Raman Study of Aluminum Chloride−Dimethylsulfone Solutions

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The Raman spectra of $AlCl_3$−LiCl−dimethylsulfone mixtures with different molar compositions have been recorded as a solid (300 K) and as a melt (400 K). In any case, only $AlCl_4^-$ ion lines at 120, 179, and 347 cm^{-1} were observed; we were unable to detect any other chloroaluminate species. Furthermore, some bands assigned to the $Al[(CH_3)_2SO_2]_3^{3+}$ octahedral coordination compound are evidence for a high $AlCl_3$ content.

Introduction

The need for high energy density and better rechargeable batteries is well known. In this way, lithium has been extensively studied, especially in organic media. Nevertheless, a lot of problems have been encountered due to its high reactivity towards most electrolytes.

Recently, the development of new high energy batteries based on systems other than lithium was investigated. In this research area, aluminum appeared to be an interesting anode material as regards its electrochemical characteristics such as its high electrochemical capacity (8,03 Ah cm^{-3}) and low standard potential (−1.66 V/ENH).

Acidic mixtures of $AlCl_3$ and organic alkyl ammonium chlorides like alkylimidazolium chlorides or alkylpyridinium chlorides have been used to study the electrochemical behavior of ambient temperature secondary batteries with aluminum anode.[1−7] In the 150−400 °C temperature range, neutral melts of $AlCl_3$/alkali chlorides have also been studied as battery electrolytes.[8−11] For these two kinds of chloroaluminate melts, the predominant Al^{III} species are tetrachloroaluminate, $AlCl_4^-$, anion in neutral melts and tetrachloroaluminate and heptachlorodialuminate, $Al_2Cl_7^-$, anions, both in acidic ones ($Al_3Cl_{10}^-$ was also detected in very acidic melts).

Previous works showed that dimethylsulfone, $DMSO_2$, is a good solvent because it barely coordinates, is stable at relatively high temperature, and is able to dissolve numerous metallic salts.[12,13] Our recent investigations of $DMSO_2$-based electrolytes containing $AlCl_3$ have shown that aluminum could be plated

and stripped from $AlCl_3$ (2 mol)/LiCl (1 mol)/$DMSO_2$ (1 kg) electrolyte while no aluminum deposition was observed in $AlCl_3$ (1 mol)/LiCl (1 mol)/$DMSO_2$ (1 kg) electrolyte.[14] Moreover, we carried out an electrochemical study of $AlCl_3$/$DMSO_2$ mixtures.[15] This study showed us that relatively high conductivities could be obtained (16 mS cm^{-1} for $AlCl_3$ (1 mol)/$DMSO_2$ (1 kg) at 400 K) and that aluminum could be reversibly deposited and reoxidized in these melts as well. Results of the latter study let us to conclude that $DMSO_2$ does not just play the role of an inert solvent. It must react with $AlCl_3$ to give ionic and perhaps neutral species containing aluminum.

In most of the $AlCl_3$/organic solvent systems, the Al-containing ionic species which are able to be formed are chloroaluminates described above for the anionic part and Al species resulting from $AlCl_3$ solvolysis for the cationic part. The latter species have the general formula $AlCl_m(solvent)_n^{(3-m)+}$ where $m < 3$ and n is between 1 and 6. Complete $AlCl_3$ dissociation ($m = 0$) leads to the formation of Al^{3+} stabilized by solvent molecules. In the case where m is 3, the Al species so formed are neutral. As shown, many Al species are then susceptible to formation depending on the characteristics of the solvent, such as basicity in the Lewis sense or its type of molecular interactions.

It was consequently of importance to study dimethylsulfone solutions containing various $AlCl_3$ and LiCl amounts in order to identify Al-containing species and particularly the one responsible for aluminum electrodeposition. This study has been performed through Raman spectroscopy. In fact, Raman spectroscopy is a good tool for this purpose as it is very sensitive to the modifications occurring in molecular bonds such as those due to complexation and can be implemented without any specific sample preparation.

