Study of aluminium halides in nonaqueous solvents. II. Effect of the excess of free halides

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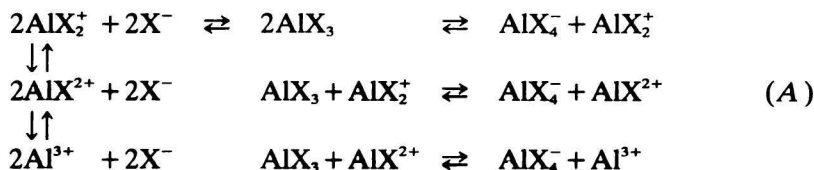
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Attention is paid to the influence of an excess of free chloride and bromide ions on the solutions of $AlCl_3$ and $AlBr_3$ in acetonitrile. The polarographic study showed no essential changes in the polarographic record when identical halides were added. The addition of bromide ions to $AlCl_3$ solution causes a remarkable positive shift of the half-wave potential of $AlCl_3$. The addition of chloride ions to $AlBr_3$ solution results in a total elimination of the negative wave of $AlBr_3$. These effects are discussed from the point of view of ionization and complex formation equilibria of the investigated systems.

Изучается влияние избытка свободных хлоридных и бромидных ионов на растворы $AlCl_3$ и $AlBr_3$ в ацетонитриле. Полярографическое исследование показало, что присутствие родственных галогенид-ионов не вызывает значительного изменения поляризационной кривой. Добавление бромидных ионов к $AlCl_3$ вызывает сдвиг потенциала полуволны в сторону положительных значений. Добавление хлоридных ионов к $AlBr_3$ вызывает полное устранение отрицательной волны $AlBr_3$. Эти эффекты обсуждаются с точки зрения ионизационных и комплексных равновесий данных систем.

In the previous paper of this series [1] the basic polarographic characteristics of aluminium halides solutions in acetonitrile and tetrahydrofuran were given and the stability of the systems with time was also studied. The equilibria formed in the dissolution process of aluminium halides in acetonitrile were discussed. With respect to the dissociation of halides as well as to the so-called self-ionization effect [2] the following reaction scheme was suggested

$$
\begin{array}{ccccc}
2AlX_2^+ + 2X^- & \rightleftarrows & 2AlX_3 & \rightleftarrows & AlX_4^- + AlX_2^+ \\
\updownarrow & & & & \\
2AlX^{2+} + 2X^- & & AlX_3 + AlX_2^+ & \rightleftarrows & AlX_4^- + AlX^{2+} \quad (A) \\
\updownarrow & & & & \\
2Al^{3+} + 2X^- & & AlX_3 + AlX^{2+} & \rightleftarrows & AlX_4^- + Al^{3+}
\end{array}
$$

(X denotes a halide.)

Abbreviations:
BDCI   Bis(diphenyl)chromium(I) iodide.
TEABr   Tetraethylammonium bromide.
TEACl   Tetraethylammonium chloride.
TEAOH   Tetraethylammonium hydroxide.

An excess of identical or different free halide ions was added to the AlCl₃ and AlBr₃ solutions in order to investigate the shift of equilibria and competitive equilibria formation between the respective halides. The electrochemical method of investigation enabled us to follow at the same time the relationship between the solution composition and its electrochemical properties.

Experimental

The apparatus, the preparation of aluminium halides and basic electrolytes, the purification of the solvents as well as drying and purification of the inert gas has been described in detail in [1].

Tetraethylammonium bromide (TEABr) was purified by shaking with active charcoal, crystallized from a mixture of acetone and methanol and finally dried in a vacuum drier.

Tetraethylammonium chloride (TEACl) was prepared from TEABr by converting it to hydroxide, TEAOH, by means of the ion exchanger DOWEX 1X8 200—400 mesh. Hydroxide was neutralized with HCl and recrystallized from water and from a water—ethanol mixture. Finally it was dried in a vacuum desiccator over magnesium perchlorate.

In order to avoid errors arising from different junction potentials between the reference aqueous saturated calomel electrode and various nonaqueous media, all the measured half-wave potentials were corrected to the value of the pilot ion reduction half-wave potential. As such compound, bis(diphenyl)chromium(I) iodide (BDCI) was taken the potential of which was considered as being equal to zero. These half-wave potential values are denoted as $E_{1/2\,corr}$.

Results

In the present work, the changes of the half-wave potential and limiting current values of aluminium chloride and aluminium bromide solutions in acetonitrile were investigated in the presence of TEACl and TEABr. In some cases, the limiting current dependence upon the mercury reservoire height was studied in order to explain the character of the limiting current.

