PROPERTIES OF SOLVATED ELECTRONS AND ASSOCIATED SPECIES
IN METAL SOLUTIONS AND KINETICS OF
ELECTRON- AND PROTON-TRANSFER REACTIONS

Progress Report

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ABSTRACT

The optical absorption spectra of thin films of $\text{Na}^+\text{C}\cdot\text{Na}^-(\text{s})$, $\text{K}^+\text{C}\cdot\text{K}^-(\text{s})$ and (presumably) $\text{K}^+\text{C}\cdot\text{Na}^-(\text{s})$ and $\text{K}^+\text{C}\cdot\text{e}^-(\text{s})$ have been measured. (C refers to 2,2,2 cryptand.) The major absorption bands of Na^+ , K^+ and e^- in the solids occur at 650, 850 and 1300 nm respectively. In the case of the Na^+ salt, two additional absorptions occur at higher energies. Preliminary static susceptibility measurements show that $\text{Na}^+\text{C}\cdot\text{Na}^-$ is diamagnetic, whereas $\text{K}^+\text{C}\cdot\text{e}^-$ is strongly paramagnetic, even down to 1.6°K. Extensive measurements of the thermodynamics and kinetics of complexation of Cs^+ by various crowns and cryptands in a number of solvents have been made by Cs-133 n.m.r. spectroscopy. The results show the formation of both 1-to-1 and 2-to-1 crown complexes and two types of 1-to-1 cryptate complexes, one centro-symmetric (inclusive) and one apparently an exterior (exclusive) complex. Solution studies of alkali metal anions and solvated electrons by n.m.r. and optical spectroscopy have been continued.

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TECHNICAL PROGRESS REPORT

Properties of Solvated Electrons and Associated Species in Metal Solutions
and Kinetics of Electron- and Proton-Transfer Reactions

U. S. Energy Research and Development Administration

Contract No. E(11-1)958

Sept. 16, 1975 through Sept. 15, 1976

Personnel and Publications

The research described in this report was carried out with the assistance of four graduate students (C. Andrews, M. DaGue, E. Mei, and M. Yemen). C. Andrews completed his M.S. degree requirements during this period. E. Mei has completed the experimental work for the Ph.D. degree and is currently writing the dissertation. The Principal Investigator (Professor J. L. Dye) spent full time during the academic year on this project as a Fulbright Hays Research Scholar and Guggenheim Fellow in the laboratory of Professor J. M. Lehn in Strasbourg, France and full time for 10 weeks during the summer at Michigan State University.

Reprints of five research papers¹⁻⁵ which have appeared in print since September 1975 are included in this report. Two papers have been accepted for publication and will appear shortly. These papers deal with the following topics:

- 1) "Cation-Electron Interactions in Metal Solutions - From Solvated Electrons to Alkali Metal Anions", J. L. Dye, accepted for publication in Pure and Applied Chemistry. This paper was presented as a Plenary Lecture at the Conference on Non-Aqueous Solutions in Leeds, England, July 5-9, 1976.

2) "Alkali Metal Anions - An Unusual Oxidation State", J. L. Dye, accepted for publication in J. Chem. Education.

One paper has been finished and will be submitted to the Journal of Physical Chemistry. This is: "Sodium-23 Nuclear Magnetic Resonance Study of Sodium Ion-Sodium Cryptate Exchange Rates in Various Solvents", J. M. Ceraso, P. B. Smith, S. Landers, and J. L. Dye.

An article for Scientific American entitled "Alkali Metal Anions" is being prepared. Three papers which deal with the Cs-133 nmr spectra of crown and cryptate complexes are in the initial stages of preparation with all experimental work completed.

The papers which comprised the program for Colloque Weyl IV - "Electrons in Fluids, the Nature of Metal Ammonia Solutions", which was held at Michigan State University June 30-July 3, 1975, were published in the Journal of Physical Chemistry, December 18 issue, 1975. The Principal Investigator served as the Chairman of this colloquium, and as coordinator of the publication of papers and discussion.

