

ELECTROMIGRATION OF CARRIER-FREE RADIONUCLIDES

XIV. COMPLEX FORMATION OF ^{241}Am –Am(III) WITH OXALATE AND SULFATE IN AQUEOUS SOLUTION

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Using a special type of on-line electromigration measurements of γ -emitting radionuclides in homogeneous aqueous electrolytes free of supporting materials, complex formation of carrier-free ^{241}Am –Am(III) has been studied in perchlorate electrolytes, $T = 298.1$ (1) K. Stoichiometric stability constants for oxalate ligand of $\log K_1 = 5.01$ (13), 5.11 (13) and 5.38 (18) as well as $\log K_2 = 3.15$ (15), 3.19 (14) and 3.58 (26) were obtained at the overall ionic strength of $\mu = 0.10$, 0.05 and 0.01, respectively. The corresponding thermodynamic stability constants are $\log K_1^0 = 5.90$ (15) and $\log K_2^0 = 3.73$ (18). The sulfate ligand values of $\log K_1 = 2.5$ (2) were obtained both in acidic and neutral solutions, $\mu = 0.10$.

Introduction

Besides investigating the hydrolysis behaviour of the actinide elements, their complex formation chemistry is also of interest. There are conventional aspects like chemical analysis and separation, and there are new aspects such as growing industrial, medical and military applications of these elements and their behaviour under natural geological conditions.

The special state of americium arises from two facts. Americium is the first member of the trivalent actinides, stable in inert aqueous solution. It is available in satisfactory amounts, so that different analytical techniques can be used to study chemical properties both for weighable amounts of the element and for carrierfree isotopes. These facts lead to a model function of americium(III) with respect to the investigations of transamericium homologues, which are difficult to produce and to handle because of their decay character. With the investigation of the complex formation of carrier-

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free $^{241}\text{Am}-\text{Am(III)}$ with oxalate and sulfate ligands in neutral and acidic aqueous electrolytes, principal possibilities of a modified version of the electromigration technique worked out in our Laboratory will be demonstrated concerning the chemical analysis of americium and transamericium radionuclides.

The oxalate and sulfate ligands were chosen because there is a lot of literature data on the complex formation parameters of Am(III) with these ligands, and our own results can be compared with them. In addition, using the $[\text{Am}(\text{ox})_n]^{3-2n}$ complexes, $n = 1, 2$, one can test the calculation of thermodynamic stability constants on the basis of the electromigration measurements. Since the sulfate ligand is relatively weakly protonated in acidic solutions, the effect of different individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in acidic and neutral aqueous inert electrolytes¹ should be investigated with respect to its consequences for (sulfate) complex formation mechanisms of the trivalent americium.

Investigations on ion mobilities and hydrolysis of the carrier-free trivalent americium in aqueous perchlorate electrolytes were described in Reference 1. The results are prerequisites for electromigration studies of the present work.

Experimental

Electromigration technique

The method used is a modified version of the continuous horizontal low-voltage electromigration measurement of γ -emitting radionuclides in homogeneous aqueous electrolyte solutions free of any supporting chromatographic materials, which was carried out in our laboratory. The design of the electromigration equipment as well as the setup and interpretation of electromigration experiments was published elsewhere.²⁻⁴

$^{241}\text{Am}-\text{Am(III)}$

The preparation of stock solutions of the carrier-free $^{241}\text{Am}-\text{Am(III)}$ in 0.10M $\text{Na}(\text{H})\text{ClO}_4$ and the demonstration of the special aptitude of this radioisotope for the electromigration measurements were described in Reference 1 in detail.

Electrolyte systems

- (1) $\text{Na}(\text{H})\text{ClO}_4/\text{Na}_2(\text{ox})_2$,
pH 5.5(5), $\mu = 0.10, 0.05$ and 0.01 , respectively,

(2) Na(H)ClO₄/Na₂SO₄,
 pH 2.8(2) and 5.5(5), respectively, $\mu = 0.10$,
 were prepared for the experiments; T = 298.1(1) K.

Chemicals were of grade p.a., water was bidistilled. The pH of the solutions was measured by means of glass electrodes, calibrated by standard buffer solutions.

