

Study of aluminium halides in nonaqueous solvents. III. Influence of the presence of water in the solvent

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The influence of water in the solvent upon the shift of the half-wave potentials of aluminium salts in acetonitrile, tetrahydrofuran and dimethylformamide has been investigated. It was found that the shift may be correlated with donicity values of the respective solvents and water. Particular attention was paid to the influence of water on the solutions of aluminium chloride and bromide in acetonitrile; this is discussed with respect to the aluminium—halogen bond stability and the related self-ionization effect.

Изучалось влияние присутствия воды в растворителе на сдвиг потенциалов полуволн солей алюминия в ацетонитриле, тетрагидрофуране и диметилформамиде. Было найдено, что сдвиг в отдельных растворителях можно коррелировать со значениями донорной способности этих растворителей по отношению к значению донорной способности воды. Специально разбирается влияние воды на растворы хлорида и бромиды алюминия в ацетонитриле, которое обсуждается с точки зрения прочности связи алюминий—галоген и с ним связанным эффектом автоионизации.

In the previous papers the basic polarographic characteristics of the aluminium halides solutions in acetonitrile and tetrahydrofuran, the stability of these systems in time [1] and the effect of an excess of free halides on the behaviour of AlCl_3 and AlBr_3 solutions in acetonitrile [2] have been investigated. In this paper attention is paid to the influence of water in the organic solvent upon the electrochemical behaviour of aluminium.

Low water contents below 100 p.p.m. ($5 \times 10^{-3} \text{ mol l}^{-1}$) may influence the electrode kinetics through adsorption effects and changes of the dielectric constant value in the interphase. It is very laborious, however, to remove these last traces of water. To some extent, it depends on the type of solvent to be purified. For example, tetrahydrofuran can be disposed of water down to 10—15 p.p.m. by distillation with alkali metals. In acetonitrile, there always remain approx. 50 p.p.m. of H_2O . Both p.p.m. values are within a milimolar concentration range.

Abbreviations:

AN	Acetonitrile.
BDCI	Bis(diphenyl)chromium(I) iodide.
DMF	Dimethylformamide.
TEACl	Tetraethylammonium chloride.
THF	Tetrahydrofuran.

At higher concentrations (above 100 p.p.m.) water usually takes part in the solvent—solute and solute—solute equilibria in solution. In this respect namely the formation of aqua complexes is to be considered which brings about changes of the diffusion coefficients of the particles transported towards the electrode and affects also the process of losing the solvation shell in the course of electroreduction. Ions forming strong aqua complexes may not get rid of the hydration shell at all during the electroreduction process which is just the case of aqua aluminium ions [3].

The stability of an ion—solvent bond is, under certain simplifying conditions, proportional to the donacity value of the respective solvent. Three organic solvents: acetonitrile, tetrahydrofuran, and dimethylformamide were applied in combination with water to verify the relation between the donacity value and the half-wave potential of aluminium ions in each solvent.

The main aim of the whole study is, however, to look for the correlations between the solution properties and composition and its electrochemical behaviour with respect to the electroreduction of aluminium. From this aspect, the critical amount of water in the organic medium is of primary importance. It is necessary to find the correlation between the high hydrophylic properties of an aluminium ion and the experimental difficulties connected with operating a totally nonaqueous system.

Experimental

All experimental conditions such as apparatus, preparation and purification of the aluminium salts, purification and drying of solvents and inert gases are described in detail in [1] and [4].

Results

The changes of the half-wave potentials and limiting currents of aluminium halides with increasing water concentration were investigated with AlCl_3 , AlBr_3 , and AlCl_3 —TEACl system in acetonitrile. Further, the effect of water addition to tetrahydrofuran on the electroreduction of AlCl_3 and to dimethylformamide on the electroreduction of aluminium perchlorate was followed. All the measured potential values were corrected with respect to the half-wave potential of bis(diphenyl)chromium(I) iodide (hereafter referred to as BDCI).

