

# The study of aluminium halides in nonaqueous solvents. I. Basic polarographic characteristics

M. GÁLOVÁ and L. LUX

*Department of Chemistry, Faculty of Metallurgy, Technical University,  
043 85 Košice*

Received 11 September 1974

Accepted for publication 5 December 1974

The aluminium halides were polarographically investigated in acetonitrile and tetrahydrofuran. Their stability with time and their basic polarographic characteristics were determined. The half-wave potentials of the studied systems in tetrahydrofuran are approximately by 700 mV more negative than in acetonitrile. The stability of aluminium halides is greater in acetonitrile than in tetrahydrofuran and in both solvents decreases with increasing halide radius.

Полярграфически изучались галогениды алюминия в ацетонитриле и тетрагидрофуране. Определились их основные полярграфические константы, а также их устойчивость со временем. Потенциал полуволны изучаемых систем в тетрагидрофуране приблизительно на 700 мВ отрицательнее, чем в ацетонитриле. Устойчивость галогенидов алюминия выше в ацетонитриле, чем в тетрагидрофуране и в обонх растворителях понижается с увеличением радиуса галогена.

The aluminium(III) ions form strong aqua complex  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  which makes the direct deposition of aluminium from aqueous solutions rather difficult [1]. Electroplating by aluminium from aqueous solutions is accompanied with hydrogen evolution and thus with poor quality of the deposit. This was one of the reasons for applying various organic media in the electrodeposition studies of aluminium and similar elements. Several of industrial patents, mainly in USA, are devoted to this problem. However, the basic relations between the solution composition and the electrochemical properties remain unexplored. The aim of this work was the study of aluminium halides in organic media from the above-mentioned point of view.

## Experimental

Three-electrode system was used for measurements in the organic solvents: DME as a working electrode, platinum wire as a counter electrode, and aqueous SCE as a reference. The DME characteristics were as follows: the mercury reservoir height  $h = 73$  cm, the drop time  $t_1 = 4.5$  s, and the flow rate of mercury  $m = 2.3$  mg s<sup>-1</sup>.

Owing to an unknown and varying junction potential value between the water and organic phase, the comparison of the measured potential values in different solvents

is almost impossible. In order to avoid this difficulty, a so-called pilot ion, bis(diphenyl)-chromium(I) iodide was applied (hereafter referred to as BDCI). Due to its small charge, large ionic radius and high symmetry, the assumption can be made of negligible solvation and thus of small differences in its reduction potential values in various solvents. The half-wave potential of the pilot ion mentioned is  $-0.625$  V *vs.* SCE in dimethylformamide. This value was chosen as reference.

The polarographic measurements were carried out on a Radelkis OH-102 polarograph. Supporting electrolytes used were lithium perchlorate, tetraethylammonium perchlorate (TEAP) and in the case of the microcoulometric determination of the charge number of the electrochemical reaction it was tetrabutylammonium perchlorate (TBAP). The water from the lithium perchlorate was removed by melting in an electrical furnace at  $350^{\circ}\text{C}$ , followed by crushing and drying in vacuum oven for 48 hrs. The preparation of TEAP was already described [2].

Due to the high reactivity of the studied aluminium halide systems towards water, all solutions were prepared in an inert atmosphere of dried argon or nitrogen. For these preparations, partly an adapted drying box originally used for work with radioactive material and partly the vacuum-line securation technique was applied [3]. Immediately before taking a polarographic record, nitrogen or argon was passed through the electrolytic vessel for 5–10 min. Before entering the vessel, the respective inert gas was passed through a column with copper catalyst for removing oxygen, then through a column with molecular sieves Nalsit 4 for removing water, and finally saturated by the solvent under investigation.

Acetonitrile (Malinkrodt) was purified according to the adapted method of *Baucke et al.* [4]. Tetrahydrofuran was distilled twice with metallic sodium, then refluxed with calcium hydride and metallic sodium again and distilled in dried nitrogen atmosphere with metallic sodium.