The L²⁻ concentration of the ligand was calculated with the stoichiometric deprotonation constants $pK_1 = 1.26$, $pK_2 = 3.82$ for oxalic acid⁵ and $pK_1 = 1.55$ for sulfuric acid.⁶

Results and discussion

To obtain stoichiometric stability constants of the [AmL_n]³⁻²ⁿ complexes, the experimental dependences of the overall ion mobility $\bar{u}_{Am(III)}$ on the ligand concentrations are to be measured:

$$\bar{u}_{Am(III)} = f([L^{2-}]) \quad (1)$$

Calculations of the complex formation parameters start from



According to the general electromigration equation, the concrete correlation of the formation of the [AmL_n]³⁻²ⁿ complexes with n = 2 is:

$$\bar{u}_{Am(III)} = \frac{u_{Am^{3+}}^0 + u_{[AmL]^+}^0 \cdot K_1 [L^{2-}] + u_{[AmL_2]^-}^0 \cdot K_1 K_2 [L^{2-}]^2}{1 + K_1 [L^{2-}] + K_1 K_2 [L^{2-}]^2} \quad (4)$$

where $\bar{u}_{Am(III)}$ — overall ion mobility of trivalent americium,

$\bar{u}_{[AmL_n]^{3-2n}}^0$ — individual ion mobilities of the ions acting in the equilibria;
 n = 0, 1, 2;

K_n — stepwise stoichiometric stability constants; n = 1, 2.

According to the electromigration results obtained in Reference 1, effects of the hydrolysis reaction of ²⁴¹Am—Am(III) on its complex formation equilibria are negligible in the electrolyte systems (1) and (2) used in the experiments.

Complex formations with oxalate ligand

Figure 1 shows the experimental results of the electromigration experiments in the electrolytes.¹

The results show that cationic and anionic (at $[\text{ox}^{2-}] > 10^{-3}\text{M}$) complex species are formed. Consequently, the interpretation must take both Eqs (2) and (3) into consideration.

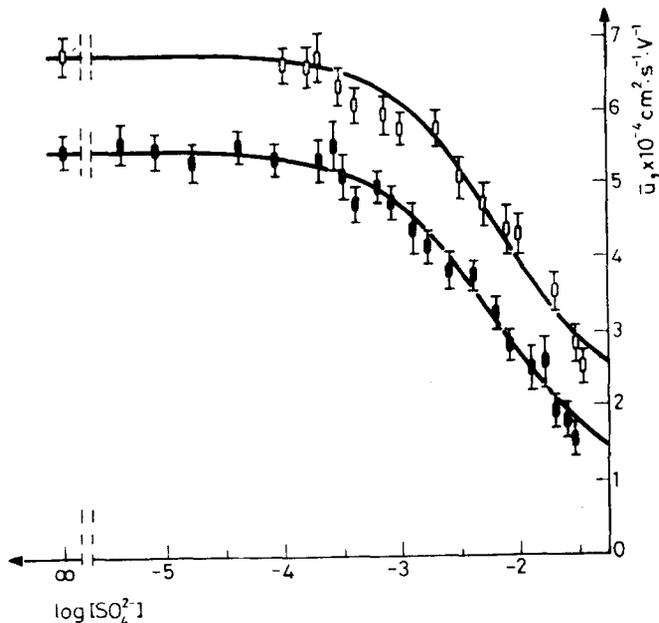


Fig. 1. Overall ion mobility of $^{241}\text{Am}-\text{Am(III)}$ as a function of the oxalate ion concentration in neutral aqueous perchlorate electrolytes of different overall ionic strength; pH 5.5(5), $T = 298.1(1)\text{K}$, $\mu = 0.01$ (\circ), $\mu = 0.05$ (\bullet), $\mu = 0.10$ (\circ).

