Conductometric study of the composition of AlCl₃—LiAlH₄ electrolyte in tetrahydrofuran

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Solution consisting of $LiAlH_4$ and $AlCl_3$ in tetrahydrofuran is suitable electrolyte for aluminium electrodeposition. The components of the solution undergo chemical reaction the products of which are ionized particles: Li^+ cation and complex anions of the general formula $AlCl_mH_{4-m}^-$, m being given by the mole ratio of both components. The conductance of the mixed solution is therefore higher than that of the single components solution. The maximum conductance is reached at the mole ratio $2LiAlH_4 : AlCl_3$ where the optimum anionic complex formation occurs. The excess of $AlCl_3$ over this ratio causes more remarkable decrease in conductance than the excess of $LiAlH_4$. Aluminium exists in this solution dominantly in the form of anions and neutral molecules. Increase in the total electrolyte concentration results, at the suitable mole ratio of the components, in a linear increase of the conductivity.

Раствор, состоящий из $LiAlH_4$ и $AlCl_3$ в тетрагидрофуране является подходящим электролитом для электроосаждения алюминия. Компоненты раствора претерпевают превращения, продуктами которых являются заряженные частицы: катион Li^+ и комплексные анионы с общей формулой $AlCl_mH_{4-0}^-$, в которой m определяется молярным отношением обоих компонентов. Электропроводность смешанного раствора, таким образом, оказывается выше, чем растворов каждого компонента в отдельности. Максимальная электропроводность достигается при молярном соотношении $2LiAlH_4 : AlCl_3$, при котором наблюдаются оптимальные условия для образования анионных комплексов. Избыток $AlCl_3$ вызывает более значительное уменьшение электропроводности, чем избыток $LiAlH_4$. Алюминий присутствует в растворе главным образом в виде анионов и нейтральных молекул. Повышение общей концентрации электролита приводит, при подходящем молярном соотношении компонентов, к линейному росту электропроводности.

The reaction between $AlCl_3$ and $LiAlH_4$ in diethyl ether was first used by *Schlesinger* [1] for aluminium hydride (alan) preparation according to the formula

$$3LiAlH_4 + AlCl_3 \quad \leftrightarrow \quad 4AlH_3 + 3LiCl \qquad (A)$$
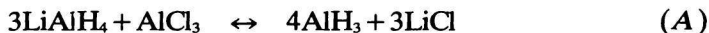
The reaction mixture has been applied as very strong reducing agent the reducing power of which could be modified and specifically directed by changing the mole ratio of both components.

Conductometric studies were carried out in order to reveal the ionization equilibria in the solution [2, 3]. The conductance of the $AlCl_3$ solution in diethyl ether is extremely low. It increases after adding $LiAlH_4$ and reaches maximum at a mole ratio $LiAlH_4 : 2AlCl_3$. The actual conductivity value in the maximum is rather low: in 0.5 molar solution it has the value 0.36 mS cm^{-1}. Further increase in the $LiAlH_4$ concentration up to the mole ratio $3LiAlH_4 : AlCl_3$ causes the precipitation of LiCl (see reaction (A)) and after few hours the precipitation of AlH_3 [4]. After overreaching this ratio, the conductance starts to increase again.

The $LiAlH_4$—$AlCl_3$—diethyl ether solution has also been studied and used as electrolyte for electrodeposition of aluminium [5—9].

Diethyl ether was later substituted by less volatile and inflammable tetrahydrofuran (THF) with higher relative permittivity [10, 11]. In THF solution $LiAlH_4$ forms solvated cations $Li(THF)_4^+$ and anions AlH_4^- [12]. Free ions exist in solution only at low concentration — up to 10^{-5} molar $LiAlH_4$. Doublets and triplets formation occurs at higher concentration with hydrogen bond between AlH_4^- hydrogen and THF oxygen in $Li(THF)_4^+$ [13]. The conductivity of 0.5 molar solution of $LiAlH_4$ in THF reaches the value of approximately 5 mS cm^{-1}. $AlCl_3$ in THF at the same 0.5 molar concentration level shows ten times lower conductivity [14]. In comparison with the diethyl ether solution of $AlCl_3$ it is much higher — about two orders — but still, it cannot be regarded as electrolyte. This is in agreement with earlier observations [15] on $AlCl_3$ dissolution in THF in the form of covalent monomer.

Yoshio et al. [16] studied conductometrically the solution of both $LiAlH_4$ and $AlCl_3$ in THF, with equimolar concentration of the components and with excess of $AlCl_3$. They observed an increase in the conductivity value with increasing $AlCl_3$ concentration.

In the present work, the conductivity of the $AlCl_3$—$LiAlH_4$ solution in THF has been studied with changing the mole ratio of both components. The measurements by *Yoshio et al.* [16] have also been repeated but not verified in the whole extent. The experiments were carried out also in solutions with excess of $LiAlH_4$ with regard to their possible application in the galvanic industry.