Aluminium chloride, anal. grade (Merck) was purified by doubled sublimation in dried nitrogen. Aluminium bromide was prepared from the bromine and metallic aluminium and then purified by distillation under reduced pressure with aluminium spoons in dried nitrogen [5]. Aluminium iodide was prepared by direct reaction of an excess of metallic aluminium with iodine at increased temperature in sealed tubes.

## Results

### *The stability of aluminium halides in acetonitrile and tetrahydrofuran solutions*

The stability of aluminium halides in the studied solvents was followed by two lines. First, the dissolution reaction of the halide itself in the solvent in the preparation of a stock solution was observed visually. Second, the stability of the depolarizer with time after dilution of the stock solution of halide by the supporting electrolyte was followed polarographically.

The stock solution of  $10^{-1}$  molar  $\text{AlCl}_3$  in acetonitrile is stable for several days. After dilution by the supporting electrolyte to the concentration of approximately  $2 \times 10^{-4}$  M- $\text{AlCl}_3$  no change of the polarographic wave height and potential is recorded with time. Contrary to this, in aqueous solutions a shift of the half-wave potential to the negative region with time was observed [1, 6].  $\text{AlBr}_3$  is less stable: approximately 24 hrs after dissolution  $10^{-1}$  molar stock solution of  $\text{AlBr}_3$  in acetonitrile gets brownish coloured. After dilution by the supporting electrolyte to the concentration  $2 \times 10^{-4}$  M of  $\text{AlBr}_3$ , the first polarographic record taken 2 min after dilution

shows two waves; in the following record taken 6 min after dilution the height of the two waves lowers. After this time, no further changes occur in the wave heights as can be clearly seen in Fig. 1. This time effect was in further experiments eliminated by recording all polarograms with fresh stock solution of  $\text{AlBr}_3$  9 min after mixing with the supporting electrolyte.

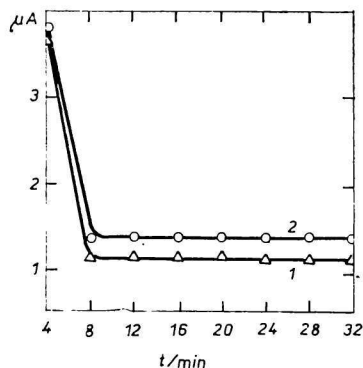


Fig. 1. The change of the limiting current of the polarographic waves of  $\text{AlBr}_3$  in acetonitrile with time. Concentration of  $\text{AlBr}_3$   $10^{-3}$  M.

1. Negative wave; 2. positive wave.

The dissolution reaction of aluminium iodide in acetonitrile is rather violent, accompanied by an increase of temperature and fast colouring of the solution. For this reason, a stock solution of aluminium iodide with defined concentration of the solute could not be prepared. The experiments were carried out with the corresponding amount of aluminium iodide dissolved directly in the supporting electrolyte. Curve 1 in Fig. 2 was recorded after a time interval passed between the dissolution of the solid  $\text{AlI}_3$  and polarization of the electrode to the reduction potential required. The curves 2, 3, and 4 are recorded in 4 min intervals. The first record shows one positive wave at the potential of  $-0.55$  V — this wave could most likely be attributed to the depolarization of oxygen absorbed in the solid

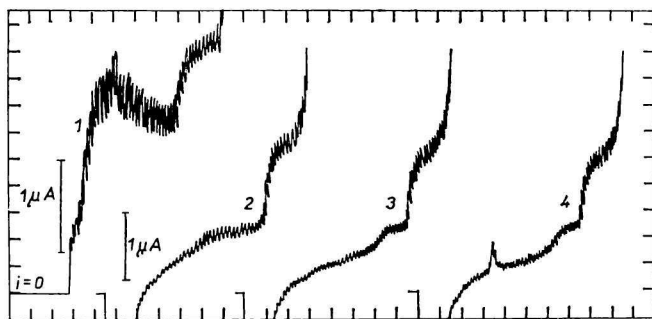


Fig. 2. The change of the polarographic record of  $\text{AlI}_3$  in acetonitrile with time. Supporting electrolyte  $0.1$  M- $\text{LiClO}_4$ ,  $100$  mV/absc. Time: 1. recorded immediately after dissolution of  $\text{AlI}_3$  in the supporting electrolyte; 2. after 4 min; 3. after 8 min; 4. after 12 min.