The calculation of K_1 and K_2 as well as $u_{[\text{Am}(\text{ox})_n]^{3-2n}}^0$, $n = 0, 1, 2$, proceeds according to Eq. (4), using a least squares computer program.⁷

Table 1 summarizes the results of the calculations. The changes in the values of $u_{\text{Am}^{3+}}^0$ which depend on the overall ionic strength are not considerable. This is understandable if one takes into account the general electromigration behaviour of the $^{241}\text{Am}-\text{Am}^{3+}$ cation in neutral aqueous inert electrolytes.¹

The ratios between the individual ion mobilities of the central ion and the mono-oxalato complex ion also follow the known regularities of electromigration studies. There is a proportionality between the individual ion mobilities and the charges of

the ions acting in the equilibrium reaction. However, individual ion mobility data of the dioxalato complex ion differ from this correlation: they are 40–50% too “slow”

Because of the decreasing activity coefficients of the species acting in the complex formation reaction, the stoichiometric stability constants K_n increase in the range of $\mu = 0.10 \rightarrow 0.01$. In the next step the stoichiometric stability constants were used to obtain the thermodynamic stability constants K_n^0 .

Mathematical formulations of correlations like $\log K_n = f(\mu)$ differ for different ranges of the overall ionic strength and physicochemical parameters considered. With respect to the experimental conditions applied we tried to use a simplified formulation according to KOHLRAUSCH

$$\log K_n^0 = \log K_n + B \sqrt{\mu} \quad (5)$$

and the DAVIES equation of the type:⁸

$$\log K_n^0 = \log K_n - A\Delta Z^2 \left[\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu \right] \quad (6)$$

Here B is a constant, A is the DEBYE-HÜCKEL constant and $\Delta Z^2 = \Sigma Z^2$ (products) – ΣZ^2 (reactants), Z is the charge on the ion. The correlations (5) and (6) are shown graphically in Fig. 2. The resulting $\log K_n^0$ data, fitted by the linear regression, are

$$\log K_1^0 = 5.54(15) \quad |0.984|, \quad \log K_2^0 = 3.74(18) \quad |0.937|$$

according to eq. (5), and

$$\log K_1^0 = 5.90(15) \quad |0.994|, \quad \log K_2^0 = 3.72(18) \quad |0.561|$$

according to Eq. (6). Correlation coefficients of the extrapolated data are given in brackets.

Table 2 compares the stability constants obtained with the corresponding literature data.

Complex formation with sulfate ligand

Figure 3 summarizes the experimental results of type (1) for acidic and neutral sulfate electrolytes.

For the acidic solutions the real sulfate ion concentrations are calculated according to the protolysis equilibrium $\text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$ and the particular mole fraction of

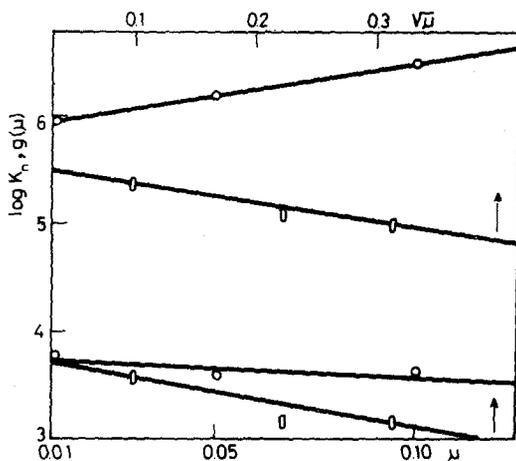


Fig. 2. Extrapolation of $\log K_n^0$ data of the $[\text{Am}(\text{ox})_n]^{3-2n}$ complexes in aqueous solution, $n = 1, 2$; (O) Eq. (4), $f(\mu)$; $g(\mu) = 0$, (o) Eq. (5), $f(\mu)$; $g(\mu) = \Delta Z^2 A \cdot \sqrt{\mu} / (1 + \sqrt{\mu})$