Alkali Metal Anions and Solvated Electrons in Solution

The use of crown and cryptand complexing agents to enhance metal solubility in a number of solvents which we pioneered⁶ in 1970 has proven to be a very general technique.⁷⁻¹³ It is possible to obtain fairly concentrated solutions ($> 0.2M$) in many cases. In general, one can expect to get both M^- and e^-_{solv} in addition to M^+C (C = complexing agent for the cations) in the solutions. However, the ratio $[M^-]/[e^-_{solv}]$ depends strongly upon the solvent, the metal, and the concentration of complexing agent. With sodium in amines and ethers, there is a strong tendency to form Na^- in preference to e^-_{solv} . By contact with excess metal, even in as good a solvent as methylamine (MA), the $[Na^-]/[e^-_{solv}]$ ratio can be made large enough that

the solutions contain essentially only Na^+C and Na^- . Indeed, in a poorer solvent such as tetrahydrofuran (THF), even the addition of a large excess of C_{222} (2,2,2 cryptand) will not give detectable amounts of e_{solv}^- .¹⁴ That is, the equilibrium

lies far to the left in THF. With K, Rb and Cs, the anion will form but the $[\text{M}^-]/[\text{e}_{\text{solv}}^-]$ ratio is not as large and with a suitable complexing agent, M^- can be converted to e_{solv}^- by the addition of C even in as poor a solvent as THF. In MA for the metals K, Rb, and Cs, some e_{solv}^- is always present even with a deficiency of C. In the case of lithium, there is no evidence for Li^- with or without complexing agents. These conclusions are based largely upon the optical spectra of solutions which show distinct absorption bands of M^- and e_{solv}^- .

We have prepared solutions of all of the alkali metals in a number of solvents by using crowns and cryptands. For example, lithium is only slightly soluble in ethylamine but the addition of C_{211} (cavity size optimum for Li^+) rapidly dissolves the solid metal to give at least 0.05 molar solutions. In many cases, the rate of solution is slow even in the presence of the cryptand. For example, K(s) dissolves only slowly in THF even in the presence of C_{222} . In order to enhance the rate of solubilization, we have found it convenient to first dissolve the metal in ammonia, evaporate the solvent to form finely divided metal and then add THF and the complexing agent. By this procedure we have been able to dissolve barium in methylamine and in ethylenediamine in the presence of C_{222} . Without a complexing agent, barium is insoluble in these solvents.

Solutions of sodium with C_{222} or with 18-crown-6 in amines and ethers show good stabilities. Apparently, Na^- does not readily react with either the solvent or the complexing agent. However, in all other cases, the stability is much lower. This has caused many problems and delays in studying solutions and solid alkali metal anion salts prepared from these solutions. By way of illustration, we have prepared solutions of $K^+C_{222} \cdot K^-$ in isopropylamine in order to grow crystals. In two out of four attempts, the solution decomposed before crystals could be grown even though the temperature was kept below $-15^\circ C$. At dry-ice temperatures, however, the solutions are stable for long periods of time.

NMR Spectra of Alkali Metal Anions and Complexed Cations

The ^{23}Na , ^{87}Rb , and ^{133}Cs nmr spectra of alkali metal anions^{3,12} provided the first proof that the anions exist in solution as "genuine" anions with two electrons in the outer s orbital. We have continued studies of the nmr spectra of Na^- in the presence of Na^+C in which C is 18-crown-6. One goal of this study was to determine the mechanism of exchange of Na^- and Na^+C . At low temperatures, separate lines are seen for these two species in the ^{23}Na nmr spectra. However, the lines coalesce at -15° to $-5^\circ C$ because of exchange. This is followed by exchange narrowing at higher temperatures. The mechanism of exchange has not been determined but it is clear that the simple exchange process

cannot explain the variation of the rate of exchange with concentration.

If we could be certain that the atom or radical, $Na^\bullet$, is not actively

participating in the exchange, then the data could be analyzed by using the two-site Bloch equations even though the minor species Na^+ may (and probably does) participate in the exchange. If however, the minor species is paramagnetic, then it would be necessary to consider the third site, even if it is only a minor species. With the assumption that sodium atoms or monomers are not involved, we conclude that Na^+ participates in the exchange via

and

The exchange data also suggest the presence of the associative pathway

but it is likely that this pathway may involve the paramagnetic species $\text{Na}^+ \cdot \text{e}^-$ ($\text{Na}^\bullet$). It will require additional studies of the effect of added 18-crown-6 on the exchange rate to determine the mechanism and the rate constants.