An addition of water to acetonitrile exhibits only a very slight effect upon the half-wave potential and limiting current of AlCl_3 , as it can be seen in Table 1. Only a negligible decrease of the wave height may be observed when adding 0.55 mol l^{-1} of water (1 volume %). The situation is different when an excess of chloride is present. As it was already stated before [2], a three-fold molar excess of TEACl over AlCl_3 causes an increase of the limiting current of AlCl_3 . This can be clearly seen also from a comparison of i values in the first lines of Tables 1 and 2. An addition of 0.55 mol l^{-1} of H_2O to the above AlCl_3 —TEACl system results in a further not very significant increase of the limiting current while the half-wave potential remains practically unchanged. At a molar ratio of AlCl_3 to TEACl 1:6 and 0.55 mol l^{-1} of H_2O a new wave is formed with a half-wave potential by 300 mV more negative than the potential of the original wave. With water content increased up to 1.65 mol l^{-1} the original and the

Table 1

Changes of the half-wave potential and limiting current of AlCl_3 in acetonitrile in the presence of water
Concentration of AlCl_3 : $5 \times 10^{-4} \text{ mol l}^{-1}$

Concentration of H_2O		$E_{1/2 \text{ corr}}$ V	i A 10^6
volume %	mol l^{-1}		
0	0	-0.395	2.04
0.1	0.055	-0.395	1.96
1.0	0.55	-0.400	1.88

Table 2

Changes of the half-wave potential and limiting current of AlCl_3 in acetonitrile in the presence of an excess of free halide and water
Concentration of AlCl_3 : $5 \times 10^{-4} \text{ mol l}^{-1}$

Molar ratio $\text{AlCl}_3 : \text{TEACl}$	Concentration of TEACl mol l^{-1}	Concentration of H_2O		$E_{1/2 \text{ corr}}$ V	i A 10^6
		volume %	mol l^{-1}		
1 : 3	1.5×10^{-3}	0	0	-0.395	2.4
1 : 3	1.5×10^{-3}	1.0	0.55	-0.400	2.48
1 : 6	3×10^{-3}	0	0	-0.400	2.84
1 : 6	3×10^{-3}	1.0	0.55	-0.430	2.64
				-0.710	
1 : 6	3×10^{-3}	3.0	1.66	-0.600	2.64

newly formed waves merge into one. The half-wave potential of this wave is by 200 mV more negative than the half-wave potential of AlCl_3 in water-free acetonitrile. The precise values of the corrected half-wave potentials and limiting current for the AlCl_3 -TEACl system in acetonitrile in the presence of water are given in Table 2.

In the case of AlBr_3 electroreduction in acetonitrile the influence of water is much more remarkable. The corrected values of the half-wave potentials of AlBr_3 two-step reduction in acetonitrile as given in [2] are the following: $E_{\text{pos corr}} = -0.230 \text{ V}$ and $E_{\text{neg corr}} = -0.630 \text{ V}$. The addition of water exhibits a crucial effect upon the positive wave. Its potential shifts towards negative values and at the same time the wave becomes ill defined. At a concentration of water 0.55 mol l^{-1} the positive wave merges completely with the negative one. The limiting current of the resulting negative wave corresponds to the sum of the positive and negative wave limiting currents in water-free acetonitrile. The maximum on the negative wave becomes lower and less sharp in the presence of water. These effects are schematically illustrated in Fig. 1.