$\text{AlI}_3$  — and one negative wave at the potential of  $-1.52$  V. The following record (curve 2) shows only a slight indication of the positive wave and a decrease of the negative one. Approximately 10 min after the dissolution, a new wave could be observed on the polarographic record at the potential of approximately  $-1.24$  V (curve 3). This wave shows no changes with time; the wave at  $-1.52$  V continues to decrease smoothly. The difficulties in preparing a stock solution of  $\text{AlI}_3$  in acetonitrile and the described continuing time effects on the polarographic record were the reasons for refraining for the present from further experiments with this compound.

The dissolution reaction of aluminium halides in tetrahydrofuran is more violent in comparison with the reaction in acetonitrile. The overall tendency, however, is the same as in acetonitrile: the most violent is the reaction of  $\text{AlI}_3$ , then  $\text{AlBr}_3$ , and less intensively reacts  $\text{AlCl}_3$ . The dissolution of  $\text{AlI}_3$  and  $\text{AlBr}_3$  is accompanied with gas evolution and brown colouring of the solution. The stock solution of  $\text{AlCl}_3$  in tetrahydrofuran is stable for several hours.

The reaction product of the  $\text{AlI}_3$  dissolution in tetrahydrofuran produces no defined polarographic wave and therefore could not be polarographically investigated. The reaction of  $\text{AlBr}_3$  after dilution with the supporting electrolyte is so fast that only the final product can be polarographically recorded. Only the dilution reaction of  $\text{AlCl}_3$  with the supporting electrolyte can be polarographically followed. Fig. 3 shows the change with time of both waves of  $\text{AlCl}_3$  in tetrahydrofuran obtained after dilution of  $10^{-1}$  molar stock solution of  $\text{AlCl}_3$  by the supporting electrolyte to the concentration of  $2.5 \times 10^{-4}$  molar. The height of both waves increases smoothly in the first time interval of approximately 15 min. This time effect was eliminated by recording all polarograms with fresh stock solution of  $\text{AlCl}_3$  20 min after mixing with the supporting electrolyte.

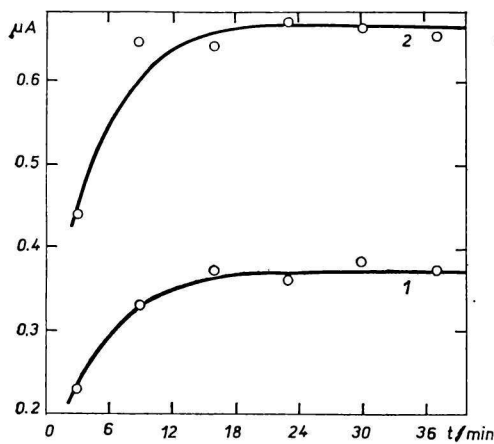


Fig. 3. The change of the limiting current of the polarographic waves of  $\text{AlCl}_3$  in tetrahydrofuran with time. Concentration of  $\text{AlCl}_3$   $2.5 \times 10^{-4}$  M.