Experimental

All experiments had to be realized in inert atmosphere due to the vigorous reaction of $LiAlH_4$ with water and hydrolysis of $AlCl_3$. The inert gas, argon or nitrogen, as well as THF and $AlCl_3$ purification was described in [17]. $LiAlH_4$ was used without further purification. The preparation and analytical control of the mixed solutions were described in [18]. The conductance measurements were realized with the Radelkis OK 102/1 Conductometer. The

conductance electrode OK 902 was sealed directly into the conductance cell adapted for measurements in inert atmosphere. All experiments were carried out at the constant temperature $25 \pm 0.1°C$.

The change of the solution composition was realized by dilution of the most concentrated electrolyte measured either by THF itself or by a solution of one of the components, LiAlH$_4$ or AlCl$_3$ in THF. In this way, either the ratio of both components or the concentration of one of them was kept constant.

Results and discussion

The results were treated by plotting the conductivity against the electrolyte concentration or by plotting molar conductivity which, in this case, was calculated as conductivity to total Al concentration against the solution composition.

In Fig. 1, the molar conductivity change with increasing mole ratio of LiAlH$_4$ and AlCl$_3$ can be seen. Curve *1* represents the change of molar conductivity with increasing excess of LiAlH$_4$ whereas curve *2* with increasing excess of AlCl$_3$ in the solution. The molar conductivity of the solution increases at first with increasing mole ratio in both cases up to the ratio value 2LiAlH$_4$: AlCl$_3$. Further change in the solution composition in either direction, *i.e.* when increasing the AlCl$_3$ or LiAlH$_4$ concentration, leads to a decrease in molar conductivity which is more remarkable in the former case (curve *2*) than in the latter one (curve *1*).
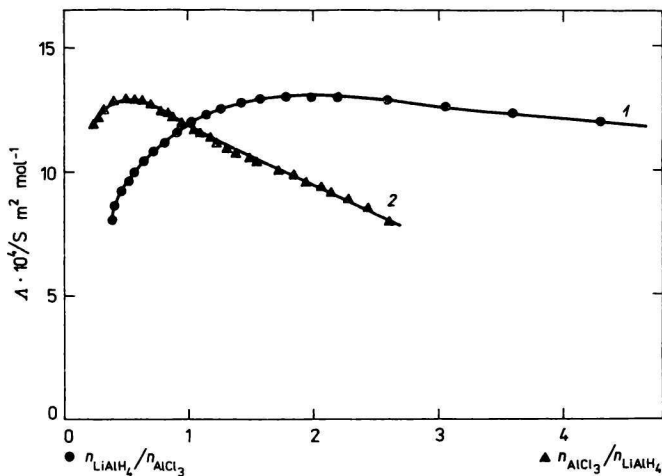

Fig. 1. Change of the molar conductivity of the AlCl$_3$—LiAlH$_4$—THF solution with the mole ratio of LiAlH$_4$ and AlCl$_3$.

1. Increasing molar excess of LiAlH$_4$ over AlCl$_3$; *2.* increasing molar excess of AlCl$_3$ over LiAlH$_4$.

The initial increase in the molar conductivity points out the fact that the presence of both components in the solution results in formation of ionic particles. The following set of equations describes the ionization processes

$$LiAlH_4 + AlCl_3 \quad \leftrightarrow \quad 2AlH_2Cl + LiCl \tag{Ba}$$

$$AlH_2Cl + LiCl \quad \leftrightarrow \quad LiAlH_2Cl_2 \tag{Bb}$$

$$LiAlH_2Cl_2 \quad \leftrightarrow \quad Li^+ + AlH_2Cl_2^- \tag{Bc}$$

$$LiAlH_4 + 3AlCl_3 \quad \leftrightarrow \quad 4AlHCl_2 + LiCl \tag{Ca}$$

$$AlHCl_2 + LiCl \quad \leftrightarrow \quad LiAlHCl_3 \tag{Cb}$$

$$LiAlHCl_3 \quad \leftrightarrow \quad Li^+ + AlHCl_3^- \tag{Cc}$$

In the (B) set of reactions, one half of the total aluminium concentration is ionized whereas in the (C) set it is only one quarter. Thus, the amount of ionic particles in solution is given basically by the LiAlH_4 concentration.

The formation of ionic particles by the reaction of chloro- and dichloroalans with LiCl according to eqns (Bb, Bc) and (Cb, Cc) is not the only source of ionic particles in solution. Both compounds undergo disproportionation reaction according to the scheme

$$2AlH_2Cl \quad \leftrightarrow \quad AlH_2^+ + AlH_2Cl_2^- \tag{D}$$

$$2AlHCl_2 \quad \leftrightarrow \quad AlHCl^+ + AlHCl_3^- \tag{E}$$

The maximum in the molar conductivity curve at the mole ratio $2LiAlH_4 : AlCl_3$ may be ascribed to the fact that at this ratio the chloroalan and the dissociated Li complex described by eqns (B) can still be formed but by further increase in LiAlH_4 concentration the formation of AlH_3 according to eqn (A) takes place. This compound is neither ionized nor forms ionic particles with other component in the THF solution similarly as in diethyl ether [19].

