Cathodic Generation and Oxidation of Lead Zintl Ion Pb_9^{4-} in Potassium Iodide Solutions in Liquid Ammonia

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The electrochemical reduction of lead and oxidation reaction of the resulting Pb_9^{4-} Zintl ions have been studied in 0.1 and 1.0 M KI solutions in liquid ammonia at −70 °C. The reduction process is a complicated multistep reaction. Under certain conditions the oxidation of Pb_9^{4-} occurs as a simple, electrochemically irreversible reaction for which the limiting current is diffusion controlled. The diffusion coefficient of Pb_9^{4-} was determined from a combination of chronoamperometry measurements on a 25 μm Pt ultramicroelectrode and chronocoulometry measurements on a 1 mm Pb disk electrode. The chronocoulometric method for the determination of Pb_9^{4-} determination is presented and used to determine the actual Pb_9^{4-} concentrations in the electrochemical cell. Side effects, which accompany the reduction and oxidation reactions, have also been studied and the ways to avoid them presented.

Introduction

The first observation of the species we call today Zintl ions[1] was reported more than 100 years ago.[2,3] These homopolyatomic anions of metals (metaloids) of group IV and V are formed by dissolution of alloys of these elements with alkali metals in liquid ammonia or ethylenediamine or by a direct reaction between the elements in one of the above solvents.[1] The first successful attempt to generate Zintl ions electrochemically dates back to the beginning of this century.[4] Since the initial studies,[2−12] our understanding of Zintl ions has significantly improved. Also, the name "Zintl ions" has been extended to include heteroatomic species, such as for example $Sb_2Te_5^{4-}$, $Sb_6Te_9^{4-}$,[13] or $Cu_4SbTe_{12}^{3-}$.[14] Products of reduction of cathodes made of mercury[15−23] and other metals[24−28] in solutions of quaternary ammonium salts in some organic solvents were suggested to be alkylammonium salts of the respective homoatomic Zintl ions.[15,28] Contemporary, well-controlled, electrochemical generation methods were applied to produce heteroatomic $Pb_xSn_{9-x}^{4-}$ species[29] as well as alkylammonium or alkylphosphonium salts of some heteroatomic[30−33] Zintl ions. Detailed electrochemical studies of reduction processes of some metal cathodes in certain organic solvents containing organic background electrolytes are also available.[17−28] These studies[17−28] generally show complicated character of the reduction processes involving the electrode material. Quite unexpectedly, no detailed studies have been performed on the electrochemical behavior of homoatomic Zintl ions in the presence of alkali metal salts. Rather simpler behavior may be expected for such systems, and we believe that a better understanding of the cathodic reduction (corrosion) of metals could be achieved with the aid of such studies. Such studies will also provide a deeper insight into some unusual chemical reactions of Zintl ions,[34−37] which are certainly electrochemical in nature. Lead, for which the Pb_9^{4-}, Pb_7^{4-}, and Pb_5^{2-} Zintl ions are known, was the first element which was selected, because of the relative ease of production of lead electrodes in variety of sizes and shapes. Liquid ammonia was selected as a solvent, because simple and very efficient purification methods of that solvent for electrochemical purposes are known.[38,39] Also, the electric permittivity of liquid ammonia is close to 25, which makes this solvent more suitable for electrochemical measurements than ethylenediamine, which has the permittivity of 12.9.

Experimental Section

A three-compartment electrochemical cell equipped with medium-porosity glass frits was used in the experiments.

A lead disk electrode was prepared by sealing of a 1 mm lead wire (Puratronic, Alfa Aesar, Ward Hill, MA) in an epoxy resin (Huntington Mechanical Laboratories Inc., Mountain View, CA) or shrinkable PVC tubing.

Large lead electrodes used for preparative electrolysis were prepared by melting lead wire and pouring the liquid into a porcelain boat. A 1.5 mm Pt wire was heated in a flame until it started melting and the hot end pressed against the lead bar which locally melted and formed a durable electrical contact. The large lead electrode was usually around 3 cm long and has a diameter of approximately 7 mm. During experiments around two-thirds of its length was immersed in the solution. Platinum disk electrodes (0.5 mm diameter) as well as Pt ultramicroelectrodes (25 μm diameter) were prepared by sealing corresponding Pt wires in a soft glass. In most experiments a silver wire (0.5 mm diameter) was used as a quasireference electrode (AgQRE). However, in order to ensure maximal stability of the reference potential in those experiments in which high concentrations of lead anionic species were generated, a regular Ag/Ag^+ reference electrode was used. This reference electrode was prepared by electrochemical oxidation of the Ag wire in situ to produce some Ag^+ cations in the reference electrode compartment. Such a procedure prevented a shift of the silver electrode potential even if some amount of Pb_9^{4-} diffused through the frits and entered the reference electrode compartment during the long-lasting experiments. Occasionally the AgQRE was placed in a small fritted compartment that was placed in the main reference electrode compartment. The potentials reported in the present paper are referenced versus the solvated electron potential. The potential used in this study is the oxidation peak potential of solvated electrons generated voltammetrically on a 25 μm Pt UME. The solvated electron was generated at a scan rate of 50mV/s with the reversal potential at which the reduction current reached approximately 12 μA. The reference potential determined in this way was virtually ohmic drop free. Sometimes a potential which corresponds to a certain cathodic current density