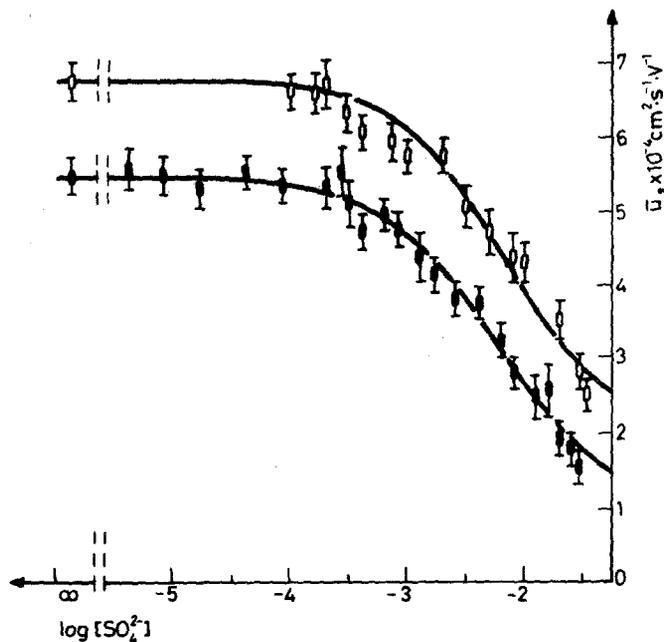


Fig. 3. Overall ion mobility of $^{241}\text{Am}-\text{Am}(\text{III})$ as a function of the sulfate ion concentration in neutral and acidic aqueous perchlorate electrolytes; $\mu = 0.10$, $T = 298.1(1)$ K, pH 5.5(5) (O), pH 2.8(2) (O)

Table 1

Parameters of the $[\text{Am}(\text{ox})_n]^{3-2n}$ complexes, $n = 1, 2$, in neutral aqueous perchlorate electrolytes of different overall ionic strength, pH 5.5 (5), $T = 298.1$ (1) K, u^0 in $10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, K_n in $\text{l} \cdot \text{mol}^{-1}$

Parameter	$\mu = 0.10$	$\mu = 0.05$	$\mu = 0.01$
$u_{\text{Am}^{3+}}^0$	+6.71 (20)	+6.82 (24)	+6.99 (22)
$u_{[\text{Am}(\text{ox})]^+}^0$	+2.65 (31)	+2.38 (29)	+2.53 (48)
$u_{[\text{Am}(\text{ox})_2]^-}^0$	-1.12 (14)	-1.28 (12)	-1.21 (26)
$\log K_1$	5.01 (13)	5.11 (13)	5.38 (18)
$\log K_2$	3.15 (15)	3.19 (14)	3.58 (26)

Table 2

Stability constants of the $[\text{Am}(\text{ox})_n]^{3-2n}$ complexes in aqueous solutions; $T = 298.1$ K

μ	Method	$\log K_1$	$\log K_2$	$\log \beta_1$	$\log K_3$	$\log \beta_3$	Reference
0	iox	7.0	4.16	11.16	—	—	9
0	iox	7.3	4.2	11.5	0.8	12.3	10
0	dis	—	—	10.8	2.2	13.0	11
0	sol	7.3	4.16	11.46	2.8	14.26	12
0	sol	6.68	3.26	9.94	1.68	11.62	13
0.1	em*	5.25	3.60	8.85	—	—	14
0.1	em*	6.14	4.4	10.54	—	—	15
0.1&	dis	—	—	8.3	2.5	—	16
0.2	iox	5.99	4.16	10.15	—	—	9
0	em	5.90 (15)	3.73 (18)	9.6 (2)	—	—	**
0.01	em	5.38 (18)	3.58 (26)	9.0 (3)	—	—	**
0.05	em	5.11 (13)	3.19 (14)	8.3 (2)	—	—	**
0.1	em	5.01 (15)	3.15 (15)	8.2 (2)	—	—	**

iox — ion exchange,
 dis — distribution between,
 sol — solubility,
 em — electromigration,
 em* — electromigration on solid materials,
 (&) — $T = 293.1$ K,
 (***) — this work.

