EPR AND ELECTROCHEMICAL STUDIES OF THE SYSTEM $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_x \cdot \text{Na}^-$

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Abstract : Very concentrated solutions of lithium and sodium can be obtained in ethylamine when these alkali metals are put in contact together in this solvent. The major species in presence are solvated lithium cations and sodium anions. The stoichiometry of the solution can be written as $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_x \cdot \text{Na}^-$. The liquid corresponding to $x = 4$ is highly viscous and has a bronze metallic luster. Impedance measurements indicate that for $x > 10$, the behavior of the solution is similar to that of ordinary sodides in the same solvent. When x becomes close to 4, highly conducting systems are obtained. EPR spectroscopy measurements show only a single line having a g -value close to that of the free electron whose width increases as the temperature is decreased. A discontinuity is observed at about the freezing temperature of the solvent, but a paramagnetic signal is still present in the solid state. Band shape analysis indicates complex systems of several gaussian lines. "Dysonian" lines, characteristic of the onset of a metallic state, were never observed.

INTRODUCTION

Alkalides - compounds containing alkali metal anions - were first prepared with the help of a non-reducible complexant of alkali metal cations such as a crown ether, a cryptate or their nitrogen equivalent. The role of the complexant was to favor the dissolution and dismutation of alkali metal atoms in an appropriate solvent following the general scheme :

where M stands for an alkali metal, C, for a complexant molecule, and (M^+C) represents a complexed cation.

The complexant prevents the reverse recombination reaction between ions of opposite charge when the solvent is removed. It must be noted that ammonia is not a proper solvent for these studies, since it promotes the formation of solvated electrons rather than alkali anions. When solid compounds are formed, via solvent removal, the complexed cation occupies a very important space in the crystal structure. Therefore in most of the cases, the anions are well separated from one another and from the cation and they form ordinary ionic salts. However, this not always the case, EPR studies have revealed that electrons trapped at anionic defects could have a large contact density on the cation (¹), X-ray crystal studies of some alkalides have shown that in compounds such as $\text{K}^+\text{C}_{222}\text{K}^-$, pairs of K^- were observed while alkali metal anion chains extending through the crystal existed in $\text{Cs}^+\text{C}_{222}\text{Cs}^-$ (²). This last phenomenon occurs because the size of the anions becomes large with respect to the complexed cation, but as yet there is no explanation for the existence of such "alkali dimers dianions" although some *ab initio* calculations tend to indicate the existence of such metastable entities (³).

It has been recently reported that lithium amine complexes such as $\text{Li}(\text{CH}_3\text{NH}_2)_4$ could assist the solubilization of various alkali metals in solvents in which they are usually sparingly soluble (⁴). Alkali metal NMR studies and optical absorption studies revealed that, in the case of the dissolution of sodium,

sodide anions were formed while Li was present as a cation. When ethylenediamine (en) was used to complex lithium, the compound $\text{Li}^+(\text{en})_2\text{Na}^-$ was identified (⁵)

Our work is focused on the use of ethylamine as a complexant to form the compound $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Na}^-$ and also as solvent of this compound. NMR studies have shown that lithium cations and sodium anions were present. This compound is diamagnetic down to 2 K as indicated by static magnetic susceptibilities measurements (⁶).

These compounds are currently the simplest sodides. Their physical aspect is shiny bronze or gold, and is very reminiscent of that of concentrated metal-ammonia solution in the metallic state. The distance between anions may become smaller than in the case of sodides involving crown ethers or cryptates; this fact joined to the high polarizability of Na^- (ionic radius : 2.6 Å) might lead to the formation of a new metallic system. Similar compounds involving K, Rb and Cs have recently been prepared (⁷)

Two techniques were used in this work, the measurement of electrical impedance as a function of the frequency and of the concentration, and EPR spectroscopy. EPR has been used for long to show the presence of conduction electrons in alkali-metals usually characterized by dysonian line shapes (⁸)

EXPERIMENTAL

Lithium and sodium metal of high purity were used as received. They were cut and weighed in a argon filled glove box. Typical quantities were 17.5 mg of Li and 57.5 mg of sodium for EPR experiments and of 140 mg Li and 460 mg of Na for impedance measurements. The metals were first dissolved in dry ammonia in order to disperse them. Ammonia was slowly removed by evaporation and the remaining metals were pumped at 1×10^{-5} torr overnight at room temperature.