Infrared and Raman spectra of dimethylsulfone and its deuterated derivative, as well as force field calculations, have been extensively studied and the assignment of the different bands observed is unquestionable.[16−20] Furthermore, the vi-

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Table 1. Molar Compositions of Solutions a−e[a]

solution	composition (mol)		
	DMSO₂	AlCl₃	LiCl
a	pure		
b	10.6	1	0
c	10.6	1	1
d	10.6	2	1
e	10.6	4	0

[a] 10.6 mol of DMSO₂ = 1 kg.

brational properties of different aluminum chlorides are known[21,22] and allow each one to be characterized unambiguously.

Experimental Section

Lithium chloride, LiCl (Fluka), was vacuum dried at 200 °C for 24 h and aluminum chloride, AlCl₃ (Aldrich), was used as received. Dimethylsulfone, (CH₃)₂SO₂ (Janssen), was first recrystallized in water and then twice from absolute methanol, air dried at 60 °C for 12 h, and dried again *in vacuo* at 60 °C for 24 h. After this procedure, the residual water content was less than 20 ppm.

The solutions were prepared in a dry glovebox filled with argon which was recirculated through drying column containing molecular sieves, by directly mixing the salts (LiCl and AlCl₃ in appropriate proportions) and DMSO₂ at ambient temperature. Mixtures were then allowed to warm slowly up to 400 K. They were kept at this temperature over pure aluminum threads for several days to remove some impurities such as iron before being transfered into sealed glass capillary tubes for analysis. Five solutions (a−e) were studied; their compositions are summarized in Table 1.

Raman spectra were recorded as solid (300 K) and molten (400 K) dimethylsulfone solutions on a computerized triple monochromator, Dilor RTI 30. The excitation light at 514.5 nm of a Spectraphysics 2000 argon ion laser was used with power of about 0.2 W. A classical furnace was used for experiments at 400 K. The resolution was 2 cm⁻¹ and wavenumber reproducibility 1 cm⁻¹.

Results and Discussion

Figure 1 shows Raman spectra of molten solutions a−e at 400 K. No difference is observed when Raman spectra are recorded at 300 K on solid solutions. So, we shall only discuss in this paper results obtained with liquid solutions in order to avoid spectroscopic crystal effects. The spectrum of pure DMSO₂ (solution a) is identical to those already published.[16−20] In particular, two strong lines are observed for the symmetric stretching vibrations $\nu_s SC_2$ and $\nu_s SO_2$, at 695 and 1130 cm⁻¹ respectively, which can be regarded as practically pure modes.[17,19] Moreover, the five bands of medium intensities corresponding to the bending modes of the tetrahedron are detected between 300 and 500 cm⁻¹.

When aluminum chloride is added to DMSO₂ (solutions b−e), three new bands are detected at 120, 179, and 347 cm⁻¹ which are readily assigned to the $AlCl_4^-$ ion. The spectrum of this tetrahedral entity gives rise to four fundamental modes. The three bands we observed correspond respectively to bendings $\nu_2(E)$ and $\nu_4(F_2)$ and to the symmetric stretching $\nu_1(A_1)$ of $AlCl_4^-$ entity. The fourth vibration expected for this species the stretching mode $\nu_3(F_2)$, is generally observed as a weak Raman line of about 490 cm⁻¹, but in our solutions, it is certainly masked by the relatively intense doublet of dimethylsulfone at 465−495 cm⁻¹.

