

# Differences in the Mechanism of Influence of Organic Cation and Anion Radicals on the Cathodic Processes in Chloroaluminate Melt\*

N. TUMANOVA\*\*, L. BOGDANOVICH, and P. RUDENOK

*Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine,  
Kiev-142, 252680 Ukraine*

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The formation of stable ion-radicals of some organic compounds during the electrolysis of chloroaluminate melt has been shown. The cathodic discharge of cadmium, cobalt ions is stimulated by the ion-radicals formation. The influence of cation radicals is catalytic in nature, and the degree of stimulation is higher than that of anion radicals, and is caused by their adsorption on the Pt-electrode surface.

The study of the adsorption of some organic compounds in molten salts and its effect on electrode kinetics [1—5] allowed us to show that the main laws governing adsorption and adsorption kinetics are, on the whole, identical for all electrolyte systems except some specific features associated with the absence of solvent in melts [2, 3]. Following the agreed-upon classification in molten salts as in aqueous electrolytic solutions, the adsorbable surface-active additives are classified into three types according to the character of their influence on electrode kinetics: neutral, cation-active (salts with organic cation), and anion-active (salts with organic anion) additives. In molten salts, this classification was confirmed by us for molten alkali nitrates, thiocyanates, and chlorides [4]. Neutral and cation-active organic additives exhibit generally inhibiting properties, and anion-active additives stimulate the electrode reaction.

The results obtained in a chloroaluminate melt turned out to be unexpected. Neutral surfactants such as diphenylamine,  $\beta$ -naphthylamine, and cation-active benzidinium sulfate stimulated the cathode discharge of aluminium and cobalt ions [1] unlike other molten media, in which these compounds naturally showed inhibiting properties. It appears that the specific action of surfactants in a chloroaluminate melt is dependent on the chemical, electrochemical, acid-base, and catalytic properties of the melt itself. It is known from literature that a number of organic compounds dissolved in a chloroaluminate melt undergo anodic oxidation. It was found that benzene, chlorobenzene, triphenylamine, naphthalene, *N,N*-dimethylamine, and others

[6—11] oxidize on the anode to form stable cation radicals. Their stability in chloroaluminate melt is higher than in acetonitrile [9].

This information suggested that it is the radicals of organic compounds formed that may be responsible for the stimulation of electrode processes.

The objective of this investigation was to enlarge the body of experimental data, which reflect the influence of organic compounds that form stable cation radicals on the kinetics (rate) of cathodic processes, to establish the general regularities as well as the reason and mechanism of action of additives. It was also of interest to find whether stable anion radicals can be formed in a chloroaluminate melt and to study the character of their influence on the discharge of depolarizer ions.

## EXPERIMENTAL

Anhydrous chemically pure  $\text{AlCl}_3$  was used in the experiments. Chemically pure sodium chloride was recrystallized twice in distilled water and dried under vacuum at  $t = 100^\circ\text{C}$ . Cobalt and cadmium chlorides were prepared in the same way. Chemically pure organic reagents were dried under vacuum at a temperature which was  $30^\circ\text{C}$  lower than the reagent melting point. *S*- and *N*-containing heterocyclic compounds were synthesized and identified at the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine. The eutectic  $2\text{AlCl}_3\text{—NaCl}$  mixture was prepared by mixing salts, then melted, and the cell was evacuated for 5 h at  $t = 100^\circ\text{C}$ . The cell was made of

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\*\*The author to whom the correspondence should be addressed.

**Table 1.** The Calculated Parameters of Adsorption of Me-CX in 2AlCl<sub>3</sub>—NaCl Containing Co<sup>2+</sup> (5 × 10<sup>-5</sup> mol cm<sup>-3</sup>) (Pt Electrodes)

$c/(\text{mol cm}^{-3})$	$C/(\mu\text{kF cm}^{-2})$	$\theta$	$a$	$B/(\text{cm}^3 \text{mol}^{-1})$
0	7.5			
$2.9 \times 10^{-3}$	7.5			
$5.8 \times 10^{-3}$	8.0	0.6	-0.81	98
$9.7 \times 10^{-3}$	8.5			

pyrex glass and hermetically sealed with a cover with built-in current leads. A special opening for organic additive inlet and inert gas inlet and outlet was provided in the cover. The electrochemical experiments were taken in argon atmosphere, temperature of experiments was 175 °C.