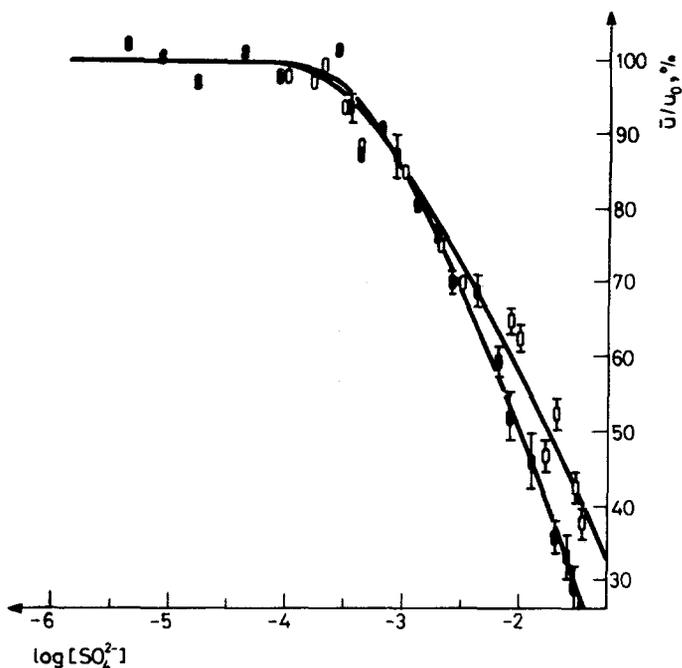


Fig. 4. Relative overall ion mobility of $^{241}\text{Am}-\text{Am(III)}$ as a function of the sulfate ion concentration in neutral and acidic aqueous perchlorate electrolytes; $\mu = 0.10$, $T = 298.1(1)$ K, pH 5.5(5) (○), pH 2.8(2) (●)

$\alpha_{\text{SO}_4^{2-}} \approx 0.9$ at pH 2.8. Two different standards of the individual ion mobility of $^{241}\text{Am}-\text{Am}^{3+}$ in the electrolyte systems are caused by different dependences of $u_{\text{Am}^{3+}}^0$ on the pH of aqueous perchlorate electrolytes. The values measured in References 1 are

$$u_{\text{Am}^{3+}}^0 (\text{pH } 3) = +5.58(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$$

and

$$u_{\text{Am}^{3+}}^0 (\text{pH } 5.5-7) = +6.85(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1},$$

respectively,

$$\mu = 0.10 (\text{ClO}_4^-), \quad T = 298.1(1) \text{ K}.$$

Compared to the complex formation of $^{241}\text{Am}-\text{Am(III)}$ with the oxalate ligand in neutral aqueous solutions, no formation of anionic complexes was found even at

Table 3
Parameters of the $[\text{Am}(\text{SO}_4)_n]^{3-2n}$ complexes, $n = 1, 2$, in neutral
and aqueous perchlorate electrolytes; $\mu = 0.10$, $T = 298.1$ (1) K, u° in $10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$,
 K_n in $l \cdot \text{mol}^{-1}$

pH	Case	$u^\circ_{[\text{Am}(\text{SO}_4)]^+}$	$u^\circ_{[\text{Am}(\text{SO}_4)_2]^-}$	$\log K_1$	$\log K_2$
5.5 (5)	A	+2.18 (14)	—	2.22 (4)	—
	B ₁	+5.1 (4)	-2.3 (2)*	3.04 (28)	1.2 (1)
	B ₂	+2.3*	-2.3*	2.23 (4)	0.0 (3)
	Mean:	—	—	2.5 (3)	0.6 (6)
2.8 (2)	A	+1.29 (13)	—	2.30 (4)	—
	B ₁	+3.2 (4)	-1.8 (1)*	2.76 (6)	1.3 (1)
	B ₂	+1.8*	-1.8*	2.39 (4)	0.9 (2)
	Mean:	—	—	2.5 (2)	1.1 (2)

*Fixed values, for cases A and B see text.

maximum sulfate ion concentrations of $3.0 \cdot 10^{-2} \text{ M}$ and $3.33 \cdot 10^{-2} \text{ M}$ for pH 2.8 and 5.5 solutions, respectively.