In collaboration with Professor A. I. Popov of this Department, we have carried out extensive studies of the complexation of Cs^+ by a number of crown and cryptand complexing agents.⁵ These experiments have yielded a wealth of information about the thermodynamics and kinetics of the complexation reaction. The results will form the basis for at least three and possibly four full papers and are too numerous to describe in detail in this report. However, the major findings are as follows:

1) The complexation of Cs^+ by 18-crown-6 in pyridine was found to proceed in two steps. A strong 1-1 complex ($K > 10^5$) forms whenever up to equimolar crown and Cs^+ are mixed. This is followed by a weaker 2-1 "sandwich" complex at higher crown concentrations. By a complete temperature-dependent nmr study of the complexation, the rate of dissociation of the 1-1 complex was measured (activation energy = 8 kcal mole⁻¹) and the thermodynamic parameters for the reaction

were also determined ($\Delta H = -6$ kcal mole⁻¹, $\Delta S = -11$ cal mole⁻¹ deg⁻¹).

2) Stability constants for the formation of 1-to-1 complexes between Cs^+ and four [2]-cryptands (C_{222} , $\text{C}_{222\text{B}}$, C_{221} , C_{211}) were measured in six solvents. (The subscripts represent the number of ether oxygens in each strand; B refers to a benzo group in one of the strands.) The solvents used were: pyridine (PY), acetone (AC), propylene carbonate (PC), N,N-dimethylformamide (DMF), acetonitrile (MeCN) and dimethylsulfoxide (DMSO). The results show that the solvent plays an important role in determining the complexation constant. For example, the values of $\log(K_f)$ for Cs^+ with C_{222} at 25°C decrease in the order: PY(> 4.6), MeCN(4.6), AC(4.0), PC(4.0), DMF(2.2), DMSO(1.4). In addition the role of the cavity size is clearly demonstrated in this study.

3) The thermodynamics and kinetics of exchange of free Cs^+ with Cs^+ complexed by 18-crown-6 (18C6), Dibenzo-18-C-6 (DBC), and Dicyclohexyl-18C6 (DCC) have been studied in six solvents (see part 2 above). "Sandwich" complexes, Cs^+C_2 , as well as 1-to-1 complexes, Cs^+C , are clearly formed in PC, PY, and AC for all of the crown compounds. In DMF, DMSO,

and MeCN, the chemical shifts also show formation of 1-to-1 and 2-to-1 complexes with 18C-6 but we can only be sure that a 1-to-1 complex forms in these solvents with DBC and DCC. The chemical shift data suggest also that 2-to-1 complexes are formed but the evidence is not conclusive. Combining these results with those in (2) above shows the marked effect of ligand on the complexation constant to form the 1-to-1 complex. For example, in DMF as solvent at 25°C the values of $\log (K_f)$ decrease in the order: 18C6(4.0), DCC(3.4), C_{222} (2.2), C_{222B} (1.7), DBC(1.5). Similar trends are found for other solvents and complexing agents although there are exceptions. In general, it appears that the crown complexes can more easily accommodate the large Cs^+ ion than can the [2]-cryptands which have too small a cavity size. In addition, in many cases, the crowns can form "sandwich" 2-to-1 complexes.

4) Extensive studies of Cs-133 nmr spectra in the presence of the [2]-cryptand, C_{222} have been made at various temperatures in six solvents (see part 2 above). Only 1-to-1 complexes are formed. The dependence of the limiting chemical shift of the complex upon solvent and temperature gives strong evidence for the existence of two types of 1-to-1 complexes. The diameter of Cs^+ ($3.3\text{\AA}$) is larger than the estimated diameter of the cavity ($2.8\text{\AA}$) in C_{222} . However, X-ray studies show that this complex is centrosymmetric in the crystalline state. At low temperatures in solution (-60°C and below) the Cs-133 nmr signal in the Cs^+C complex is separated from that due to Cs^+ because of slow exchange. The chemical shift of Cs^+C at these temperatures is independent of solvent and that due to Cs^+ occurs at the same shift as for simple salts. However, the limiting shift of Cs^+C depends strongly upon the solvent at higher temperatures. The results can be