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is used as a reference potential in liquid ammonia,[38] a condition that moves us to also quote the corresponding value for the reference potential. The reference potential corresponds to the reduction current density of 22.6 mA/cm^2. The experiments were performed using a EG&G PARC 273A potentiostat. Unless otherwise stated, a positive feedback was used as a method of *iR* drop compensation.

In a typical experiment the electrochemical cell was loaded with KI Reagent, ACS (MCB, Cincinnati, OH) and connected to a vacuum line. It was dried at 120−130 °C under vacuum for 2 or 3 days. Before the electrodes were placed in the cell, a fresh surface of Pb was exposed either by a brief grinding with a triangular file (epoxy) or by cutting off a tip of the electrode with a razor blade (PVC). Grinding of the Pb/epoxy electrodes required some skill to prevent the lead from spreading all over the epoxy. The freshly prepared electrodes were loaded into the cell, which was then evacuated under vacuum at 110 °C for 1−2 h. The reason for not heating the electrodes for a long time was a possible damage to their surface or shell. The Pb/PVC electrodes could not be heated above 120 °C and/or for long periods of time, since such a treatment resulted in irreversible loss of PVC elasticity and consequently in a poor Pb−PVC seal. The lead surface of the Pb/epoxy electrodes, on the other hand, was easily oxidized at elevated temperatures by the moisture accumulated in the epoxy. Because of that possibility, the Pb/epoxy electrodes were predried under vacuum in a separate vessel and kept under vacuum until they were used in an experiment. Ammonia (anhydrous grade, Matheson) was condensed under vacuum in a trap containing metallic sodium with liquid nitrogen. After condensation three freeze−pump−thaw cycles were applied to remove any gaseous impurities left after purification with sodium. Finally, the purified ammonia was vacuum-distilled into the electrochemical cell. Ammonia solutions obtained by this process were usually sufficiently pure for electrochemical experiments as demonstrated by cyclic voltammogram on a Pt disk electrode. In very rare cases, however, some reducible impurities were still present as manifested by the lowered reoxidation current of solvated electrons generated at the cathodic potential limit. In such cases small concentrations of solvated electrons were generated at a constant potential in order to reduce the impurities. This procedure was repeated as many times as necessary, i.e., until the light blue color of a diluted e^- solution could be seen for more than 5 min.

All the experiments were performed at the dry ice/2-propanol bath temperature (−70 °C).

Results

Preparation of Pb_9^{4-} Solutions in Liquid Ammonia. Preparative electrolysis in 0.1 M KI solutions was performed at selected cathodic potentials more positive than the solvated electron potential. The potentials were not corrected for *iR* drop and therefore apply only to the specific cell geometry. Compensation for *iR* in the preparative experiments case is of rather limited usability, because of the large surface area of the electrode. Some parts of the electrode would remain undercompensated, some other would be overcompensated, and comparison of the potentials with the corresponding voltammetric data would still be doubtful. The reduction produced a very dark solution which initially appeared violet and then brownish red. The lead electrode had a shiny appearance after electrolysis, and a characteristic corrosion pattern could be seen on its surface irrespective of the reduction potential applied. No solid deposit formation was detected in contrast to voltammetric data (see below). This discrepancy is most likely due to *iR* drop effects. During a similar study with RbBr and CsI solutions,[40] in which formation of a solid compound occurs at a lower overpotential, solid products of a preparative electrolysis were easily detected. Stoichiometry of the dissolved products was determined using a gravimetric method. The lead cathode was weighed before and after preparative electrolysis, and the number of electrons (*n*) associated with removal of a single lead atom from the electrode was calculated from the electrolysis charge and the electrode weight loss. The plot of *n* versus the electrolysis potential, shown in Figure 1, suggests that the dark colored species generated was Pb_9^{4-} ($Pb^{0.44(4)-}$). That Pb_9^{4-} was the only reduction product was further confirmed by voltammetric experiments described below. The Pb_9^{4-} solution could be reoxidized at 1.254 V (see below) with an efficiency exceeding 95%, thus suggesting that the oxidation product was metallic lead. The deposit was black, spongelike, and did not adhere well to the electrode surface. Identical behavior was observed when PbI_2 solution was reduced under similar conditions and is rather typical for electrochemical deposition of lead both in liquid ammonia[41] and in water.[42]