The influence of the presence of water in tetrahydrofuran on the half-wave potentials of AlCl_3 reduction is summarized in Table 3. It should be noted that both waves of the AlCl_3 reduction in

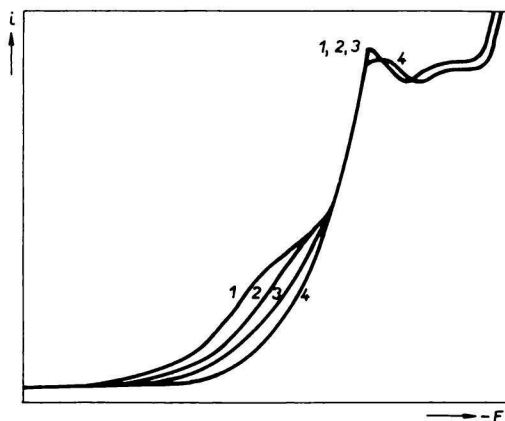


Fig. 1. Schematic diagram of the influence of water additions on the polarographic record of AlBr_3 in acetonitrile.

Concentration of AlBr_3 : $5 \times 10^{-4} \text{ mol l}^{-1}$.

1. Polarogram of AlBr_3 in water-free acetonitrile; 2. $0.055 \text{ mol l}^{-1} \text{ H}_2\text{O}$; 3. $0.11 \text{ mol l}^{-1} \text{ H}_2\text{O}$; 4. $0.55 \text{ mol l}^{-1} \text{ H}_2\text{O}$.

tetrahydrofuran are ill defined, therefore the given half-wave potential values are only approximate. Despite of this, it can be stated unambiguously that in the presence of water the half-wave potential of the negative wave shifts positively while the positive wave diminishes. The limiting current of the resulting negative wave is lower than the sum of both waves in water-free tetrahydrofuran.

In dimethylformamide, the influence of the presence of water upon the reduction of aluminium perchlorate was investigated. The effect is entirely opposite to that in both above-mentioned solvents: the peaks shift towards more positive values of potential (Table 4).

Note: This system was studied by cyclic voltammetry on the hanging mercury drop electrode. The presented peak potential values are the actually measured values, not the corrected ones. At a concentration of $0.275 \text{ mol l}^{-1} \text{ H}_2\text{O}$ in dimethylformamide the positive peak of $\text{Al}(\text{ClO}_4)_3$ shifts by

Table 3

Changes of the half-wave potentials of AlCl_3 in tetrahydrofuran in the presence of water
Concentration of AlCl_3 : $5 \times 10^{-4} \text{ mol l}^{-1}$

Concentration of H_2O		$E_{1/2 \text{ pos corr}}$ V	$E_{1/2 \text{ neg corr}}$ V
volume %	mol l^{-1}		
0	0	-0.560	-0.980
1.0	0.55	—	-0.930
2.0	1.10	—	-0.920
3.0	1.65	—	-0.910
4.0	2.20	—	-0.900

Table 4

Changes of the peak potentials of Al(III) in dimethylformamide
in the presence of water*
Concentration of $\text{Al}(\text{ClO}_4)_3$: $10^{-3} \text{ mol l}^{-1}$

Concentration of H_2O		$E_{p\text{pos}(1)}$ V	$E_{p(2)}$ V	$E_{p(3)}$ V	$E_{p\text{neg}(4)}$ V
volume %	mol l^{-1}				
0	0	2.0	—	—	2.2
0.5	0.278	1.8	—	—	2.05
1.0	0.55	1.3	—	—	2.0
1.95	1.08	1.3	—	1.8	2.0
4.75	2.64	—	1.65	1.8	2.03
9.1	5.05	—	1.7	—	2.03
16.7	9.28	—	1.65	—	2.03

* See Experimental.

200 mV, the negative one by 150 mV positively as compared with a water-free solvent. An increase of the water concentration causes a further positive shift of the positive peak but no further shift of the negative peak was observed. The heights of both peaks undergo remarkable changes. The negative peak current increases up to a maximum at $0.55 \text{ mol l}^{-1} \text{ H}_2\text{O}$, when it reaches a value by 60% higher than the peak in water-free dimethylformamide. With a further increase of H_2O content this peak height decreases. The positive peak height decreases in the whole followed water concentration range; at $1.1 \text{ mol l}^{-1} \text{ H}_2\text{O}$ it disappears completely.