The relative changes of the overall in mobility $\bar{u}_{\text{Am(III)}}$ at maximum sulfate ligand concentrations of about 40% (pH 2.8) and 30% (pH 5.5) should be interpreted in such a way that the formation of the disulfato complex is negligible under the experimental conditions applied. Consequently, the parameters of the $[\text{Am}(\text{SO}_4)_2]^-$ are not computable by means of Eq. (4), (case A in Table 3). Nevertheless, they were considered in the calculations in terms of fixed values of $u^\circ_{[\text{Am}(\text{SO}_4)_2]^-}$, based on general regularities of correlation between individual ion mobilities and charges of central and complex ions acting in the equilibrium reaction of the element. As an alternative, a calculation mechanism was also tested, using fixed values of both $u^\circ_{[\text{Am}(\text{SO}_4)_2]^-}$ and $u^\circ_{[\text{Am}(\text{SO}_4)]^+}$ (cases B). The results of computer calculations⁷ are summarized in Table 3. The stoichiometric stability constant ($K_1^{\mu=0.10}$) data should be discussed in detail; the ($K_2^{\mu=0.10}$) values are of a tentative character. First it has to be stated that the complex formation tendency of ^{241}Am —Am(III) with sulfate in acidic aqueous solutions seems to be a little stronger than in the neutral ones. This is illustrated in Fig. 4. Here, the relative changes in the electromigration of the trivalent americium in sulfate electrolytes are compared by introducing a normalized individual ion mobility of the type

$$\bar{u}'_{\text{Am(III)}} = \frac{\bar{u}_{\text{Am(III)}}}{u^\circ_{\text{Am}^{3+}}} \quad (7)$$

The normalized individual ion mobility of the central cation is given with

$$u_{\text{Am}^{3+}}^{0'} \equiv 1. \quad (8)$$

However, the effect is weak and may be reduced to the effect of hydrogen sulfate complexing of $^{241}\text{Am}-\text{Am}(\text{III})$ in the acidic solution. The difference between the stoichiometric stability constants in the acidic and neutral electrolyte systems (2) is not significant: $\log K_1 = 2.58(20)$ and $\log K_1 = 2.60(44)$, respectively.

The stoichiometric stability constants calculated are compared with the literature data in Table 4.

Unless available in the literature, thermodynamic stability constants were extrapolated, using Eq. (6). Most of the $\log K_1$ data have been obtained in weakly acidic solutions and at higher values of the overall ionic strength. Extrapolations of the

Table 4
Stability constants of the $[\text{Am}(\text{SO}_4)_n]^{3-2n}$ complexes,
 $n = 1, 2$, in aqueous perchlorate electrolytes, $T = 298.1 \text{ K}$

μ	pH	$\log K_1$	$\log K_2$	Reference
0		3.76		17
0		4.20		18
0		4.01		19
0		3.85 (30)		*
0.1	2.8 (2)	2.5 (2)	1.1 (2)	*
0.1	5.5 (2)	2.5 (3)	0.6 (6)	*
0.5		1.86		20
0.75	3.5–4.0	1.78		9
1.0 ^a		1.72		21
1.0	3–4	1.57	1.09	11
1.0 ^b		1.49	0.87	22
1.5	3.5–4.0	1.76	0.35	9
2.0	3	1.43	0.42	18

*This work.

^a303.1 K.

^b300.1 K.

corresponding K_1^0 data are complicated under these conditions. Consequently, the $\log K_1^0$ values given differ. Nevertheless, the stoichiometric stability constants $\log K_1^{\mu=0.10}$ of the present work agree with the tendency $\log K_1 = f(\mu)$ as to the data summarized in Table 4. This correspondence is also true for the $\log K_1^0$ data.

Conclusions

The possibilities of the modified technique of continuous electromigration measurements of carrier-free γ -emitting radionuclides in homogeneous aqueous electrolytes free of any supporting materials were demonstrated using the complex formation reactions of the carrier-free $^{241}\text{Am}-\text{Am(III)}$ with oxalate in neutral aqueous solutions and with sulfate in acidic and neutral aqueous solutions. The stoichiometric stability constants of $[\text{AmL}_n]^{3-2n}$ complexes were obtained for L = oxalate, $n = 1, 2$, $\mu = 0.01, 0.05$ and 0.10 , and for L = sulfate, $n = 1$, $\mu = 0.10$, $T = 298.1(1)$ K. Extrapolations of the thermodynamic stability constants were carried out. The values of the stability constants agree with the corresponding literature data. Finally, the results could be used for further investigations of the complex formation chemistry of the actinides by means of this electromigration technique.

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