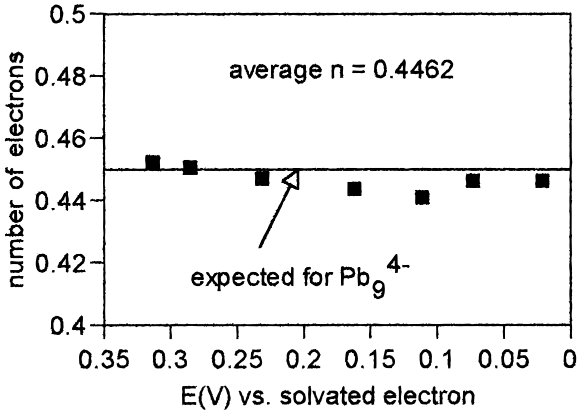

Figure 1. Number of electrons associated with the removal of a single lead atom during the cathodic reduction of lead plotted against the reduction potential.

It has to be noted that a long electrolysis can result in accumulation of NI_3 on the Pt anode. Since NI_3 is explosive when dry, care has to be exercised when removing the counter electrode from the cell and when cleaning it.

Cyclic Voltammetry. The electrochemical behavior of Pb_9^{4-} was studied using both pure KI solutions and solutions containing Pb_9^{4-} produced by preparative electrolysis using a large lead cathode (see above). All the data described below were obtained after electrochemical activation of the lead surface. The activation procedure was not always necessary, but ocassionally the surface of the electrode was partially oxidized. The activation consisted of a potential scan in the cathodic potential region until the steady state cyclic voltammogram was obtained. The potential range applied was that in which no solid reduction products were generated (see below). For 0.1 M KI solutions potentials between approximately +0.5 and +0.3 V fulfilled this requirement. Usually, fewer than 10 cycles at a scan rate of 50 mV/s were necessary to activate the surface. Once activated, the surface remained active during experiments.

At relatively low cathodic potentials (*E*) the Pb reduction current in 0.1 M KI is independent of the scan rate and follows approximately exponential increase with *E* (Figure 2) as expected for a completely irreversible process. A single reoxidation peak can be seen at around 0.6 V. No other products could be detected for scan rates ranging from 20 mV/s to 20 V/s. However, the reoxidation currents recorded for scan rates $v \leq 0.1$ V/s were lower than expected (curve 2 in Figure 2 and Figure 3), suggesting instability of the product. However,

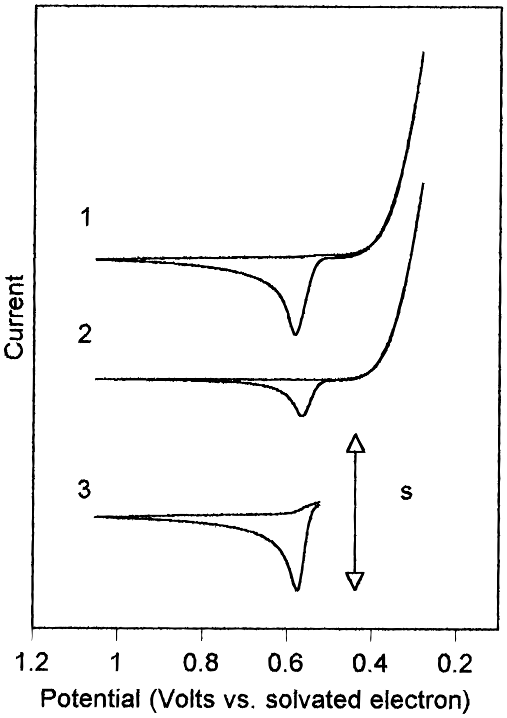

Figure 2. Cyclic voltammetric curves recorded using a 1 mm Pb disk electrode in 0.1 M KI solution in liquid ammonia at −70 °C without (curves 1 and 2) and with 0.4 mM concentration of Pb_9^{4-} (curve 3). Starting potential: +0.494 V (curves 1 and 2); 0.526 V, i.e., open-circuit potential (curve 3). Scan rate (V/s): 0.05 (curve 2); 0.2 (curves 1 and 3). Direction of the forward scan: cathodic (curves 1 and 2); anodic (curve 3).