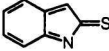
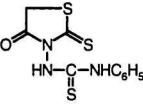
All the organic additives studied are soluble in chloroaluminate melt and thermally stable. The organic compounds under investigation are listed in Tables 1—3.

Polarization curves were taken on a P-5848 potentiostat and cyclic voltammograms on a PI-50-1 potentiostat. Chronopotentiometric measurements were made with an SV-14 oscillograph. An R-5021 as bridge was used to study adsorption. All electrochemical measurements were performed on platinum electrodes. The length of Pt wire which served as the cathode in all measurements was 0.5 cm and its diameter 0.05 cm. When taking polarization curves, the anode was a platinum plate of 1 cm<sup>2</sup> area; when taking chronopotentiograms, the anode was a Pt wire ( $l = 0.5$  cm,  $d = 0.05$  cm); when taking differential capacity curves, the anode was a platinum cylinder located coaxially around the cathode. The Ag/2AlCl<sub>3</sub>—NaCl—AgCl half-cell was used as the reference electrode.

The electrochemical behaviour of organic compounds was studied by the voltamperometric method. Several representatives of classes of heterocyclic compounds and aromatic amines as well as new compounds of *S*- and *N*-containing heterocycles were chosen as objects under investigation.

Oxidation of organic compounds was revealed in

**Table 2.** Comparative Characteristics of the Effect of Neutral and Anion-Active Organic Compounds on Discharge of Cations in Molten Salts\*

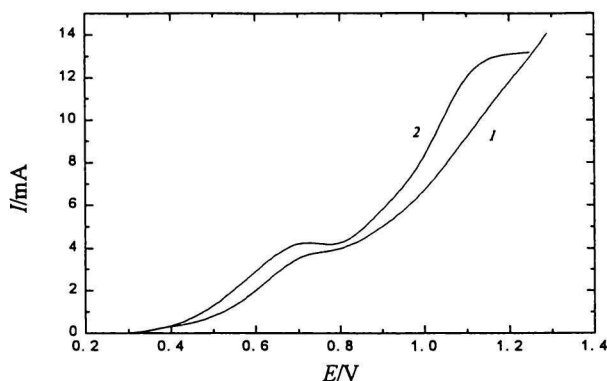
Electrolyte	Depolarizer	Organic additive	Additive concentration	$E/V$	$I_0/\text{mA}$	$I_0/I$
			10 <sup>-6</sup> mol cm <sup>-3</sup>			
2AlCl <sub>3</sub> —NaCl	Co <sup>2+</sup>	—	—	0.90	1.8	—
		Carbamide	2.9	1.1	—	2.3
		Na acetate	4.6	0.82	—	0.83
		Al stearate	4.0	0.80	—	0.72
		Anthracene	3.0	0.85	—	0.40
		Naphthalene	3.0	0.71	—	0.40
	Cd <sup>2+</sup>	Na ascorbate	3.0	0.84	—	0.44
		$\beta$ -Naphthylamine	4.0	0.85	—	0.46
		Diphenylamine	3.0	0.85	—	0.45
		Anthracene	3.0	0.74	—	0.38
		Anthraquinone	4.0	0.75	—	0.48
		Benzidine	3.0	0.75	—	0.48
			3.0	0.70	—	0.42
	3.0	0.70	—	0.42		
KCl—NaCl—LiCl—CsCl	Co <sup>2+</sup>	—	—	0.95	2.32	—
		Anthracene	2.5	1.0	—	1.2
		Diphenylamine	2.9	1.0	—	1.45
		Benzidine	1.5	1.1	—	1.8
KSCN—NaSCN	Co <sup>2+</sup>	—	—	0.92	2.08	—
		Anthracene	1.97	0.96	—	1.69
	Cd <sup>2+</sup>	—	—	0.95	1.92	—
		Benzidine	1.5	0.99	—	2.4

\*Electrodes — platinum, reference electrode Ag/Ag<sup>+</sup>, depolarizer concentration 5 × 10<sup>-5</sup> mol cm<sup>-3</sup>.