analyzed on the basis of an equilibrium between inclusive and exclusive complexes. In the former, the Cs^+ ion is located centrally within the cavity but is sterically unfavorable so that an equilibrium concentration of outside, exclusive complexes exists. Because the Cs^+ ion is still accessible to the solvent in the exclusive complex, its chemical shift depends upon the solvent, just as for the solvated ion and for 1-to-1 crown complexes of Cs^+ . Lineshape analysis yields information about exchange rates. The variation of the chemical shift with concentration of C_{222} and with temperature gives the equilibrium constant for complex formation and an estimate of the thermodynamic parameters for the inclusive $\rightleftharpoons$ exclusive equilibrium.

Solid Compounds which Contain Alkali Metal Anions or Electrons

The isolation and identification of a salt which contains the sodium anion^{10,11} together with the cryptated cation presented us with the opportunity to examine an entire family of new compounds. It is now clear both from the thermodynamics involved² and from experiment that the formation of alkali metal anions is common to all of the alkali metal family except lithium. All of the systems which we have examined to date contain as the counter-ion an alkali metal cation complexed by either a crown or a cryptand molecule. Therefore, the salts could be looked upon formally as containing M^0 , the metal in a zero oxidation state. However, the properties are clearly those of a salt $\text{M}^+\text{C}\cdot\text{M}^-$. The function of the cation is to provide charge neutralization by a non-reducible species. In principle, any non-reducible cation should suffice for this purpose. The choice of cation is not simple, however, because M^- is such a powerful reducing agent that most cations are unsuitable. In addition to the complexed alkali cations, carefully purified tetra-alkyl ammonium ions should be usable. However, the ease of cleavage of the C-N bond makes the problem of their use non-trivial.

In addition to a more detailed study of the properties of $\text{Na}^+\text{C}_{222}\cdot\text{Na}^-(\text{s})$, we have prepared powdered samples of other salts by rapid evaporation of solutions which contain K^- , Rb^- , and Cs^- . So far it has only been possible to grow crystals^{10,11} of $\text{Na}^+\text{C}_{222}\cdot\text{Na}^-$ (which forms thin hexagonal plates) and, within the past year, crystals which apparently contain $\text{K}^+\text{C}_{222}\cdot\text{K}^-$ (these grow as thin needles). The stability of the latter solid is very poor compared with the sodium compound. While $\text{Na}^+\text{C}_{222}\cdot\text{Na}^-(\text{s})$ is even stable enough to allow rapid measurement of its decomposition temperature (83°C) (at which molten C_{222} and solid metallic sodium are formed), crystals of $\text{K}^+\text{C}_{222}\cdot\text{K}^-$ decompose irreversibly within a few minutes above about -20°C even in a good vacuum system. This, and comparable experience with films produced by solutions of the other alkali metals has hampered studies of these reactive solids. It is necessary not only to rigorously exclude air and moisture and to clean the glassware scrupulously but also to keep the temperature low at all times. It has been reported¹⁴ that solution stability in THF is markedly improved by first following our cleaning procedures, then flaming all glassware under high-vacuum, and pre-rinsing the glassware with a metal solution. We may be forced to adopt this procedure which requires break-seals to be used in place of stopcocks.

During the past few months, we have been able to prepare thin deposits of $\text{Na}^+\text{C}\cdot\text{Na}^-(\text{s})$, $\text{K}^+\text{C}\cdot\text{K}^-(\text{s})$, and $\text{K}^+\text{C}\cdot\text{Na}^-(\text{s})$ on the walls of quartz absorption cells. These microcrystalline films are thin enough to permit us to measure the absorption spectra. The results are remarkably similar to the solution spectra of the corresponding alkali metal anions except that the bands are narrower and the spectrum of $\text{Na}^+\text{C}\cdot\text{Na}^-(\text{s})$ shows additional peaks. The principal peak at 655 nm compares with the single peak in ethers

and amines at 650-720 nm (depending upon the solvent and temperature). The width of the band in the solid is less than half that in liquid solutions and shows a pronounced shoulder at 520 nm and a small but reproducible peak at 400 nm. The variation of peak position with temperature is 3-5 times less pronounced than in solution. The simplest interpretation is an excitation from the ground state of Na^- to at least three excited states. Since the powder conductivity indicates a band-gap of 2.5 to 3.0 e.v., a direct transition from the ground state to the conduction band may also be present.