The basic concentration of both aluminium halides used was 5×10^{-4} mol l   All polarograms were

Table 1

Changes of the half-wave potential and limiting current of AlCl₃
in acetonitrile in an excess of free chloride
Concentration of AlCl₃: 5×10^{-4} mol l⁻¹

Molar ratio AlCl₃ : TEACl	Concentration of TEACl mol l⁻¹	$E_{1/2\,corr}$ V	i A 10⁶
1 : 0	0	−0.395	2.20
1 : 1	5×10^{-4}	−0.390	2.25
1 : 3	1.5×10^{-3}	−0.385	2.40
1 : 6	3×10^{-3}	−0.395	2.84

recorded at least six times with regard to the relatively low reproducibility of the limiting currents. The reported values of the half-wave potentials and limiting currents are arithmetic means of all six measurings.
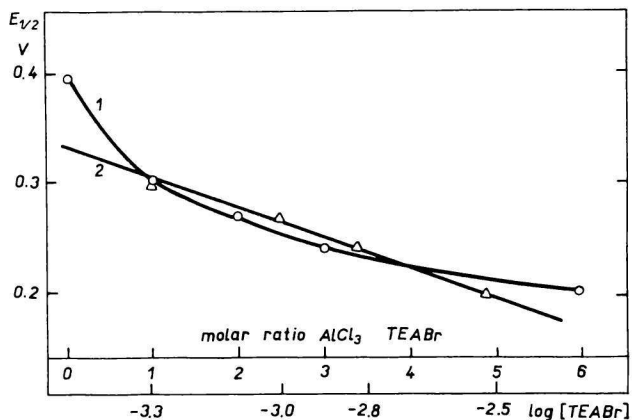

Fig. 1. Influence of free bromide ions addition to the half-wave potential of $AlCl_3$ in acetonitrile.
$AlCl_3$ concentration: 5×10^{-4} mol l^{-1}
1. The shift of $E_{1/2}$ with the change of molar ratio $AlCl_3$: TEABr; *2.* the shift of $E_{1/2}$ with the logarithm of Br^- concentration.

In Table 1 the values of the half-wave potential and limiting current changes of $AlCl_3$ solution in acetonitrile caused by the addition of free chlorides are given. The molar ratios are related to the $AlCl_3$ concentration. The half-wave potential of $AlCl_3$ in acetonitrile in the presence of free Cl^- ions changes only in the limits of experimental errors. The limiting current increases slightly with increasing chloride excess.

Table 2

Changes of the half-wave potentials and limiting currents
of both polarographic waves of $AlBr_3$ in acetonitrile in an excess
of free bromide
Concentration of $AlBr_3$: 5×10^{-4} mol l^{-1}

Molar ratio $AlBr_3$: TEABr	Concentration of TEABr mol l^{-1}	$E_{1/2 \, pos \, corr}$ V	$E_{1/2 \, neg \, corr}$ V	i_{pos} A 10^6	i_{neg} A 10^6	i A 10^6
1:0	0	−0.230	−0.630	2.0	3.5	5.5
1:1	5×10^4	−0.210	−0.690	2.1	3.5	5.6
1:2	10^{-3}	−0.200	−0.700	2.4	3.3	5.7
1:3	1.5×10^{-3}	−0.190	−0.720	2.3	3.25	5.55
1:4	2×10^{-3}	−0.195	−0.750	2.3	3.2	5.5
1:5	2.5×10^{-3}	−0.185	−0.755	2.5	3.05	5.55
1:6	3×10^{-3}	−0.175	−0.765	2.3	3.3	5.6

The situation changes when bromide ions in the form of TEABr are added to the AlCl₃ solution in acetonitrile. The half-wave potential shifts remarkably towards the positive values. Already at an equimolar excess of bromide the half-wave potential shifts positively by 115 mV, at a six-fold bromide excess the positive shift reaches 200 mV. The dependence of the AlCl₃ half-wave potential change on the bromide concentration is shown in Fig. 1. The limiting current of AlCl₃ shows no changes with an increasing bromide concentration.
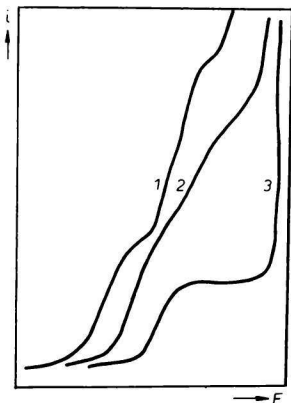

Fig. 2. Schematic diagram of the influence of free chloride ions addition on the polarographic record of AlBr₃ in acetonitrile.
1. AlBr₃ without addition of chloride; 2. AlBr₃ + TEACl in molar ratio 1 : 1; 3. AlBr₃ + TEACl in molar ratio 1 : 4.