**Table 3.** The Comparison Data of Influence of Me-CX and other Compounds on Cathodic Discharge of Cations in Chloroaluminate and other Melts

Electrolyte	Depolarizer	Organic additive	Additive concentration	<i>E</i> /V	<i>I</i> <sub>0</sub> /mA	<i>I</i> <sub>0</sub> / <i>I</i>
			10 <sup>-6</sup> mol cm <sup>-3</sup>			
2AlCl <sub>3</sub> —NaCl	Co <sup>2+</sup>	—		0.9	1.88	
		Calixarene	3.0	0.8		0.82
	Cd <sup>2+</sup>	Calixarene	3.0	0.75	1.72	0.80
		Al stearate	9.0	0.8		0.82
KSCN—NaSCN	Co <sup>2+</sup>	—		0.92	2.08	
		Na acetate	7.8	0.92		0.78
KNO <sub>3</sub> —NaNO <sub>3</sub>	Cd <sup>2+</sup>	Na acetate	6.6	0.95	1.92	0.78
		—		0.95		
	Co <sup>2+</sup>	—		1.4	0.6	—
		Na acetate	6.0	1.3		0.80
KCl—NaCl—LiCl—CsCl	Co <sup>2+</sup>	—		0.95	2.4	—
		Al stearate	2.0	0.85		0.90

\*Electrodes – platinum, reference electrode Ag/Ag<sup>+</sup>, depolarizer concentration 5 × 10<sup>-5</sup> mol cm<sup>-3</sup>.



**Fig. 1.** Potentiodynamic curves on Pt electrodes against Ag/Ag<sup>+</sup> reference electrode in chloroaluminate melt with diphenylamine (1) and anthracene (2) at 175°C.

the anodic region of potentiodynamic curves when electrolyzing the melt 2AlCl<sub>3</sub>—NaCl—organic compound. The cathodic portion of the polarization curve exhibited no electrochemical effects up to the supporting electrolyte decomposition potential.

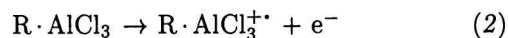
The anodic polarization curve obtained on Pt electrodes in a chloroaluminate melt containing organic additives exhibits oxidation waves: one or two depending on the nature of additive. The oxidation curves were obtained for all compounds studied. Fig. 1 shows as an example a diphenylamine oxidation curve (1). The oxidation wave is reversible and corresponds to one-electron process. The calculation of the curve in

semilog coordinates showed the slope ( $\text{tg } \alpha = 86 \text{ mV}$ ) to correspond to the theoretical coverage ( $2.3 RT/nF = 88 \text{ mV}$ ) at  $n = 1$ .

It is known that organic compounds: cyclic hydrocarbons [6—8] and aromatic amines [9—11] are able to form coloured complex compounds with aluminium chloride according to the scheme



which readily oxidize on the anode with removal of one electron, leading to the formation of cation radicals



Depending on melt acidity, the equilibrium of reaction (1) may shift to the left (when acidity decreases), and the melt may contain either a mixture of hydrocarbons and their complexes or pure hydrocarbons. However, both complexes with aluminium chloride and uncomplexed compounds are oxidized to cation radicals. Stable cation radicals may undergo further oxidation to dication. Therefore, the anodic polarization curve exhibits a second oxidation step when the positive potential increases *e.g.* for anthracene (Fig. 1, curve 2). Both oxidation waves are reversible and correspond to one-electron process ( $\text{tg } \alpha_{1\text{st wave}} = 0.85$ ,  $\text{tg } \alpha_{2\text{nd wave}} = 0.88$ ), indicating a stepwise oxidation of organic compounds first to cation radical and then to dication. Cyclic hydrocarbon and amine dications possess a low stability and a high reactivity [12].