1. Positive wave; 2. negative wave.

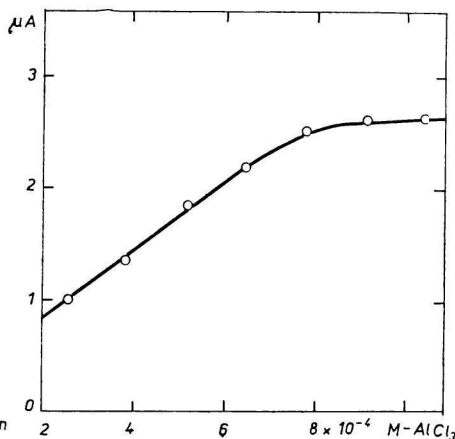


Fig. 4. The limiting diffusion current of  $\text{AlCl}_3$  in acetonitrile as a function of the concentration of  $\text{AlCl}_3$ .

*The basic polarographic characteristics of aluminium halides  
in acetonitrile and tetrahydrofuran*

Aluminium chloride in acetonitrile gives one well defined wave; its half-wave potential found by logarithmic analysis is  $-1.08$  V *vs.* SCE at the depolarizer concentration of  $8 \times 10^{-4}$  M. The wave is proportional to the depolarizer concentration up to the concentration value of  $8 \times 10^{-4}$  M- $\text{AlCl}_3$ ; above this value no change of the wave height could be observed with the change of the depolarizer concentration. The graphical illustration of this dependence is given in Fig. 4. At higher concentration of  $\text{AlCl}_3$  — approximately  $2 \times 10^{-3}$  M — the formation of a very fine precipitate can be observed. It is worth mentioning that at higher concentrations of  $\text{AlCl}_3$  — above  $5 \times 10^{-2}$  M — the substance is again completely dissolved in acetonitrile. This could be caused by the formation of a soluble dimer  $(\text{AlCl}_3)_2 \cdot \text{AN}$ , the existence of which is known [7]. This concentration region, however, is not suitable for polarographic investigation. The UV-VIS spectroscopy technique was applied. In the mentioned concentration region new absorption peaks were observed (at 310 and 360 nm) that are not present in the lower concentration region of  $\text{AlCl}_3$  in acetonitrile. The i.r. spectroscopy could not be applied to the large-scale study owing to the high reactivity of all studied systems towards the cell material.

The reduction of aluminium bromide in acetonitrile proceeds in two steps. The half-wave potentials estimated by logarithmic analysis of the waves are

$$E_{1/2 \text{ pos}} = -0.85 \text{ V,}$$

$$E_{1/2 \text{ neg}} = -1.19 \text{ V.}$$

Fig. 5 shows the change of current intensity with the depolarizer concentration for both waves. At the concentration value  $4 \times 10^{-4}$  M of  $\text{AlBr}_3$  the slope of both

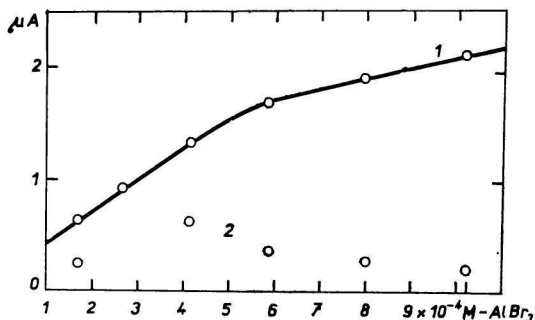


Fig. 5. The limiting diffusion current of  $\text{AlBr}_3$  in acetonitrile as a function of the concentration of  $\text{AlBr}_3$ .

1. Positive wave; 2. negative wave.

straight lines changes. The value of the exponent of the wave height dependence on the mercury reservoir height for the positive wave is  $y = 0.85$ , for the negative one  $y = 0.00$ . The polarographic record of the mercury reservoir height dependence for  $\text{AlBr}_3$  in acetonitrile is in Fig. 6.

In tetrahydrofuran, aluminium chloride exhibits two poorly defined waves with a potential difference of roughly 150 mV. The positive wave is highly irreversible.