Solvents were dried over alkali metals or sodium-potassium liquid alloy. They were transferred by evaporation under vacuum from a blue solution. Quantities were determined either by gas volumetry or gravimetrically for large quantities.

EPR samples were prepared in small spherical vessels to which the EPR sample tube (SUPRASIL 4 mm OD) was attached via a Pyrex to silica graded seal. Appropriate quantity of ethylamine was condensed in the bulb and the assembly was sealed off the vacuum line. The solvent was left in contact with the alkali metals at -40 °C for a period of several days. The resulting bronze liquid was poured into the EPR tube taking care to keep the whole cell at the same low temperature. The volume of the solution was small enough that all of the liquid was inside the EPR dewar. EPR spectra were measured on a BRUKER ESP 300 spectrometer using X-band. Temperature was regulated by a stream of cold nitrogen.

The cell used for impedance measurements was a modification of the standard "K-cell" used for alkali and electride synthesis (⁹). A small extension equipped with two facing tungsten electrodes sealed through Pyrex (2 mm or 4 mm in diameter) was added to the bottom of one side. Tungsten electrodes were cleaned by electrodisolution in a 1 M aqueous KOH solution. After rinsing with conductance water, the cell was dried by evacuation at better than 1×10^{-5} torr for several hours. Alkali metals were introduced on the side having no electrodes where the solution was prepared. After the step of ammonia dispersion, a large measured quantity of ethylamine was distilled. Alkali metals and solvent were kept in contact at -40 °C for several days to ensure the formation of the complex while minimizing the possibilities of decomposition. The resulting liquid was poured on the measurement side through a coarse frit to avoid metal carry over. More concentrated were obtained through removal of the solvent taking care to keep the system at low temperature to prevent decomposition. Impedance were measured in the frequency range 10^4 to 10^{-2} Hz using a Solartron (Schlumberger) frequency response analyzer.

RESULTS

The only solvent used in this work was ethylamine, accordingly we shall call dilute solutions systems such as $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_x\text{Na}^-$ when x becomes larger than 4.

Very high concentrations of Na^- can be reached in these systems, when $x=4$ it can be as high as 0.1 mole/kg. This about two orders of magnitude larger than the concentration obtained via dissolution of $\text{Na}^+\text{C}_{222}\text{Na}^-$ in the same solvent. These liquids have a very high "wetting" ability of the glass system, very much higher than that of $\text{Li}(\text{NH}_3)_4$ or $\text{Li}(\text{CH}_3\text{NH}_2)_4$. Bronze films formed on the walls have no tendency to flow. Accordingly, all the liquid transfers had to be performed very slowly with the whole apparatus kept at the same low temperature.

Figure 1 : Impedance diagram of a dilute $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4.\text{Na}^-$ sample at two temperatures : $\square$: $-20\text{ }^\circ\text{C}$; $\circ$: $-40\text{ }^\circ\text{C}$

Impedances

Tungsten electrodes were found to be compatible with sodide solutions; platinum catalyzes decomposition, gold is reduced by alkali metals ⁽¹⁰⁾ as well as by alkalides. The response of the cell was calibrated by using standard solutions of $\text{Fe}(\text{CN})_6\text{K}_4/\text{Fe}(\text{CN})_6\text{K}_3$ and comparing the diagrams to those obtained in cells having a known geometry.

Since the aim of this work was to study properties of highly concentrated systems, no support electrolytes were used. The impedance diagram in the Nyquist plane of a dilute solution of $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_x.\text{Na}^-$ having $x = 16$ are shown in figure 1. When the excess ethylamine is removed and that overall stoichiometry gets closer to that of $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4.\text{Na}^-$, the whole diagram collapses to a single point. In this last case, the resistance is analogous to that of a short circuit between the two electrodes. Similar experiments were run for concentrated lithium solutions ($\text{Li}/\text{amine} = 0.1$) These solutions are dark blue and do not show any metallic shine. Their diagram consists of a single point situated on the real axis. (Dilute solutions of lithium in methylamine have also the same behavior).

EPR Spectra

The EPR spectra of a variety of samples having the stoichiometry $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4.\text{Na}^-$, $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_{16}.\text{Na}^-$ and pure lithium in ethylamine in the temperature range 150-250 K have been recorded. In every case a single symmetrical line is observed. Its position is close to that expected for solvated electron. Under no circumstances, "dysonian" lineshapes were observed. Hyperfine structure characteristic of the existence of alkali metal monomer or of others radicals could not be detected. The

saturated Li-ethylamine solutions are strongly paramagnetic and do not show any tendency to form metallic systems.