While the formation of stable cation radicals of var-

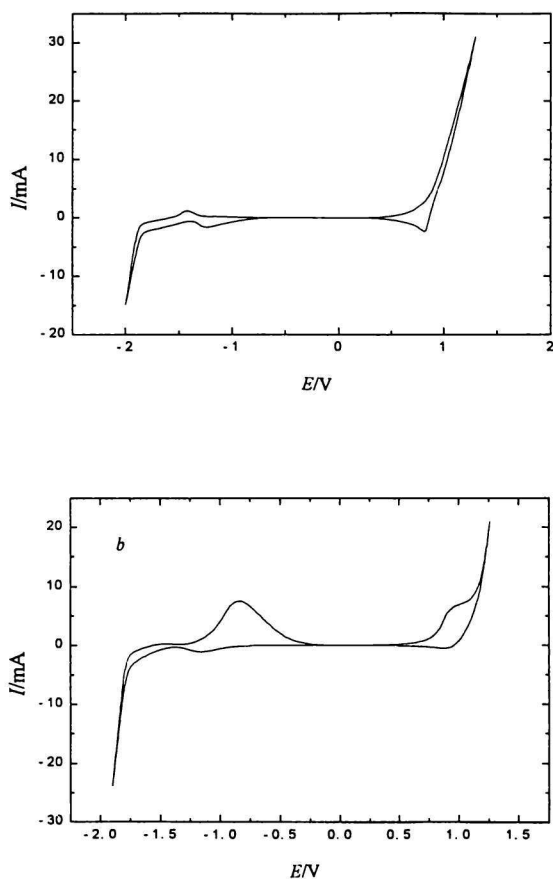


Fig. 2. Cyclic voltamperograms on Pt electrodes against Ag/Ag<sup>+</sup> reference electrode in chloroaluminate melt (a) and with added Me-CX (b) at 175 °C.

ious organic compounds during chloroaluminate melt electrolyses was established for a large number of organic compounds of different classes, it was proved to be difficult to find compounds that form stable anion radicals. Up to date the formation of stable anion radicals was found only for representatives of the class of calixarenes: methyl calixarene (Me-CX) and butyl calixarene (Bu-CX) were added to a chloroaluminate melt. But Bu-CX has a low solubility, therefore all results concerning this compound are qualitative in character and can merely serve as an additional corroboration of the conclusions that were drawn on the basis of the quantitative results, obtained when studying Me-CX solution in chloroaluminate melt.

No effects reflecting oxidation or reduction of calixarene were observed either in the cathodic or anodic potential region when taking potentiodynamic curves. Only when the cyclic voltammetry method was employed, the electrochemical transformation of calixarene was revealed. Comparison of cyclograms taken in chloroaluminate melt (Fig. 2a) and in melt, containing Me-CX (Fig. 2b) shows electrochemical process to occur in the negative potential region. Cathodic Me-CX reduction reaction takes place at more negative

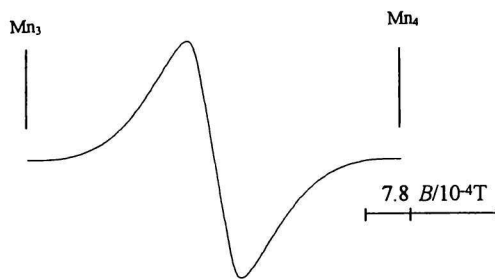


Fig. 3. ESR spectra of chloroaluminate melt with added Me-CX.

potentials than supporting electrolyte decomposition potential. Therefore, the formation of the Me-CX anion radical can be only observed in retracing the cathodic branch of the cyclic voltammogram.

The conclusion about anion radical formation was confirmed by an ESR spectral method. ESR spectrum of quickly frozen solution of Me-CX in 2AlCl<sub>3</sub>—NaCl exhibited after electrolysis has a signal which showed the presence of an unpaired electron and radical formation (Fig. 3).

In terms of transition energy, which is expressed by the equation

$$E = h \cdot \nu = g \cdot \beta \cdot H \quad (3)$$

where  $\beta$  is the Bohr magneton,  $H$  the field strength,  $\nu$  radiation frequency, and  $h$  Planck's constant, we calculated the spectroscopic splitting factor  $g$  to be 2.005 at a line width of  $7 \times 10^{-7}$  J.

It was interesting to determine the adsorption properties of organic additives. The adsorption of representatives of all classes of the compounds under investigation was studied on a Pt electrode using differential capacity curves. C—E curves were taken in the molten supporting 2AlCl<sub>3</sub>—NaCl electrolyte and in the presence of three different organic additive concentrations. To determine the main adsorption parameters, a graphic method was employed [13] by which the applicability of Frumkin's isotherm to the experimental data obtained was assessed

$$B \cdot c = \frac{\theta}{1 - \theta} \cdot \exp(-2 \cdot a \cdot \theta) \quad (4)$$

where  $B$  is the adsorption equilibrium constant in dm<sup>3</sup> mol<sup>-1</sup>,  $\theta$  the electrode surface coverage by adsorbed substance,  $a$  the attraction constant characterizing the interaction between adsorbed molecules, and  $c$  the additive concentration in dm<sup>3</sup> mol<sup>-1</sup>. Thus, the main adsorption parameters ( $a$ ,  $B$ ,  $\theta$ ) were calculated.

