Solvation of Alkali Metal Ions

Solvent molecules always surround a metal ion in solution. This is referred to as solvation. If the solvent is water, then it is called hydration. The alkali metal ions are extensively hydrated. A small ion has high charge density and attracts the solvent molecules strongly, resulting in extensive hydration. The energy evolved during hydration is called hydration energy. Li^+ being smallest is most heavily hydrated and has highest hydration energy. The extent of hydration decreases down the group. Hydration directly affects ionic mobility. Li^+, the smallest ion is expected to be highly mobile, but in fact the reverse is time. This is because the hydrated radius of Li^+ is the largest and is least mobile and least conducting in solution.

The decrease in hydration from Li^+ to Cs^+ is revealed by the fact that most crystalline salts of lithium are hydrated. Most salts of alkali metals are soluble in water. For any substance to dissolve the hydration energy must exceed lattice energy.

Solution of Metals in Liquid Ammonia

The alkali metals dissolve in liquid ammonia and other amines to give blue solution believed to contain solvated electrons.

$$Na + x\,NH_3 \longrightarrow Na^+ + e\,(NH_3)^-_x$$

Due to the presence of these solvated electrons, dilute solution of alkali metals conduct electricity far better than completely dissociated electrolytes. As the concentration of the metal increases the conductivity decreases initially and then increases. At sufficiently high concentrations the solution develops a bronze metallic luster and the conductivity approaches the value of a molten metal. The dilute solutions are paramagnetic but the paramagnetism decreases with increase in concentration. The blue colour is attributed to the solvated electrons. These solutions are excellent reducing agents.

$$RC \equiv CR + e^- \longrightarrow RC \equiv C^- + \tfrac{1}{2} H_2$$

$$S + 2e^- \longrightarrow S^{2-}$$

The solutions undergo slow decomposition to give amides.

$$M + NH_3 \longrightarrow MNH_2 + \tfrac{1}{2} H_2$$

The Group 2 metals and some lanthanides also dissolve in liquid ammonia. ✓

Alkyls and Aryls

Lithium shows a stronger tendency to covalency than the other alkali metals. It forms covalent alkyls and aryls.. These compounds are frequently tetrameric or hexameric and are made by reaction of lithium with the alkyl / aryl halide.

$$RCl + Li \longrightarrow Li\,R + LiCl.$$

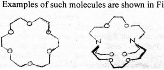
The methyl derivative is tetrameric [$(LiCH_3)_4$], covalent and soluble in organic solvents. The four Li atoms occupy the corners of a tetrahedron with the methyl groups above the face of the tetrahedron. The classical theories of bonding cannot explain the formation of these compounds, which involve multi-centred bonds. These compounds are starting materials for synthesis of organometallic and organic compounds. The alkyls of Na, K, Rb and Cs are ionic.

Complexation Behaviour of Alkali Metals ✓

The alkali metals generally have weak complexing ability. This is because the factors that favour complexation viz, small size, high nuclear charge and availability of empty orbitals of low energy are lacking in alkali metals.

Aqua complexes like $[Li(H_2O)_4]^+$, $[Cs(H_2O)_6]^+$ are known. A number of chelates are known e.g. those with salicylaldehyde and acetyl acetone.

An important development in the field of alkali metal chemistry is the discovery of complexes with cyclic ethers and cryptands (cryptates) i.e. with macro cyclic molecules containing nitrogen and oxygen. The cyclic ethers are called crown ethers; they have varying sizes of rings and form complexes with alkali metal ions by donating electron density through the oxygen atoms. Examples of such molecules are shown in Fig. 1.



The cryptates are more selective and stronger complexing agents than the crown ethers, with eight donor atoms (nitrogen and oxygen) surrounding the metal ion completely. The ability of crown ether or a cryptands to trap a metal ion depends on the size of both the cavity and the metal ion.

The chemistry of alkali metals is almost exclusively of the M^+ ion, but examples of anions of the type M^- (alkalide) have been reported. The first such ion to be reported was Na^- formed by cooling a solution of Na in ethylamine with 2, 2, 2 – crypt. A crystalline compound, $[Na(2,2,2 - crypt)]^+ Na^-$ was obtained. The K^- ion was made in a similar way but is less stable. Very recently (2002), a compound "inverse sodium hydride" has been reported containing Na^- and H^+.