No other lines are observed in the Raman spectra of solution d where the presence of $Al_2Cl_7^-$ could have been assumed from the stoichiometric composition of the melt (AlCl₃ (2 mol)/LiCl (1 mol)).
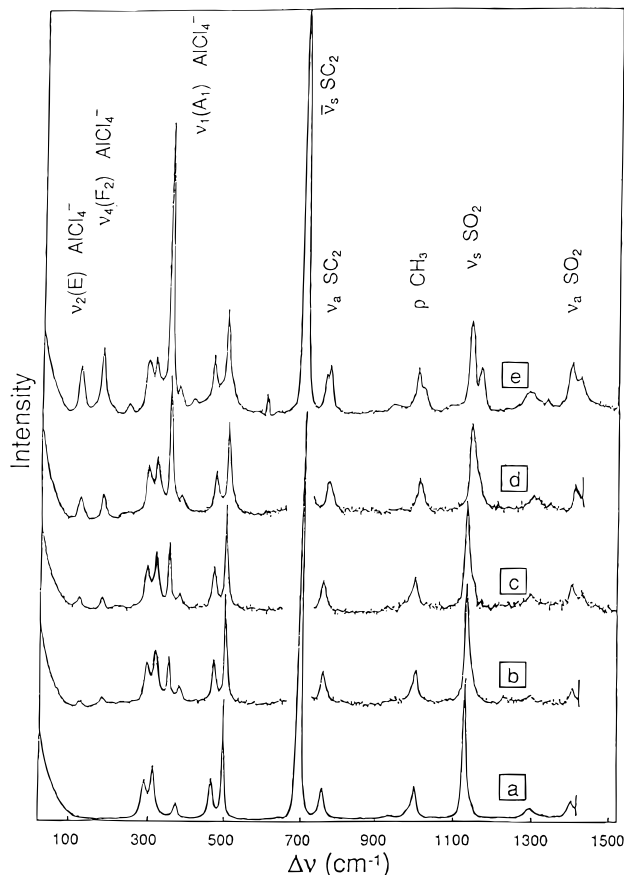
Figure 1. Raman spectra of molten dimethylsulfone solutions a−e at 400 K.

On the contrary, the following additional lines are observed in the Raman spectrum of solution e with the highest AlCl₃ content: two weak lines at 245 and 409 cm⁻¹. Moreover, several lines assigned to (CH₃)₂SO₂ modes split in doublets (e.g. $\nu_a(SC_2)$, $\nu_s(SO_2)$, and $\nu_a(SO_2)$ at about 770, 1160, and 1410 cm⁻¹ respectively). The splitting of the band at 1000 cm⁻¹ is less interesting to point out as several $\rho_s(CH_3)$ modes are expected at this wavenumber.[16−18]

All these results indicate that the $AlCl_4^-$ ion is the main aluminum chloride species present in DMSO₂-based melts investigated here. The presence of this species, obviously expected for solution c, is more surprising for the other mixtures, in particular for solutions b and e, which contain no LiCl. The splitting pointed out for some DMSO₂ vibrations in solution e can be justified only if a reaction between AlCl₃ and DMSO₂ occurs, such as

$$4AlCl_3 + n(CH_3)_2SO_2 \rightleftharpoons 3AlCl_4^- + Al[(CH_3)_2SO_2]_n^{3+}$$

So, a coordination compound between Al^{3+} ion and DMSO₂ is supposed to be generated although this molecule is known to barely coordinate. However, several DMSO₂ complexes have already been obtained and characterized.[23−26]

The free dimethylsulfone $\nu_s(SO_2)$ mode at about 1130 cm⁻¹ was used in order to indicate the stoichiometry and structure of the coordination compound. The $\nu_s(SC_2)$ band at 695 cm⁻¹ was used as a reference insofar as its linear intensity is assumed to be unaffected by complexation. The intensity ratio $I(\nu_s(SO_2)\text{-free})/I(\nu_s(SC_2))$ was calculated for pure sulfone and for solution e. Its value is 0.321 for pure sulfone and 0.222 for solution e.

