M⁻
Anionic solvation energies depend upon some of the same factors, dielectric constant, polarity of the solvent molecules, etc. which affect cation solvation. However,the high polarizability expected for these large anions will also play a role and polarizable solvents should be favored. Again ion size is important and we expect the solvation energy of M⁻ to decrease from Li⁻ to Cs⁻.

7. Spin-pairing interaction
The influence of the solvent and metal on this process are unknown. One might expect that long-range screening of electron-electron repulsions would be favored by solvents of high dielectric constant.

It is evident from the profusion of species found in metal solutions that these interactions are in a rather delicate balance. In a good donor solvent such as ammonia, the solvation energies are large enough that the identifiable species are the solvated cation and the solvated electron. Even the spin-pairing interaction does not seem to destroy these basic units. Of course, as for a normal electrolyte, ion-pairing will occur. Because of the large size and relatively weak solvation of e_s^- we expect easy formation of solvent-shared ion pairs. Of the species shown schematically in Fig. 3, only 1, 2, 3, and 5 are expected in ammonia.
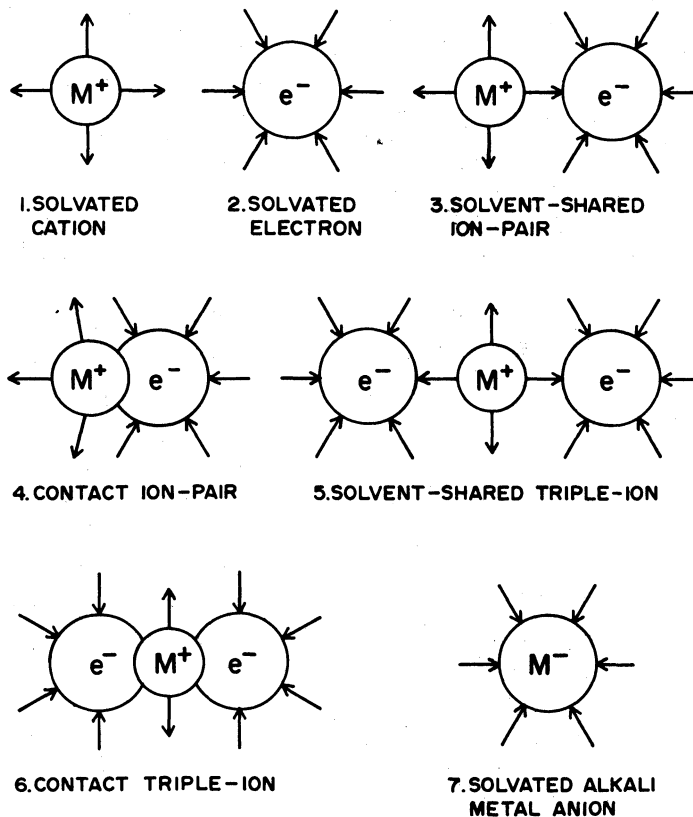

Figure 3.   Schematic representation of seven
             possible species in metal solutions.

The relative concentration of alkali metal anions compared with solvated electrons increases as the solvent donicity and dielectric constant decrease. Within a given solvent, the order of relative importance of M^- is Na >> K > Rb >>Cs >> Li. That is, in spite of the larger solvation energy of Na^+ compared with the heavier alkali metal cations, Na^- is by far the most stable with respect to the dissociation reaction

$$Na^- \; \underset{\leftarrow}{\rightarrow} \; Na^+ + 2e_s^- \tag{5}$$

This results from a combination of interactions 4, 5, and 6 which must be large enough to overcome the greater solvation energy of Na^+. Evidently, for the case of lithium, the favorable interactions 4, 5, and 6 cannot overcome the very important cation solvation free energy.

A schematic representation of the various species described in this paper is shown in Fig. 3. Although we have no evidence for the existence of the contact triple-ion, it is included for completeness, and seems to be a plausible species for some solvents.

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