Addition of anthracene, naphthalene,  $\beta$ -naphthylamine, and diethylamine ( $c = 1-10 \times 10^{-2}$  mol cm<sup>-3</sup>) did not affect the zero-charge potential value of the differential capacity curve for the supporting

2AlCl<sub>3</sub>—NaCl electrolyte containing the ions of metals. Addition of the calixarenes Me-CX and Bu-CX increased the double-layer capacity at zero-charge potential along the entire length of the differential capacity curve over a wide potential range: from -1.0 V to +0.4 V. There were no substantial differences of the shape of the curves with additives from that of the curve for the supporting electrolyte. For Me-CX quantitative measurements of capacity were made, and the main adsorption parameters, which are listed in Table 1, were determined. The increase in capacity at the zero-charge point indicates the adsorptive activity of calixarenes. This effect is usually exhibited by anion-active surfactants.

## DISCUSSION

Addition of organic compounds to a chloroaluminate melt leads to an increase in Co<sup>2+</sup> and Cd<sup>2+</sup> discharge current. The ratio of depolarizer discharge current in the presence of an additive (*I*) to ion discharge current in a pure solvent (*I*<sub>0</sub>) determines the degree of inhibition (*I*/*I*<sub>0</sub> < 1) or stimulation (*I*/*I*<sub>0</sub> > 1) of the electrochemical process. Tables 2 and 3 list the experimental data obtained; Table 2 reflects the effect of compounds that form cation radicals, and Table 3 the effect of compounds that form anion radicals. For comparison, the tables give the data obtained by us earlier [1–5], which concern the behaviour of the same additives in other molten media. They illustrate the specific peculiarities of the action of additives in the case where organic compounds form radicals.

Table 2 lists the data obtained at the highest additive concentration. It follows from the table that:

- the investigated compounds (polycyclic, aromatic hydrocarbons and amines) differently affect discharge of ions in the chloroaluminate melt (*I*<sub>0</sub>/*I* < 1) and other molten media (*I*<sub>0</sub>/*I* > 1);
- the stimulating effect of the investigated neutral additives is greater than that of anion-active additives, not belonging to this class of organic compounds (sodium acetate, aluminium stearate);
- the effectiveness of salts, containing the anion of the studied class of compounds (sodium ascorbate), is more expressed in comparison with sodium acetate and aluminium stearate;
- values of the degree of stimulation of discharge of metals (*I*<sub>0</sub>/*I* < 1) by additions of the investigated compounds are similar among themselves and amount to a value of 0.43 on the average. From this it follows that the reason for the stimulation of each process has the same physicochemical nature independently of the composition and structure of the additive (CH—N and *S*,*N*-containing heterocycles, amino compounds);
- carbamide, which does not belong to the class of heterocyclic compounds, has the same inhibiting effect on Co<sup>2+</sup> discharge in all molten electrolytes studied.

The chronopotentiometric method, the theoretical

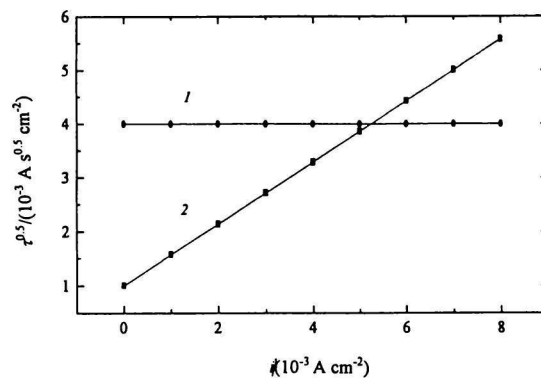
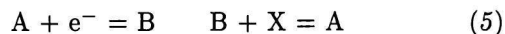


Fig. 4. The results of calculation of the chronopotentiograms on Pt electrodes in chloroaluminate melt, containing CoCl<sub>2</sub> ( $5 \times 10^{-5}$  mol cm<sup>-3</sup>) (1), and with added  $\beta$ -naphthylamine ( $4.0 \times 10^{-5}$  mol cm<sup>-3</sup>) (2) at 175°C.