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Table 2: Amounts of $AlCl_4^-$ (mol/kg of $DMSO_2$) Worked out from Relative Intensity (Linear I and Integrated A) of the 347 cm^{-1} Raman Line for Solutions b−e at 400 K

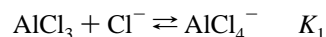| solution	I_{347}/I_{293}	$nAlCl_4^-$ (mol)	A_{347}/A_T	$nAlCl_4^-$ (mol)	$nAlCl_4^-$ expected (mol)
b	1.1	0.8	0.25	0.78 ± 0.05	0.75
c	1.4	1.0	0.32	1.00	1.00
d	2.9	2.1	0.53	1.70 ± 0.10	1.75
e	5.4	3.9	1.07	3.30 ± 0.30	3.00

Assuming that the 0.321 value corresponds to 100% of the free sulfone, the 0.222/0.321 ratio value allowed us to conclude that solution e contains 69% of the free sulfone and attributes the value of 3 to n (3.3 calculated). Another way to indicate the stoichiometry of the coordination compound is to calculate the intensity ratio between $\nu_s(SO_2)$ with a free $DMSO_2$ at 1130 cm^{-1} and a $\nu_s(SO_2)$ with an Al-bonded $DMSO_2$ at 1160 cm^{-1}, as far as the polarizability of $\nu_s(SO_2)$ in the two entities is assumed to be the same. The experimental ratio deduced from Raman spectra is 2.5. This value is in agreement with the theoretical value of 2.53, assuming $n = 3$ (7.6/3 = 2.53). This n value justifies that no splitting can be observed for solution b: indeed, with a molar ratio $AlCl_3/DMSO_2$ of 0.094, only 7% of the sulfone coordinates; the lines of the coordination compound cannot emerge from the free solvent ones and appear only as shoulders.

The coordination compound $Al(DMSO_2)_3^{3+}$, must be similar to those obtained with dimethyl sulfoxide,[27,28] or with propylene carbonate[29] ($Al(DMSO)_6^{3+}$ or $Al(PC)_6^{3+}$). It is assumed to be an octahedral complex like that formed between Co^{2+} ions and dimethylsulfone.[26] The two bands at 245 and 409 cm^{-1} on the Raman spectrum of solution e are in accordance with the formation of such a complex between $DMSO_2$ and Al^{3+} ions. This might be due to the bending and the stretching Al−O cage vibrations respectively. Besides, $\nu(Al-O)$ is observed at about 545 cm^{-1} for dimethyl sulfoxide complex.[27] The lower wavenumber of the sulfone complex indicates, as expected, a weaker coordination strength with $DMSO_2$. The stoichiometry of this complex indicates that sulfone acts as a bidentate ligand. However, in this case, the S−O distance, 1.45 Å,[30] leads to a strongly distorted octahedral neighborhood for the Al^{3+} ion. Furthermore, the OSO angle of the coordinated sulfone is certainly larger than that of the free sulfone. This larger OSO angle can explain why the coordination slightly increases the $\nu_s SO_2$ wavenumber, contrary to the behavior usually observed, as for monodentate coordinated dimethyl sulfoxide.[23]

In order, to confirm the n value, $AlCl_4^-$ amounts in solutions b to e were quantitatively estimated from the intensity of the strong Raman line at 347 cm^{-1}, $\nu_1(A_1)$, which is approximately proportional to the mole fraction of this species.[22] Two calculations were made to minimize the experimental deviations. First, the linear intensity of $\nu_1(A_1)$ (I_{347}) was compared to that of $\delta(SC_2)$ at 293 cm^{-1} (I_{293}). $\delta(SC_2)$ at 293 cm^{-1} is assumed to be constant and is consequently used as a reference. Second, the integrated intensity of $\nu_1(A_1)$ (A_{347}) was determined and the ratio A_{347}/A_T calculated; A_T represents the total integrated intensity of the three bands at 293, 313, and 375 cm^{-1} taken as a whole. This procedure avoids hypothetical variations due to complexation. The results are reported in Table 2 for solutions b−e. Solution c was taken as a reference as it is assumed to contain 1 mol of $AlCl_4^-$/kg of $DMSO_2$. Its ratio values were compared with those obtained for the other solutions (b, d, e) in order to determine their $AlCl_4^-$ content. These $AlCl_4^-$