Discussion

The differences between the half-wave potentials in the respective solvents may be ascribed to the different changes in the Gibbs solvation energy values. This thermodynamic quantity is under certain simplifying conditions in a direct relation to the donacity value of the solvent. The donacity was defined by *Gutmann* [5] as the positive value of the reaction heat of reaction between one mole of antimony pentachloride and one mole of the solvent in question in an inert medium. The simplifying conditions are: The depolarizer forms no complexes and ionic pairs and its activity coefficient in the solvent approaches one. The last condition is actually fulfilled with the depolarizer concentration applied: 5×10^{-4} and $10^{-3} \text{ mol l}^{-1}$. The ionic pairs formation, most likely with the supporting electrolyte ions which are in a large excess, could not be excluded in tetrahydrofuran because of its low dielectric constant values. The complex formation may occur with aluminium halides in acetonitrile as a result of self-ionization [6]. The reaction was discussed elsewhere [1, 2]. The formation of complex particle AlX_4^- competes with the

formation of simple solvated ions $\text{Al}(\text{AN})_6^{3+}$ dependent on the stability constants of both compounds and the solution composition.

The relation between the half-wave potentials of aluminium halides in acetonitrile and tetrahydrofuran as well as their shift in the presence of water is in a good agreement with the donacity values of the respective solvents despite the fact that the required simplifying conditions are not entirely fulfilled:

Solvent:	DMF	>	THF	>	H ₂ O	>	AN.
Donacity value:	26.6		20		18		14.1.

The small shift of the half-wave potential of AlCl_3 in tetrahydrofuran in the presence of water (Table 3) corresponds to the slight difference between the donacity values of tetrahydrofuran and water. The donacity value of dimethylformamide is much higher than that of water; the solvates in DMF are more stable. This fact is reflected in a remarkable positive shift of the Al(III) peak potentials in DMF when water is added (Table 4). The high stability of the bond between aluminium ion and dimethylformamide is confirmed by other observation, too. The Al(III) ion is reduced in DMF on a hanging mercury drop by three electrons but it is not disposed of its solvation shell and, consequently, cannot diffuse into mercury and remains adsorbed on the electrode surface [4].

In acetonitrile, the opposite is true. The addition of water causes always a negative shift of the halides reduction (Table 2; Fig. 1). The half-wave potential values of both AlCl_3 and AlBr_3 in the presence of water are very close to each other though in the case of AlCl_3 higher water concentration is required to shift the reduction potential. The explanation of these effects is to be found in the substitution reactions of aluminium halide complexes with water molecules. According to [1], in the solution the particles $\text{AlX}_n^{(3-n)+} \cdot \text{AN}$ ($n=1$ to 4) are present. First, the substitution of the loosely bound acetonitrile molecules in the outer sphere of the complex by water molecules takes place. The substitution of halide is different depending on the stability of aluminium—halogen bond. The aluminium—chlorine bond is very stable, therefore relatively high water concentrations are needed for substitution: 10^3 -fold molar excess of water over aluminium chloride. Aqua complex is formed and reduced in a new negative wave



The aluminium—bromine bond is evidently less stable than the aluminium—chlorine one. Therefore, the substitution (A) starts from the lowest measured water concentrations and continues gradually with increasing water concentration. Consequently, a continuous shift of the AlBr_3 positive wave in the negative direction can be observed.

As suggested earlier [2], the reduced particle in the case of chloride reduction is

assumed to be the AlCl_4^- anion. In the case of the two waves of AlBr_3 reduction, in the positive wave the reduction of the AlBr_4^- anion is assumed whereas in the negative wave the cations AlBr_2^+ , AlBr^{2+} or Al^{3+} solvated by acetonitrile are reduced. The half-wave potential of the cation reduction coincides with the half-wave potential of the aqua complex and, consequently, no shift of the negative AlBr_3 wave can be observed in the presence of water.

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