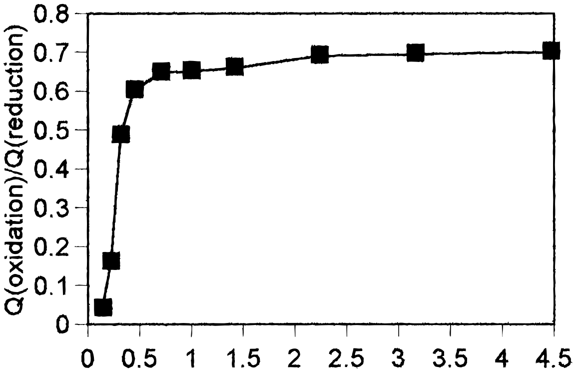

Figure 3. Ratio of the oxidation charge of Pb_9^{4-} to the reduction charge of 1 mm lead disk electrode (Pb_9^{4-} generation) in 0.1 M KI solution under voltammetric conditions plotted versus the square root of the scan rate. Starting potential +0.494 V. Cathodic reversal potential +0.284 V. Anodic reversal potential +1.054 V.

coulometric data (see above) confirmed stability of the lead reduction product. The decrease in the reoxidation charge is then interpreted as being due to a natural convection. The effect occurs at relatively slow scan rates (long reduction times)[43] when significant amounts of the product of an electrode reaction are generated and is caused by the density gradients in the vicinity of the electrode surface. The density gradient results in convection which enables faster transport of the product away from the electrode surface. At the low scan rates, at which the lowered reoxidation charges were seen (Figures 2 and 3), the reduction process was accompanied by dark streamers going downward from the Pb disk surface, in accordance with our interpretation of the lowered reoxidation charges. As expected, the effect occurred to a lesser extent in more viscous and denser 1.0 M KI solutions. The natural convection effect seems to be especially strong[43] in the present case, and the most probable reason for that is the high molecular weight of the metal clusters generated.

When the cathodic scan limit is extended up to 0 V, the reduction current does not follow exponential increase. At low scan rates ($v \leq 0.05$ V/s) a peak current followed by some current increase could be seen in the cathodic scan (Figure 4a). The cathodic current in the reverse scan exhibits hysteresis behavior and suggests chemical modification of the surface by an intermetallic compound of lead and potassium. Our other studies[40] indicate that the molar ratio of lead to potassium in the compound is close to one. The modified surface is oxidized in a broad irregular surface peak (a2) between 0.5 and 0.9 V, which overlaps with the oxidation peak (a1) of the dissolved species as described above. A relatively small oxidation current is also seen at the anodic potentials preceding the broad peak ($0.4\ V < E < 0.6$ V). This current transforms into a diffuse peak (a3) at approximately 0.5 V at higher scan rates ($v \geq 0.1$ V/s). At the same time the broad peak (a2), centered around 0.7 V, disappears. At still higher scan rates ($v \geq 0.2$ V/s) the peaks a1 and a2 merge, or peak a2 disappears and a small anodic peak (a4) appears at around 0.35 V ($v \geq 0.5$ V/s). For scan rates in the range 0.5 V/s−5 V/s the peaks a1 and a4 are the only well-resolved peaks. The ratio of their heights does not seem to vary with the scan rate. Voltammetric behavior of Pb in 1.0 M KI was essentially similar; however, some differences were found. As many as three cathodic peaks could be seen at low scan rates for 1.0 M solutions (Figure 4b). The anodic peak a4 was much better resolved, and larger amounts of the solid compound were formed (Figure 4b). The last two effects are probably associated with generally higher reduction currents measured in 1.0 M KI solution.

Voltammograms of the solutions prepared by the preparative electrolysis exhibited only a single oxidation peak whose position and slope matched well with the same parameters for peak a1 (Figure 2). This fact strongly suggests that a single dissolved species is generated during preparative electrolysis, since, due to structural differences and kinetic factors, the known lead Zintl ions (Pb_9^{4-}, Pb_7^{4-}, and Pb_5^{2-}) are expected to oxidize at different potentials. Therefore, in view of the coulometric results, the peak a_1 is attributed to the oxidation of Pb_9^{4-}. The electrochemically irreversible oxidation of Pb_9^{4-} on a lead electrode is diffusion controlled (Figure 5) in both 0.1 and 1.0 M KI solution. We found, however, that recording a large number of Pb_9^{4-} oxidation curves resulted in some increase of the oxidation current, especially when higher concentrations of Pb_9^{4-} were employed. This effect suggests that the active electrode surface area increases during subsequent oxidation scans. Examination of the electrodes after performing multiple oxidations revealed the presence of the fine black Pb deposit on the surface (see also coulometric data). When the electrode potential was scanned cathodically up to +0.3 V at a scan rate of 50 mV/s, the black lead deposit dissolved easily, exposing a fresh, shiny bulk lead surface. Therefore, such a pretreatment (in fact identical with the activation procedure described above) of the lead disk was performed occasionally during Pb_9^{4-} oxidation studies to ensure reproducible surface area of the electrode. As would be expected, the presence of the fine lead deposit on the electrode surface also leads to an increase in the lead reduction currents (Figure 6). The effect is especially significant when the lead is reduced immediately after oxidation of the solid formed at the potentials close to solvated electron generation (Figure 7). A similar phenomenon was reported for Sb cathodes reduced in dimethylformamide solutions of qua-