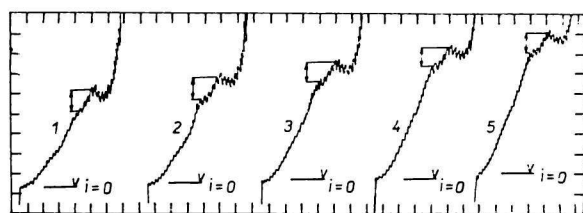


Fig. 6. The dependence of the negative wave height for  $\text{AlBr}_3$  in acetonitrile on the mercury reservoir height.

1. 48 cm; 2. 56 cm; 3. 64 cm; 4. 72 cm; 5. 81 cm.

The logarithmic analysis of both waves gives the half-wave potential values:

$$E_{1/2 \text{ pos}} = -1.72 \text{ V},$$

$$E_{1/2 \text{ neg}} = -1.86 \text{ V}$$

The positive wave increases proportionally to the depolarizer concentration up to the value  $2 \times 10^{-3} \text{ M}$  of  $\text{AlCl}_3$ . The negative wave dependence on the depolarizer concentration changes its slope at the value  $1.5 \times 10^{-3} \text{ M}$  of  $\text{AlCl}_3$ . The depolarizer concentration dependence for both waves of  $\text{AlCl}_3$  in tetrahydrofuran is shown in Fig. 7.

The half-wave potential of both waves shows no changes with time and depolarizer concentration. With decreasing concentration of the supporting electrolyte, however, a remarkable differentiation of both waves can be observed. The effect of the change of the supporting electrolyte concentration upon the half-wave potentials of  $\text{AlCl}_3$  in tetrahydrofuran is summarized in Table 1.

Aluminium bromide exhibits in tetrahydrofuran also two poorly defined waves. Their half-wave potentials calculated from the logarithmic analysis are:

$$E_{1/2 \text{ pos}} = -1.52 \text{ V},$$

$$E_{1/2 \text{ neg}} = -1.62 \text{ V}$$

Aluminium bromide is thus reduced in tetrahydrofuran more positively than aluminium chloride, similarly as in acetonitrile.

The basic polarographic characteristics of the studied systems in both aprotic solvents are given in Table 2. In the third column the experimentally measured half-wave potential values are listed. In the fourth column are the half-wave potentials corrected for the value of half-wave potential of  $\text{BDCI}$  according to the relationship

$$E_{1/2 \text{ corr}} = E_{1/2 \text{ meas}} - [E_{1/2 \text{ BDCI}} - 0.625].$$

(See Experimental.)

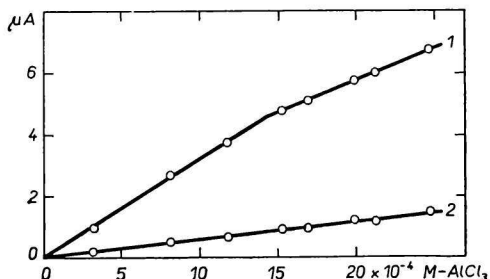


Fig. 7. The dependence of the limiting current of  $\text{AlCl}_3$  in tetrahydrofuran on the depolarizer concentration.

1. Negative wave; 2. positive wave.

Table 1

The change of the half-wave potential of  $\text{AlCl}_3$  in tetrahydrofuran with the concentration of supporting electrolyte

Concentration of $\text{LiClO}_4$ mol l <sup>-1</sup>	$-E_{1/2}$ pos V	$-E_{1/2}$ neg V
0.5	1.717	1.865
0.4	1.708	1.850
0.3	1.697	1.892
0.2	1.690	1.920
0.1	1.680	1.950

Table 2

The basic polarographic characteristics of the studied systems

Compound	Solvent	$-E_{1/2}$ meas V	$-E_{1/2}$ corr V	$n\alpha$	$I_d^*$ A/mM	$y$
$\text{AlCl}_3$	AN	1.08	0.96	0.48	3.4	0.9
$\text{AlBr}_3$	AN	0.85	0.73	0.71	1.5	0.85
		1.19	1.07	0.71	3.5	0.00
$\text{AlI}_3$	AN	1.24	1.01	0.45		0.80
		1.52	1.26			0.30
Reference compound BDCI**	AN	0.74	0.62	0.83		
$\text{AlCl}_3$	THF	1.72	1.68	0.50	3.2	0.46
		1.86	1.83	1.35		
$\text{AlBr}_3$	THF	1.52	1.48	1.0	2.02	
		1.62	1.58	0.63	1.79	
Reference compound BDCI**	THF	0.66	0.62	1.1		

\*  $I_d$  — diffusion current constant.

