ALKALI METALS ORGANIC SOLUTIONS – ^{39}K AND ^{23}Na NMR STUDY

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Abstract - Blue potassium and potassium/sodium solutions in tetrahydrofuran or tetraglyme containing various complexing agents were investigated by means of ^{39}K and ^{23}Na NMR. The ionic composition of the systems was determined. Relaxation behaviour of potassium solutions was presented and interpreted. A great influence of complexing agent on the magnitude of ionic interactions was revealed. The utility of $\text{Me}^+(\text{crown ether})$, Me^- complexes as chemical reagents and homogeneous catalysts was demonstrated.

1.- Introduction.

Over 130 years ago Weyl demonstrated the solubility of alkali metals in liquid ammonia¹. Almost 100 years later Ottolenghi² and Dye³ succeeded to solubilize alkali metals in organic solvents like amines and ethers. Due to crown ethers, cryptands and other synthetic and natural ligands abilities⁴⁻⁶ to complex alkali metal cation concentrated alkali metal solutions can be obtained. Nowadays so called organic alkali metal solutions are still a subject of extensive research because of their interesting properties and very important potential applications. Lacoste and Schue⁷ observed that solvated electrons are formed initially when potassium is dissolved in THF containing a crown ether. Our work rationalized their findings.¹⁰ It has been confirmed that electrons along with complexed metal cations are the initial products of potassium solubilization in THF containing 18C6. The experimental results suggest that the process of metal dissolution is facilitated by the crown ether adsorption on the metal surface and process of metal dissolution can be roughly described by the following equations:

Indeed the removal of K^+ from the metal lattice is expected to be a relatively slow process involving a potential energy barrier which could be reduced by adsorption of the crown ether and formation of soluble $\text{K}^+(\text{crown ether})$ complex. Then solvated electrons yield diamagnetic K^- anions (Eq.2). The process is strongly dependent on temperature, contact time of a ligand with metal surface, nature of a ligand, etc..

The aim of our work was to characterize potassium and mixed potassium/sodium solutions in various solvents and etheral ligands by means of ^{39}K and ^{23}Na NMR spectroscopy. Some new applications of well defined solutions have been proposed.

2.- Experimental.

The potassium and potassium/sodium solutions containing 18-crown-6, 15-crown-5, cryptand[2.2.2] or tetraglyme as the potassium cation complexing agent were prepared from potassium mirror¹⁰ or K/Na alloy¹¹. The total concentration of metallic ions was 0.2 M and the concentration of electrons under chosen conditions of preparations was negligibly small.

The measurements were carried out on a Varian VXR-300 spectrometer at the ^{39}K resonance frequency of 14 MHz and the ^{23}Na resonance frequency of 79 MHz in broad temperature ranges (173 - 313 K).

3.- Results and Discussion.

Potassium solutions

Figure 1 displays the representative ^{39}K NMR spectra of metallic potassium solutions in THF containing 18C6, C222 and 15C5 at 223 K.

Fig.1.- ^{39}K NMR spectra of potassium solutions in THF containing 18C6, C222 and 15C5 at 223 K.

All the spectra exhibit two resonance lines: a narrow line identified as a signal due to potassium anion and a broader one arising from complexed potassium cation. The widths of the lines are influenced by quadrupolar and exchange broadening effects^{7,12-16}. The large difference in the widths of the lines attributed to K^+ and K^- is probably due to the higher spherical symmetry of the electric field at the nucleus in the case of K^- and/or to an increased rotational correlation time characterizing the fluctuations of the K^- environment. In the entire temperature range of study the linewidth due to K^+ decreases in the order: 18C6 > C222 > 15C5 which can be related to an increasing ability of K^+ complexing agent to separate K^+ from interactions with its counterion¹⁴⁻¹⁶. In the case of 15C5 a relatively narrow line is observed also for K^+ in contrast to the other systems under study which confirms reduced availability for interionic interactions.

The results of the relaxation measurements of K^- and K^+ for $K^+(15C5)_2, K^-$ system in THF are presented in Figure 2.