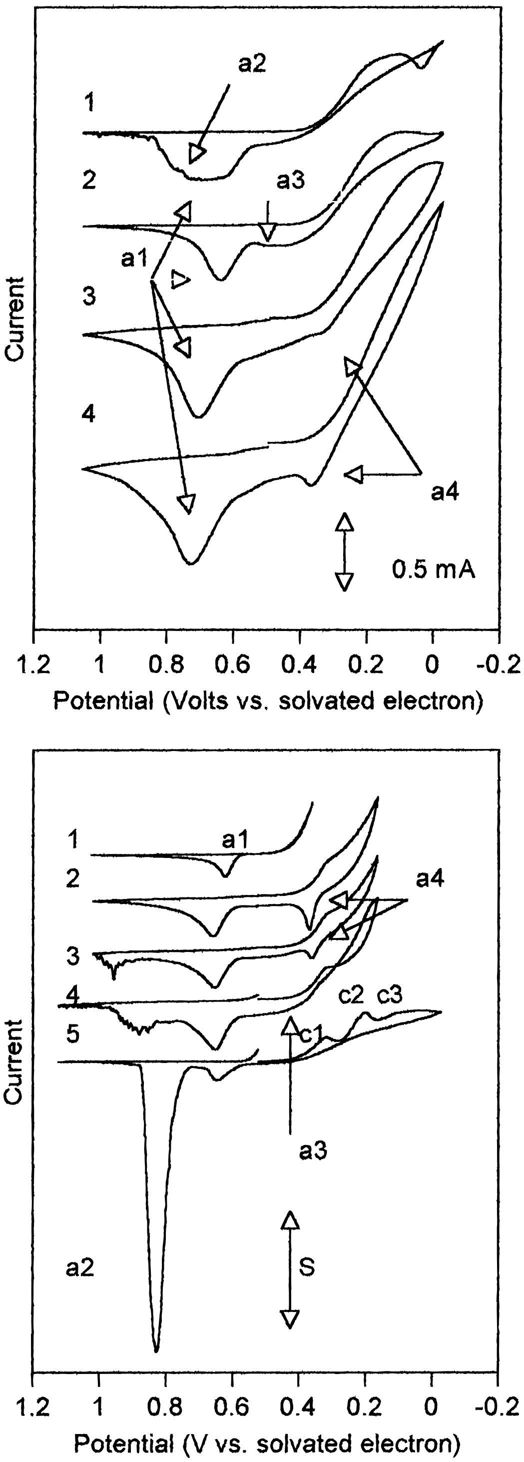

Figure 4. (a, top) Cyclic voltammograms recorded using 1 mm lead disk electrode in 0.1 M KI solution in liquid ammonia at −70 °C. Starting potential +0.494 V. Cathodic reversal potential −0.026 V. Anodic reversal potential +1.054 V. Scan rate (V/s): 0.05 (1); 0.1 (2); 0.5 (3); 2.0 (4). (b, bottom) Cyclic voltammograms recorded using 1 mm lead disk electrode in 1.0 M KI solution in liquid ammonia at −70 °C. Starting potential +0.524 V. Cathodic reversal potential (V): +0.344 (1); +0.164 (2−4); −0.026 (5). Scan rate (V/s): 0.02 (5); 0.1 (1); 0.2 (4); 0.5 (3); 1.0 (2). Anodic reversal potential (V): +1.024 (1−3); +1.124 (4, 5).

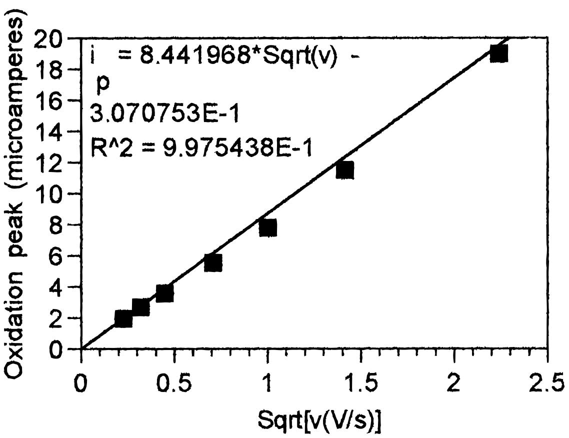

Figure 5. Plot of the peak current for oxidation of 0.4 mM Pb_9^{4-} in 0.1 M KI solution on a 1 mm Pb disk electrode versus the square root of the scan rate. The starting potential was the open-circuit potential of the lead electrode in the solution studied.