After the mole ratio of LiAlH_4 and AlCl_3 exceeds 3 the whole AlCl_3 in the solution is used in reactions (A), (B), and (C). LiAlH_4 remaining in the solution keeps the molar conductivity at roughly constant level, represented by curve 1 in Fig. 1, given by the ionization of LiAlH_4 [12] according to the equation

$$LiAlH_4 + 4THF \quad \leftrightarrow \quad Li(THF)_4^+ + AlH_4^- \tag{Fa}$$
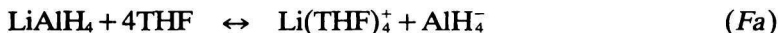
or at higher LiAlH_4 concentrations

$$3LiAlH_4 \quad \leftrightarrow \quad LiAlH_4Li^+ + AlH_4LiAlH_4^- \tag{Fb}$$

The multiplet ions formation may explain the small decrease in molar conductivity seen in this part of the curve 1.

The molar conductivity of the solution with mole ratio of AlCl₃ and LiAlH₄ exceeding 0.5 represented by the decreasing part of the curve *2* in Fig. 1 is completely in accordance with the statement about the prevailing covalent monomers formation in the AlCl₃ dissolution process in THF [15].

The particles existing in the solution at various mole ratios of LiAlH₄ and AlCl₃ are summarized in Table 1. Small amounts of $AlCl_2^+$ and $AlCl_4^-$ ions in AlCl₃

<p align="center">Table 1</p>

<p align="center">Summary of particles occurring in the LiAlH₄—AlCl₃—THF solution</p>

Mole ratio of AlCl₃ and LiAlH₄	Compounds	Ions
AlCl₃ only more than 3:1	AlCl₃	small amount of $AlCl_2^+$, $AlCl_4^-$
3:1	AlHCl₂	$AlHCl_3^-$ $Li(THF)_4^+$
1:1	$\hat{A}lH_2Cl$	$AlH_2Cl_2^-$ $Li(THF)_4^+$
1:3	AlH₃, LiCl	—
more than 1:3 LiAlH₄ only	LiAlH₄	$Li(THF)_4^+$ AlH_4^- $LiAlH_4Li^+$ $AlH_4LiAlH_4^-$

solution in THF come from the disproportionation reaction according to the equation [14]

$$2AlCl_3 \leftrightarrow AlCl_4^- + AlCl_2^+ \qquad (G)$$
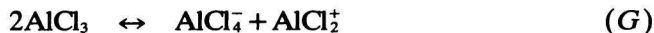
which is shifted strongly to the left.

The reactions (*A*) to (*E*) are equilibrium reactions. The change of the solution composition is obviously continuous: at a given mole ratio of LiAlH₄ and AlCl₃ the reactants and products of more reactions exist together in the solution. This is confirmed by the fact that no breaks can be seen in the molar conductivity to mole ratio plot in Fig. 1.

The conductivity of the LiAlH₄ + AlCl₃ solution in THF in dependence on the total Al concentration can be seen in Fig. 2. The mole ratio of both components is kept constant. The conductivity increases almost linearly up to the total Al concentration 0.8 mol dm⁻³. This shows that the total electrolyte concentration
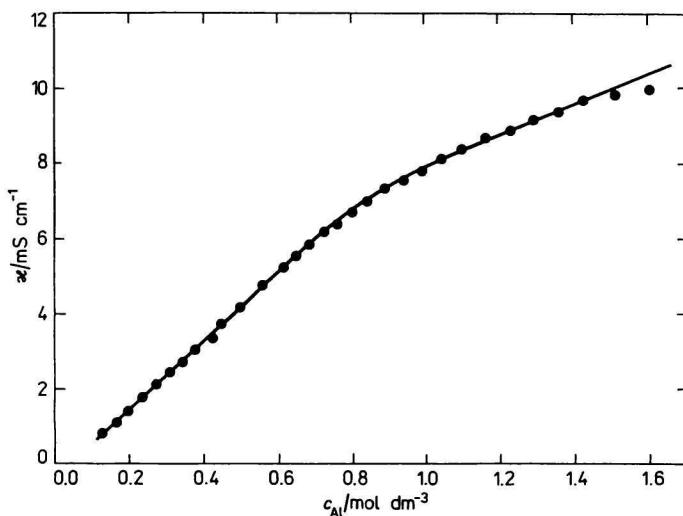
Fig. 2. Dependence of the conductivity of the $AlCl_3$—$LiAlH_4$—THF solution upon the total Al concentration.

exhibits smaller effect upon the change of the solution conductivity than the mole ratio of the components.

Worth noticing is that aluminium in this solution exists predominantly in the form of anions and neutral molecules. This fact was observed also in experiments carried out in order to determine the transference numbers in this electrolyte [20] and later respected in the interpretation of the electrode mechanism of the aluminium deposition process.

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