The influence of an excess of bromide ions upon the reduction of AlBr₃ in acetonitrile is summarized in Table 2. It can be said that by an increasing bromide ions concentration (in the form of TEABr) the half-wave potential of the positive wave shifts towards the positive values and the half-wave potential of the negative wave shifts negatively. The limiting current of the positive wave increases on the account of the negative one; the sum of both waves remains unchanged. The study of the limiting current dependence on the mercury reservoire height showed the diffusion character of the sum of both waves in the whole TEABr concentration range investigated.

The addition of chloride ions as TEACl to the solution of AlBr₃ in acetonitrile causes even at an equimolar excess with respect to the AlBr₃ concentration such a remarkable deformation of the negative wave that its half-wave potential cannot be evaluated. At a four-fold excess of Cl⁻ ions the negative wave disappears completely. The effect is schematically illustrated in Fig. 2.

Discussion

The scheme (A) given in the introductory part includes all consecutive equilibria of the halides dissociation and self-ionization. The solvation of ions is not included in the equation.

The presence of TEACl in the AlCl₃ solution in acetonitrile causes no significant shift in the half-wave potential, but only an increase of the limiting current. As the limiting current in this concentration range is diffusion controlled, this increase may result from an increasing bulk concentration of the reducing particles. Free chloride ions shift the equilibrium of the reaction (A) to the right and cause the bulk concentration of the AlCl₄⁻ ions to increase. The bulk concentration of the

positive particles, on the other hand, decreases in order to preserve a constant overall concentration of aluminium in the solution.

All the given experimental facts lead to the conclusion that the reducing particle in an $AlCl_3$ polarographic reduction wave in acetonitrile is most likely the $AlCl_4^-$ anion. This assumption is also confirmed by the $AlBr_3$ reduction in acetonitrile in the presence of an excess of TEABr. The limiting current of the positive wave increases and the limiting current of the negative wave decreases as compared to the solution with no excess of TEABr. The explanation is as follows: the addition of free bromide ions shifts the equilibrium of the reaction (A) to the right which results in an $AlBr_4^-$ anion concentration increase and therefore also in an increase of the positive wave height. The concentration of the positive $AlBr_n^{(3-n)+}$ particles decreases; these are the particles reduced in the negative wave, therefore a decrease of the negative wave limiting current follows.

Since the halide excess is added in the form of an adsorbable tetraethylammonium salt, a possible adsorption of the TEA^+ cation in the double layer and the subsequent change in the electrode potential is to be considered [3]. This fact may also contribute to the shift of the polarographic potentials of AlX_3 waves in acetonitrile. The positive shift of the positive wave of $AlBr_3$ (see Table 2) confirms the above assumption of anion particle which is reduced in this wave.

The addition of a sufficient amount of chloride ions to the $AlBr_3$ solution in acetonitrile (four-fold molar excess) causes a total disappearance of the negative wave. At the same time, the positive wave potential remains unchanged (see Fig. 2). This is obviously caused by substitution of bromide for chloride according to the reaction

$$AlBr_n^{(3-n)+} + n\,Cl^- \quad \rightleftarrows \quad AlCl_n^{(3-n)+} + n\,Br^- \tag{B}$$
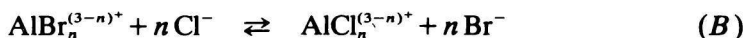
The formed particle is not reducible polarographically under given experimental conditions which is in accordance with the experimental finding that $AlCl_3$ is reduced in acetonitrile in a single wave. The substitution described by eqn (B) concerns only positive particles on both sides of eqn (A). Therefore neither the equilibrium is shifted nor the $AlBr_4^-$ particles concentration is changed. The substitution in the negative particles, e.g. of bromide anion for chloride in the $AlBr_4^-$ complex is hindered by the electrostatic repulsion forces; due to this fact, the positive wave corresponding to the $AlBr_4^-$ reduction remains unchanged.

References

1. Gálová, M. and Lux, L., *Chem. Zvesti* **29**, 279 (1975).
2. Gutmann, V., *Coordination Chemistry in Non-Aqueous Solutions.* Springer-Verlag, Wien, 1968.
3. Hayter, J. B. and Hunter, R. J., *J. Electroanal. Chem.* **37**, 71 (1972).

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