Fig.2.- Temperature dependence of T_1 and T_2 for K^- and K^+ in potassium solution in 1 THF containing 15C5.

Similar relaxation behaviours of K^- were also observed for other ligands^{14,15}. For all the solutions quadrupolar interactions appear to have an overwhelming influence on the relaxation process over the whole temperature range. The correlation time seems to determine the relaxation mechanism at low temperatures, whereas variations in the magnitude and direction of the electric field gradients can be assumed to dominate at higher temperatures. Any chemical exchange process is believed to modify the relaxation behaviour. The exact nature of exchange processes in alkali metal solutions is not known. A simple cation-anion two-site exchange would require that the signals due to K^+ and K^- shift towards each other and broaden by the same amount with temperature. In contrast to the systems containing 18C6¹⁴ or C222¹⁵ for the solution with 15C5 a tendency of the K^+ and K^- resonance lines to coalesce along with a similar broadening of both signals was observed above 250 K¹⁶. It suggests that in this case both types of ions are simultaneously involved in the exchange processes at higher temperatures.

A very similar spectrum to those of the potassium solutions in THF was obtained for the potassium solution in tetraglyme containing 18C6 (Fig.3A)¹⁷. It is interesting to note that even without the crown ether it was possible to

dissolve metallic potassium in tetraglyme, however a maximum K^- concentration of 0.01 M could only be achieved (Fig.3B)¹⁷.

Fig.3.- ^{39}K NMR spectra of potassium solutions in (A) tetraglyme containing 18C6 and (B) tetraglyme without the crown ether.

This indicates that potassium cations can be complexed also by tetraglyme molecules (although less efficiently) presumably in a pseudo-crown ether fashion. The observed increase in the K^- linewidth reflects the expected decrease in the degree of separation between K^+ and K^- in tetraglyme as compared to other systems.

Mixed metal solutions.

The advantage of the mixed metal solutions obtained from K/Na alloy over the pure potassium solutions derives from the ease of their preparation. The ^{39}K and ^{23}Na NMR spectra of solutions in THF containing 18C6 or 15C5 and in tetraglyme with 18C6 enabled to determine the ionic composition of the systems. The NMR spectra reveal that solutions contain mainly complexed potassium cations and sodium anions, however in THF a small amount of potassium anions is also present. Figure 4 displays the ^{39}K and ^{23}Na NMR spectra of the solution in THF with 15C5.

Fig.4.- ^{23}Na and ^{39}K NMR spectra of potassium/sodium solution in THF containing 15C5 at 243 K.

^{39}K and ^{23}Na NMR provide also the opportunity to follow the kinetics of an alkali metal dissolution.

Novel applications of potassium solutions.

Dye utilized alkali metal organic solutions for preparation of alkalides and electrides¹⁸. Potassium solutions, although not precisely characterized, were also applied previously for reduction of some aliphatic and aromatic hydrocarbons and acid derivatives, like esters, nitriles, etc.¹⁹⁻²¹. Our study on metal solubilization and composition of obtained solutions revealed that under proper conditions solutions with high concentration of anions and negligible amount of electrons can be produced. Well defined solutions containing potassium or sodium anions as anionically active species have been employed as reagents for organic synthesis. The great utility of this reagent, especially for the enolization of ketones²², ring opening reactions of lactones and cyclic ethers²³, metalation reactions²⁴ has been demonstrated, the mechanism of these reactions being also studied. It turned out that depending on the nature of a substrate potassium anion can react in different manner. Transfer of one or two electrons towards a suitable acceptor is possible, as well as proton abstraction, as shown schematically:

The unexpected new reaction involving two electrons transfer from potassium anion to the β -lactone molecule resulting in C-C bond scission of the β -lactone ring was also demonstrated²³. It is the first example of carbon-carbon bond cleavage that occurs in heterocyclic compounds.

The alkali metal complexes like K^+ (crown ether), K^- are also novel interesting homogeneous catalysts, e.g. for polymerization processes²⁵.

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