aspects and main results of use of which for the investigation of kinetics and mechanism of electrode processes were discussed in [14], was used to determine the reasons for the stimulating effect of aromatic amines and cyclic hydrocarbons. Kinetics of discharge of Cd<sup>2+</sup> and Co<sup>2+</sup> ions in the pure chloroaluminate melt and in the presence of additives were investigated by this method. The diffusion character of discharge of metal ions in the chloroaluminate melt was concluded on the basis of the  $i \cdot \tau^{1/2}$  dependence on *i*, parallel to the abscissa axis, where  $\tau$  is the transition time. Upon introduction of the investigated additive the value  $i \cdot \tau^{1/2}$  initially decreases significantly and then increases in proportion to an increase of current (Fig. 4). Such a form of the dependence of  $i \cdot \tau^{1/2}$  on *i* is explained in the literature [15] by the catalytic character of the studied process.

During the explanation of the appearance of a catalytic current in the investigated systems it was considered that when the product of the electrochemical reaction B reacts quite rapidly with a certain solution component X the initial, electrochemically active form A is regenerated. In that case electrochemical catalysis [16–18] takes place



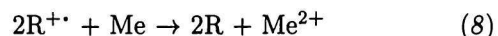
Thus, in our systems the cathodic process can be presented as



the anodic process as



and the chemical reaction as



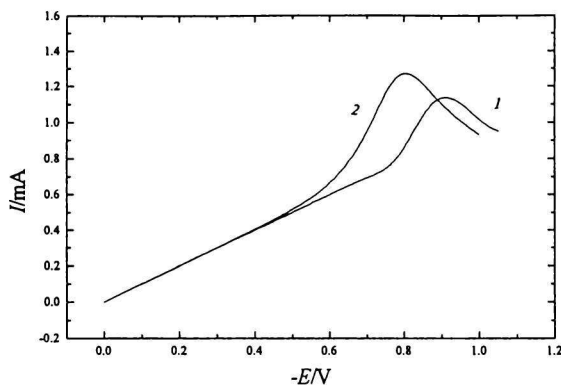


Fig. 5. The cathodic portions of the forward run of cyclic voltamperograms on Pt electrodes against Ag/Ag<sup>+</sup> reference electrode in chloroaluminate melts, containing CoCl<sub>2</sub> ( $5 \times 10^{-5}$  mol cm<sup>-3</sup>) (1), and with added Me-CX ( $3 \times 10^{-6}$  mol cm<sup>-3</sup>) (2) at 175°C.

Regeneration of electrochemically active species (metal ions) occurs in the electrode layer and leads to increasing the concentration of ions and reaction current.

Table 3 and Fig. 5 present the results of studying the effect of Me-CX on the discharge of Co<sup>2+</sup> and Cd<sup>2+</sup>. The table also contains data on the effect of anion-active surfactants in other molten electrolytes [2–5].

It follows from Table 3 that:

- addition of calixarenes stimulates the cathodic discharge of Co<sup>2+</sup> and Cd<sup>2+</sup>;
- the degree of cathodic process stimulation by calixarene is comparable to the action of anion-active surfactants in a chloroaluminate melt;
- the degree of stimulation by calixarene and anion-active surfactants in a chloroaluminate melt and in other melts is approximately the same (0.8), which may reflect the fact that the nature of the effect of additives on the cathodic process is the same.

The results obtained suggest that there is Me-CX adsorption on solid electrodes in the 2AlCl<sub>3</sub>–NaCl melt, and this compound is anion-active surfactant. The same effect was observed also for Bu-CX (qualitatively). This conclusion is corroborated by the results of studying Me-CX adsorption on a Pt electrode, which are listed in Table 1.

## CONCLUSION

The cathodic discharge of metal ions is stimulated (depolarization, current increase) by the formation of

organic compounds ion-radicals during chloroaluminate melt electrolysis. The degree of stimulation and the nature of the influence of radicals are different. The influence of cation radicals is catalytic in nature and more effective than the action of anion radicals, which is caused by their adsorption on the Pt electrode surface.

The method for stimulating electrode processes by means of radicals is simple and effective and can become widespread since the possibilities of accelerating electrode reactions are very limited.

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