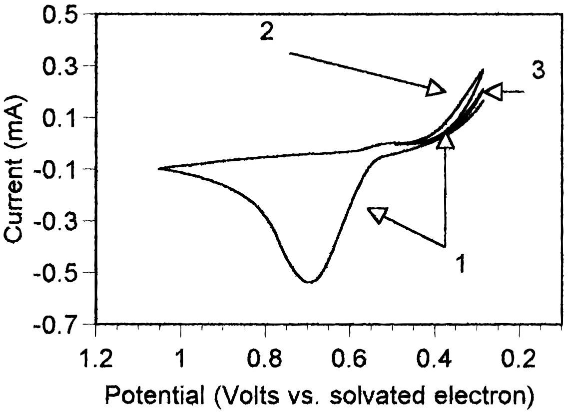

Figure 6. Effect of oxidation of large quantities of Pb_9^{4-} on the 1 mm Pb disk reduction currents in 0.1 M KI solution. Curve 1: Starting potential +0.284 V for 20 s, then the potential scanned anodically up to +1.054 V and cathodically to +0.494 V. Curves 2 and 3: two subsequent scans between +0.494 and +0.284 V recorded immediately after recording curve 1. Scan rate 0.5 V/s.

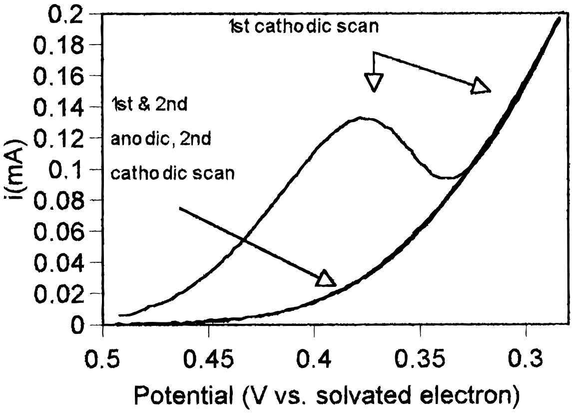

Figure 7. Two subsequent cathodic and anodic scans (0.02 V/s) on a 1 mm Pb disk electrode between +0.494 and +0.284 V in 0.1 M KI solution recorded immediately after voltammetric reduction of the electrode between +0.494 V and 0 V and reoxidation of the products (Pb_9^{4-} and a solid phase, see text and curve 1 in Figure 3). The peak seen in the first cathodic scan originates from reduction of finely divided lead produced upon oxidation of the solid compound.

ternary ammonium salts.[28] The large magnitude of the effect is easily understood if the surface compound formed is an intermetallic compound of lead and potassium. Deintercalation of K upon oxidation of the compound would leave a layer of a very porous, probably amorphous lead characterized by an exceptionally large surface area. After a few potential cycles between 0.5 and 0.3 V (0.1 M KI) the original reduction currents can be restored (Figures 6 and 7). The cathodic dissolution of the porous lead deposit was employed to clean the electrode surface after the oxidation of the surface compound.

The peak potential of Pb_9^{4-} oxidation at 50 mV/s is 0.57 V in 0.1 M KI and 0.61 V in 1.0 M KI. The difference between the peak potential and the potential at the half-height is 18 and 16 mV, respectively, which corresponds to an anodic transfer coefficient βn close to 2 and suggests that the structure of the transition state is intermediate between the structures of the metallic lead and the Pb_9^{4-} in solution. The peak a4, which is most probably a surface peak, corresponds to oxidation of some transition product of the electrolysis. Our other studies[40] show that the peak a_3 corresponds to oxidation of an intermetallic compound other than the one oxidized in peak a2. The detailed analysis of the solids formed during the reduction of a lead cathode in liquid ammonia solutions of KI, RbBr, and CsI will be presented in a subsequent paper.[40]

Chronocoulometry and Chronoamperometry. Determination of the Diffusion Coefficient of Pb_9^{4-}. Chronocoulometry is known to be a reliable method for determining the diffusion coefficient of the electroactive species when the number of electrons transferred and concentration of the electroactive species are known. Alternatively, the concentration of the electroactive species can be easily determined chronocoulometrically if the diffusion coefficient is known. The actual volume of the solution in our small three-compartment cell could only be estimated, because of the relatively large void volume associated with presence of the electrodes as well as partial diffusion of the reduction products into the frits which separated the cell compartments. As a result, neither the concentration of Pb_9^{4-} nor its diffusion coefficient could be determined precisely using just chronocoulometry. Therefore, we tried to apply a method, suggested recently by Bard and co-workers,[44] which is based on a measurement of an ultramicroelectrode current vs time transient at a potential where the current is limited solely by the rate of diffusion. This chronoamperometric method is accurate and allows for the determination of the diffusion coefficient without knowing the number of electrons transferred or concentration of the electroactive species. In a simplest approach the diffusion of a species toward an ultramicroelectrode can be regarded as a sum of a linear (time dependent) and convergent or spherical (time independent) components. The linear component is proportional to the reciprocal square root of time, while the spherical component is a constant which depends on the electrode radius. At the very beginning of electrolysis the current is mainly determined by the linear component ($1/t^{1/2} \rightarrow \infty$). After sufficiently long time the spherical component is predominant ($1/t^{1/2} \rightarrow 0$), and the current is referred to as a steady state current. The current normalized with respect to the steady state current is then given by[44]