\*\* Reference compound bis(diphenyl)chromium(I) iodide.

The comparison of the data in Table 2 shows that the half-wave potential values of the studied systems in tetrahydrofuran are approximately by 700 mV more negative than in acetonitrile.

The apparent values of  $n\alpha$  in the next column were obtained from the logarithmic analysis of the polarographic curves and can be interpreted only in terms of the relative irreversibility of the studied systems. The actual charge number of the

electrochemical reaction,  $n$ , was determined microcoulometrically according to *Gilbert and Rideal* [8]. The calculated value for the electroreduction of  $\text{AlCl}_3$  in tetrahydrofuran is  $n = 3.03$ . The microcoulometric analysis of  $\text{AlCl}_3$  in acetonitrile provides a charge number  $n = 3.01$ ; this value being in accordance with the value measured by *Kolthoff* [9].

In the last two columns of Table 2, the diffusion current constant  $I_d$  for the region of proportionality between the current and depolarizer concentration and the values  $y$  of the exponent of the wave-height dependence on the mercury reservoir height are listed.

### Discussion

Different polarographic behaviour of aluminium halides in acetonitrile and tetrahydrofuran can be chiefly attributed to different properties of both solvents. For characterization of an organic solvent it is necessary to consider several factors:

1. The localization of the negative charge on the solvent molecule. In tetrahydrofuran, the negative charge fraction is localized on oxygen, whereas in acetonitrile it is on nitrogen. From the standard free enthalpy values of aluminium oxide and aluminium nitride formation it can be concluded that the Al—O bond is more stable than the Al—N bond; owing to this fact, the solvate complexes with tetrahydrofuran can be considered as more stable than those with acetonitrile. This assumption is well in agreement with the experimentally found half-wave potential values of the studied systems in both respective solvents.

2. The donacity value of the solvent defined by *Gutmann* [10]. This value characterizes the solvent ability of forming solvates, molecular complexes, and coordination compounds. Both solvents applied in this work belong to the group of solvents the donacity value of which is close to that of water (see Table 3). In such solvents either the dissociation and ion solvation or autocomplex formation of the type  $\text{AlX}_4^-$  would take place according to the stability of metal—halide bond [11]. In fact, an equilibrium is established between the particles coordinated by halide and by solvent (see eqn (A)). The equilibrium constant values in individual solvents depend also on further solvent properties such as dielectric constant and steric factors.

3. The dielectric constant of the solvent is important from the point of view of its dissociation and dissolution ability. The dielectric constant value of tetrahydrofuran is very low, equal to 7.6. The acetonitrile molecule is much more polar which is reflected in the relatively high value of the dielectric constant 38.6.

Table 3

The donacity and dielectric constants of the solvents used

Solvent	Donacity $\text{kcal mol}^{-1}$	Dielectric constant
Acetonitrile (AN)	14.1	38.6
Tetrahydrofuran (THF)	20.0	7.6
Water	18.0	81.0



The donacity and dielectric constants of the solvents under consideration according to [10] are listed in Table 3.

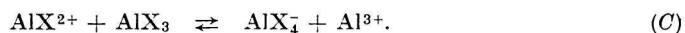
4. The steric factors, as *e.g.* the relation between the aluminium(III) ionic radius and the solvent molecule size, should not be neglected.