contents were then compared to the theoretical contents with $n = 3$, taking into account the initial composition in $AlCl_3$ and LiCl. For solution b, the two $AlCl_4^-$ contents deduced from experimental data are in agreement with the theoretical value. For the other solutions, experimental data are more dispersed but the $AlCl_4^-$ contents deduced from the A_{347}/A_T ratio compare well with the theoretical values. The results are in favor of the chemical reaction mentioned above and show that in the presence of dimethylsulfone, aluminum chloride transforms into $AlCl_4^-$ in a wide range of concentrations.

The Raman study we performed shows that (i) $AlCl_4^-$ is always present even when no LiCl is added to the melt, (ii) $Al_2Cl_7^-$ is never observed, and (iii) the complex $Al(DMSO_2)_3^{3+}$ is observed for a molar ratio $AlCl_3/LiCl$ which is greater than one. $DMSO_2$ is therefore found to act as a Lewis base weaker than Cl^- but stronger than $AlCl_4^-$ leading to the following equilibria in $DMSO_2$-based electrolytes:

$$AlCl_3 + Cl^- \rightleftarrows AlCl_4^- \qquad K_1$$

$$AlCl_3 + {}^3/_4 DMSO_2 \rightleftarrows {}^1/_4 Al(DMSO_2)_3^{3+} + {}^3/_4 AlCl_4^- \qquad K_2$$

Judging from our results on the Al^{3+} complex and $AlCl_4^-$ amounts, these equilibria are completely displaced to the right: $K_1 \gg K_2 \gg 1$.

The $Al(DMSO_2)_3^{3+}$ complex is analogous to $Al(PC)_6^{3+}$ or $Al(DMSO)_6^{3+}$ In fact, in each case, Al^{3+} is in an octahedral neighborhood of six oxygen atoms. However, the electrochemical behavior of the $DMSO_2$ complex differs from the two other complexes: while aluminum deposition is possible from the former,[12,13] the latter are not reducible.[31] By comparing complexes obtained from $DMSO_2$ and DMSO, this can be partially explained in terms of donor number. DMSO has a donor number value 29.8;[32] the $DMSO_2$ donor number value might be close to the one of tetramethylenesulfone, $TMSO_2$, 14.8.[32] Guttman showed that in most of the systems (M^{n+})-solv $+ ne^- \leftrightarrows M^0$, the greater the donor number of the solvent, the more negative the standard potential.[32] For example, a potential shift of 0.6 V between $TMSO_2$ and DMSO was reported for the Tl^+/Tl system. Nevertheless, this explanation is insufficient in the case of the Al^{3+} complex formed with PC whose donor number value is 15.1. As a matter of fact, the main difference seems to come from the coordination number of Al^{3+} which is 3 in $DMSO_2$ while it is 6 in DMSO and PC complexes. This implies a greater stabilization of the latter complexes in comparison with the $DMSO_2$ complex. Moreover, the electrochemical behavior of the $Al(DMSO_2)_3^{3+}$ species can also be explained by steric effects. In fact, the $DMSO_2$ molecule contains two S=O bonds; the approach by the two oxygen atoms of each of the three $DMSO_2$ molecules required for complexing Al^{3+} is therefore hindered because of OSO angular strains. So, the three $DMSO_2$ molecules will remain relatively far from Al^{3+}, implying a weak coordination complex. Contrary to $DMSO_2$, PC and DMSO do not encounter any similar strains and their oxygen atoms will be able to form strong coordination links with Al^{3+}. These strong Al−O links prevent the complexes so formed from being electrochemically reducible to metallic aluminum.

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