The solid state spectrum provides an explanation for the remarkably metal-like appearance of the crystals. The absorption at 650 nm is very strong but drops rather precipitously at shorter wavelengths to give characteristics in the visible region which mirror fairly well the short-wavelength plasma edge characteristic of metals. Under such circumstances the crystals can have a distinctly metallic appearance¹⁵ without the high conductivity of metals.

We have recently measured (in collaboration with Professor Robert of the University of Strasbourg, France) the magnetic susceptibility of $\text{Na}^+\text{C}\cdot\text{Na}^-(\text{s})$ from 4°K to room temperature. Only a temperature-independent diamagnetism of "normal" magnitude was observed, in accord with our expectation that the two 3s electrons in Na^- are spin-paired.

In summary, the unusual compound, $\text{Na}^+\text{C}\cdot\text{Na}^-(\text{s})$ has all of the properties expected of an ionic solid with an anion which binds the electrons weakly enough to yield an absorption band in the red region of the spectrum. The conduction band lies at low enough energies that the salt is a semi-conductor with a band-gap of 2.5-3.0 e.v. Further studies of the optical spectrum,

photo-emission spectrum and photo-conductivity should permit an even more detailed picture of the nature of Na^- .

As indicated above, absorption spectra have also been measured for the solids $\text{K}^+\text{C}\cdot\text{Na}^-(\text{s})$ and $\text{K}^+\text{C}\cdot\text{K}^-(\text{s})$. The former shows a narrow band with a peak at 660 nm but in the one sample examined so far, the shoulder and peak observed with $\text{Na}^+\text{C}\cdot\text{Na}^-(\text{s})$ are absent. The solid which contains K^- has an absorption band at about 850 nm with no clean-cut peaks at shorter wavelengths. Two samples have given the same results but the rate of decomposition was so high that the experiments must be repeated. Because of the way in which the film are made (solvent evaporation) they tend to be heterogeneous. This gives broader peaks than would be the case for a homogeneous film.

We have been trying for some time to make "electride" salts by evaporation of a solution which contains M^+C and e_{solv}^- . Such solutions are prepared in a solvent such as methylamine by using equimolar amounts of metal and the cryptand C_{222} . Because of the high stability of Na^- compared with K^- , Rb^- and Cs^- , the conversion of Na^- to Na^+C and e_{solv}^- by the addition of C_{222} is generally not complete. Therefore to prepare "electride" salts, metals such as K, Li or Ba must be used. When the appropriate solutions are evaporated at low temperatures, dark blue solids are produced which are extremely unstable above about -40°C . We have made preliminary measurements on the potassium system which is presumably $\text{K}^+\text{C}_{222}\cdot\text{e}^-$ with one trapped electron per positive center. The optical spectrum (one sample) shows a broad absorption band at 1300 nm. The susceptibility from 1.6°K to 4°K (one sample) shows strong paramagnetism approximately as expected for one unpaired spin per electron. If the spectrum and susceptibility prove to be correct,

this would suggest that the electrons are localized rather than metallic. The absorption band at 1300 nm, if verified, would correspond to a trapped electron rather than, for example, a radical produced by decomposition of the cryptand.

It appears that it might be possible to prepare a full complement of solid salts with various reactive anions from a simple trapped electron to various alkali anions. It is clear that the study of the sodium salt, $\text{Na}^+ \text{C}_{222} \cdot \text{Na}^-(\text{s})$ is an order of magnitude easier than that of the other compounds. However, it would be very desirable to determine crystal structures, conductivities, and other properties of the other members of this new class of compounds.

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