$$i(t)/i_{ss} = (\pi^{1/2}/4)r(Dt)^{-1/2} + 1 \qquad (1)$$

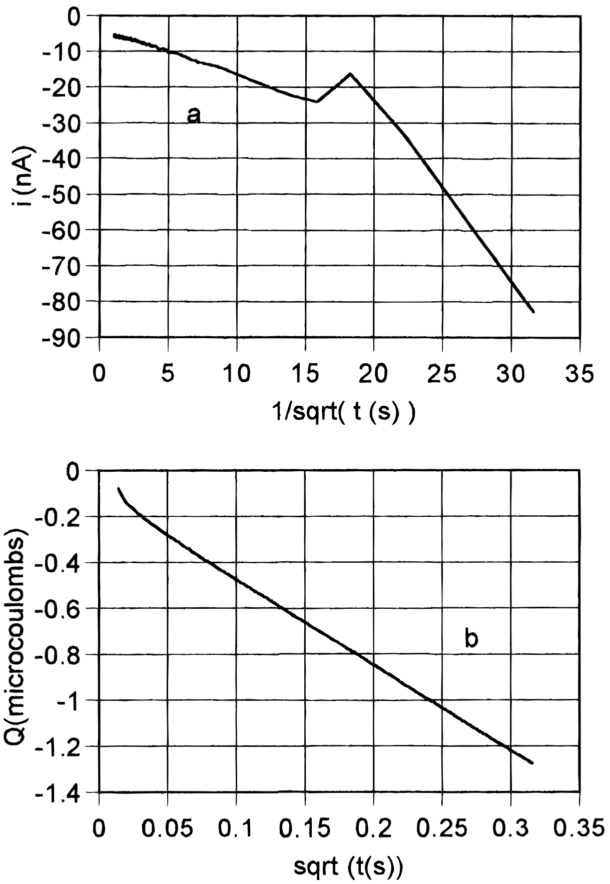

Figure 8. (a) Plot of a current versus inverse square root of time for a potentiostatic oxidation of 0.4 mM Pb_9^{4-} in 0.1 M KI solution at +1.054 V on a 25 μm Pt ultramicroelectrode. Initial potential +0.494 V. Anodic pulse duration 1 s. Current measured every 1 ms. Nonlinear section of the plot at highest $1/t^{-1/2}$ (first 3 ms) is believed to originate from the electrode surface charging and a delayed beginning of the lead deposition due to a slow nucleation process. (b) Chronocoulometric charge vs square root of time plot obtained for the potentiostatic oxidation of 0.4 mM Pb_9^{4-} in 0.1 M KI at +1.054 V on a 1 mm Pb disk electrode. Initial potential corresponds to the open-circuit potential of the disk in the solution studied. Anodic pulse duration 0.1 s. The charge measured every 0.1 ms.