From the summation of criteria 1. to 4. the following conclusions can be drawn: In acetonitrile preferentially aluminium ions stabilized by the solvent molecules would be formed but in dependence on the halide type also autocomplexes may occur in the solution. On the other hand, in tetrahydrofuran preferentially molecular solvate of the type  $\text{AlX}_3 \cdot n\text{THF}$  would be formed; the eventually occurring ions of the solute would be stabilized considering the low dielectric constant of tetrahydrofuran — by ionic pairs formation with the ions of the supporting electrolyte. At higher halide concentrations also dimers can be formed.

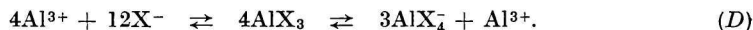
By the conductivity measurements, the ionic form of  $\text{AlCl}_3$  in acetonitrile has in fact been confirmed [12]. Among the three studied aluminium halides, the  $\text{AlCl}_3$  disposes of the most stable metal—halide bond. At the same time, with respect to its electron configuration, it is a strong Lewis acid. The chloride ion acts toward this compound as an electron donor; in this function competes with the molecules of solvent. A so-called self-ionization effect occurs, *i.e.* one  $\text{AlCl}_3$  molecule attracts a  $\text{Cl}^-$  anion from the coordination sphere of another  $\text{AlCl}_3$  molecule. In this way, a relatively strong  $\text{AlCl}_4^-$  complex is formed. (The chloride and bromide complexes of aluminium have a maximum coordination number of 4, only fluorides may form complexes with a coordination number of 6 [13, 14].) The very existence of the  $\text{AlCl}_4^-$  complex in acetonitrile was proved by the present authors by *i.r.* spectroscopy. Absorption peaks at 495 and 540  $\text{cm}^{-1}$  which are attributed to this configuration [15] were identified in the solution and even in the solid complex of  $\text{AlCl}_3$  with acetonitrile. On the other hand, no such peaks were found in tetrahydrofuran: neither in the solution, nor in the solid complex.

Thus in the diluted solution of  $\text{AlCl}_3$  in acetonitrile the following particles could be assumed to exist: the undissociated aluminium chloride molecules loosely bound to the molecule of solvate  $\text{AlCl}_3 \cdot \text{AN}$ ,  $\text{Al(III)}$  ions stabilized by the solvate molecules  $\text{Al}(\text{AN})_6^{3+}$  and the products of the self-ionization reaction,  $\text{AlCl}_4^-$ ,  $\text{AlCl}_2^+$ ,  $\text{AN}$ , and  $\text{AlCl}^{2+} \cdot \text{AN}$  (see eqns (A—D)). The concentration of the individual particles in the solution is determined by the dissociation and stability constant values of the corresponding reactions.

The dissociation and self-ionization equilibria of aluminium halides in acetonitrile could generally be expressed in the following way (the function of the solvent is neglected):



Summarized:



The acetonitrile molecules, considering the high donacity value of acetonitrile, act as coordination agents for ions  $\text{Al}^{3+}$ ,  $\text{AlX}_2^+$ , and  $\text{AlX}^{2+}$ . The existence of the molecule  $[\text{Al}(\text{AN})_6]^{3+}$   $[\text{AlCl}_4^-]_3$  in the solution is known [15].

The concentration of the individual particles in  $\text{AlBr}_3$ —acetonitrile system would differ from the  $\text{AlCl}_3$  solution. The  $\text{Al}-\text{Br}$  bond is less stable than the  $\text{Al}-\text{Cl}$  one, therefore the aluminium bromide would be more dissociated than aluminium chloride. On the other hand, the bromide ion is a weaker coordination agent because of its lower donacity value and larger ionic radius as compared to the chloride ion. A shift of the equilibrium of the reaction (D) to the left would result in higher concentration of  $\text{Al}(\text{AN})_6^{3+}$  ions and lower concentration of  $\text{AlBr}_4^-$  ions as products of the self-ionization reaction.