Figure 2 : EPR spectra of $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4.\text{Na}^-$ at various temperatures : (a) : 253 K; (b) : 243 K; (c) : 213 K; (d) : 183 K; (e) : 173 K; (f) : 153 K

In figure 2, spectra obtained at various temperatures for a sample having a stoichiometry close to $x=4$ are reported. The main feature is that the signal does not disappear at temperatures below the freezing point of the solvent at 192 K. For Li solutions or for some diluted systems corresponding to $x=16$, the signal disappears almost completely at this temperature.

In figure 3, the variation of the experimental peak-peak separation of the derivative curve is plotted as a function of the temperature for several samples. A sharp break is observed at a temperature of the order of 170-180 K whose position is independent of the cooling rate. Data points obtained with dilute solutions fall also on the same curve, but they are limited to 192 K. In the same figure, the ΔH_{pp} for Li solution is also drawn. The variation of the total number of paramagnetic species that can be obtained via double integration of the signal is not reproducible from sample to sample.

The power dependence of the signal is shown in figure 4. The shape of the spectrum is not modified when RF power is increased, no new peaks appear and the width of the signal does not change.

Lineshapes were analyzed with the general nonlinear least-squares program KINFIT (¹¹). It was found that lorentzian lineshapes or combinations of them could not fit the experimental spectrum. Good agreement was obtained with a sum of two independent gaussian lines that was found to fit properly data obtained with 8 different samples and more than 15 temperatures in each case. Both gaussian curves are located to almost the same resonance position down to the melting point of the compound, at which point, important variations are noticed. The variation of the width at half height with temperature of each component reproduces the experimental data.

Figure 3 : Variation of the width of the EPR signal as a function of temperature. $\circ$ represent data for Li in ethylamine Triangles and squares correspond to two samples of $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4.\text{Na}^-$.

DISCUSSION

Previous measurements on the system $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_x.\text{Na}^-$ have shown that the ions in presence were the cation Li^+ and the anion $\text{Na}^-(4)$. At the sensitivity of alkali metal NMR, no metal could be detected. The impedance diagrams show that these solutions behave like electrolytic systems. The striking feature, observed when the stoichiometry $x = 4$ is reached, is that the complete diagram is reduced to a single point. This can be attributed to several reasons, metal precipitating and shorting the electrodes, production of solvated electrons or formation of a highly conducting liquid.

Figure 4: Power saturation measurements on a sample of $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4.\text{Na}^-$. $\blacksquare$: 213 K; $\bullet$: 243 K

Measurements of the static magnetic susceptibility (6) have shown that $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Na}^-$ was diamagnetic. As it is the case with the alkalides, EPR signal is due to defect electrons contained in the structure. For all the systems studied, there is no apparition of lineshapes characteristic of conduction electrons either in $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Na}^-$ or in lithium solutions.

EPR spectra of defect electrons trapped in $\text{Na}^+\text{C}_{222}\text{Na}^-$ have been previously reported (¹²). They consisted of two lines, having widths of 4 and 14 gauss, centered near the g-value of the electron, but there was no variation of the width of the signal with the temperature. These two lines were strongly influenced by the RF power being used. In this work, the width was found to increase drastically when the temperature was decreased. A sharp discontinuity was noticed at a temperature slightly below that of the solidification of the solvent. For the time being, it is not possible to decide whether this corresponds to the melting point of the compound or to surfusion artefacts. Below that point the linewidth becomes narrow and remains constant. In the concentrated lithium - ethylamine the lines are wide but remain constant on the whole temperature range. This dependence upon temperature indicates that this system is different from lithium solution (sodium can be ruled out since it is virtually insoluble in ethylamine in the absence of lithium).

The resonance lineshapes are complex consisting of a combination of gaussian, furthermore the saturation experiments indicate that the broadening of the lines is inhomogeneous. Accordingly the system is complex and even in the liquid phase, there exists a distribution of the nature of the interaction of the electron with the surroundings.

This study has shown a few unique properties of $\text{Li}^+(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Na}^-$. In spite of the results obtained from electrochemical impedance measurements, no transitions to a metallic state could be established from EPR spectroscopy. More physical properties of these systems are needed to be measured before a reasonable understanding of their structure can be reached.

The support of NATO grant 0106/88, CNRS and HEI is gratefully acknowledged.

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