where D is the diffusion coefficient and r is the electrode radius. The diffusion coefficient can be determined from the slope of the $i(t)/i_{ss}$ vs $t^{-1/2}$ plot. This method requires that the steady state current and the ultramicroelectrode radius are known. However, determination of the steady state current in the present case is problematic, because of the accumulation of the metallic lead on the electrode surface (see below). The same problem remains for more accurate methods[44] where nonlinear equations are used to describe $i(t)/i_{ss}$. Therefore, we decided to use the linear approximation (eq 1) with an assumption that the steady state current can be determined from the intercept of the $i(t)$ vs $t^{-1/2}$ plot with the current axis. Such a method is expected to minimize the effect of the deposited metal on the electrode radius (see below), since the steady state current is obtained by extrapolation from the short time region, where the size of the electrode has not been altered yet. The method also allows for a simple reliability test based on comparison of the slope of the $i(t)$ vs $t^{-1/2}$ plot with the slope of a charge vs $t^{1/2}$ plot for chronocoulometric experiment with the large lead disk in the same solution. The ratio of the chronocoulometric to the chronoamperometric slope should be twice the ratio of surface areas of the electrodes used in both experiments. Since preparation of a lead ultramicroelectrode (UME) of a specific geometry is not an easy task, we decided to employ 25 μm Pt UMEs for the Pb_9^{4-} diffusion coefficient determination. In this case, however, the Pb_9^{4-} oxidation on Pt had to be studied in more detail to establish the possibility as well as conditions of using Pt UME for such a purpose. Almost instantaneous nucleation[45] of lead on the whole Pt surface followed by a diffusion-controlled oxidation was found during potentiostatic oxidation of 0.7 mM Pb_9^{4-} solution on a 0.5 mm Pt disk at a high anodic potential of +1.254 V. However, the very next transient recorded with the same electrode exhibited slightly higher currents as well as current spikes even though the cathodic cleaning (see above) was employed. Experiments with a more concentrated Pb_9^{4-} solution and Pt wire electrode, which could be easily observed during experiment, revealed that part of the lead deposit looses its electrical contact with Pt during the cathodic cleaning, but it is still mechanically attached to it. During subsequent oxidation of Pb_9^{4-}, the electrical contact can be reestablished which results in generally higher oxidation currents and occasionally current spikes. Therefore, Pt electrodes could only be used to record a single transient. Similar effects were expected to be even more pronounced with the UMEs because of generally larger amounts of Pb deposited per unit surface area of the electrode due to the increased transport rate in the spherical diffusion field. Indeed, a progressive increase of the oxidation current has been observed when a single microelectrode was used to perform multiple oxidations. However, the very first transients recorded for relatively less concentrated Pb_9^{4-} solutions produced results that were concordant with the chronocoulometric data obtained with a 1 mm Pb disks. The slope of the chronoamperometric (i vs $t^{-1/2}$) plot obtained in such a case was typically 3000−3300 lower than the slope for corresponding chronocoulometric (Q vs $t^{1/2}$) plot, while the expected ratio was 1:3200. Such results (Figure 8) were used to determine the diffusion coefficient of Pb_9^{4-} in 0.1 M KI solution. The average value obtained from six independent experiments is $(4.13 \pm 0.23) \times 10^{-6}$ cm^2/s. The Pb_9^{4-} concentrations in freshly prepared solutions which were calculated using the above diffusion coefficient as well as chronocoulometric data agreed within 10% with the corresponding values calculated from the electrolysis charge and approximate volume of the solution. In a few cases, the concentrations were lower than the estimated ones, most probably because of partial oxidation of the Pb_9^{4-} solution to zerovalent lead by products generated in the anodic compartment which may have diffused into the cathodic compartment during long experiments. One should note that no decomposition can be detected by visual examination of the solution in the cell, since the solution appears almost black even at submillimolar concentrations. Consequently, chronocoulometry on a lead disk electrode can be recommended as an accurate method for determination of Pb_9^{4-} concentration in KI solutions, especially in cases when partial decomposition has occurred.

Discussion

To our knowledge, this is the first study of electrochemical behavior of homoatomic Zintl ions. Among the systems studied by us so far, including lead[40,46] and bismuth[47] Zintl ions in liquid ammonia solutions of alkali metal salts, the present system is the simplest one. Even though, only the oxidation reaction of Pb_9^{4-} in the KI solution can be regarded as a simple process. In addition, the simple character of the reaction is limited to certain experimental conditions. However, the fact that Pb_9^{4-} can be oxidized both in a simple way and with accompanying side effects allowed us to determine the nature of the side effects and to define the conditions required to avoid or minimize them. The effects associated with fine crystalline morphology of the lead deposits formed upon oxidation of Pb_9^{4-} and lead−potassium intermetallic compounds affect both the lead reduction and Pb_9^{4-} oxidation processes and are especially dangerous, since the results distorted by these effects quite often look normal. Understanding these effects has already made the interpretation of our other results[46,47] easier. It also allows us to determine correctly the diffusion coefficient of Pb_9^{4-} in 0.1 M KI solution and apply the obtained value in a simple chronocoulometric method of Pb_9^{4-} determination. The method is very simple and much more convenient than other methods which could be applied for analysis of Pb_9^{4-} solutions in liquid ammonia. For instance, a spectrophotometric method using the visible region may be inferred to be useful, because Pb_9^{4-} is a colored species. Instead, its use is rather limited in the millimolar concentration range because the light absorption by Pb_9^{4-} is very strong.

The fact that Pb_9^{4-} was detected as the only stable product of the reduction suggests that the other possible anions, i.e., Pb_7^{4-} and Pb_5^{2-}, are rather unstable under our experimental conditions. This finding can be associated with the use of an excess of the KI electrolyte in the present study and possible ion association effects.[1] The Pb_7^{4-} was produced[9] by a titration of sodium solution in liquid ammonia with PbI_2. In such an experiment, not only was the countercation different than in the present study but also its concentration was comparable with the Zintl ion concentration. The Pb_5^{2-}, on the other hand, was detected in the solid state[48] rather than in solution.

As already mentioned, the electrochemical reduction of lead, which produces Pb_9^{4-}, is a complicated reaction. No detailed mechanism of that reaction can be deduced from the present data. However, our studies including other electrolytes, e.g., NaI, $NaClO_4$, RbBr, and CsI,[40,46] are in progress, and some important conclusions have already been reached. These studies will be published soon.

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