The experimental results indicate that ion  $[\text{Al}(\text{AN})_6]^{3+}$  or  $[\text{AlX}_m(\text{AN})_n]^{(3-m)+}$  is most likely the electroactive particle in the solutions of aluminium halides in acetonitrile. This assumption will further be experimentally verified by the study of the electrochemical behaviour of  $\text{AlCl}_3$  and  $\text{AlBr}_3$  in the presence of excess of the respective halide.

The time effects connected with the dilution of the stock solution of  $\text{AlCl}_3$  and  $\text{AlBr}_3$  in acetonitrile by the supporting electrolyte solution may be presumably attributed to the decomposition of the dimer and equilibrium constitution with participation of the electroactive particle (see eqns (A—D)).

It has been found by conductivity measurements of  $\text{AlCl}_3$  in tetrahydrofuran [16] that one undissociated molecule of the halide is solvated by two molecules of tetrahydrofuran. The assumption on the participation of a solvolytic reaction is supported also by the intensity of  $\text{AlCl}_3$  dissolution in tetrahydrofuran. The authors [16] assume the opening of one ring of tetrahydrofuran as a result of the catalytic action of aluminium chloride. The product of solvolysis is then the molecule  $\text{Cl}_2\text{AlO}(\text{CH}_2)_4\text{Cl}$   $\text{C}_4\text{H}_8\text{O}$ .

The difference of the half-wave potentials of the aluminium halides in acetonitrile and tetrahydrofuran could thus be attributed also to the formation of a very stable particle in tetrahydrofuran resulting from the solvolytic reaction. The reaction product of  $\text{AlBr}_3$  with tetrahydrofuran is less stable which explains the more positive values of the half-wave potentials of the  $\text{AlBr}_3$  reduction in tetrahydrofuran as compared to  $\text{AlCl}_3$ .

## References

1. Heyrovský, M., *Collect. Czech. Chem. Commun.* **25**, 3120 (1960).
2. Kumar, G. P. and Pantony, D. A., *J. Polarogr. Soc.* **14**, 84 (1968).
3. Herzog, S. and Dehner, J., *Z. Chem.* **4**, 1 (1964).
4. Baucke, F. G. K., Bertram, R., and Cruse, K., *J. Electroanal. Chem.* **32**, 247 (1971).
5. Nicholson, D. G., Winter, P. K., and Fineberg, H., in *Inorganic Synthesis, III*. Academic Press, New York, 1950.
6. Gálová, M. and Szmereková, V., *Chem. Zvesti* **27**, 437 (1973).
7. Schmulbach, C. D., *J. Inorg. Nucl. Chem.* **26**, 745 (1964).
8. Gilbert, G. A. and Rideal, E. K., *Trans. Faraday Soc.* **47**, 369 (1951).
9. Kolthoff, I. M. and Coetzee, J. F., *J. Amer. Chem. Soc.* **79**, 1852 (1957).
10. Gutmann, V., in *New Pathways in Inorganic Chemistry*. (E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Editors.) Cambridge University Press, 1968.
11. Gutmann, V., *Coordination Chemistry in Non-Aqueous Solutions*. Springer-Verlag, Wien, 1968.

12. Libus, W., Puchalska, D., and Walcsak, M., *J. Phys. Chem.* **11**, 3549 (1967).
13. Gutmann, V. and Hengge, E., *Allgemeine und anorganische Chemie*. Verlag Chemie, Weinheim, 1971.
14. Cotton, F. A. and Wilkinson, G. *Advanced Inorganic Chemistry*. Interscience, New York, 1962.
15. Jones, D. E. H. and Wood, J. L., *J. Chem. Soc. (A)* **1971**, 3132, 3135.
16. Evans, G. G., Gibb, T. R. P., Kennedy, J. K., and Del Greco, F. P., *J. Amer. Chem. Soc.* **76**, 4861 (1954).

Translated by M. Gálová