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Antistatic properties of dicarboxylic acid esters

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Abstract: In the present study, the electrophysical properties of dicarboxylic acid esters and cyclohexenylsuccinic acid esters were investigated. Surface resistivity and electrical conductivity were measured using a two-electrode method with a teraohmmeter (E6-13A). The relationship between molecular structure and electrical conductivity were established. It was shown that an increase in the hydrocarbon chain length in both the alcohol and acid fragments leads to a decrease in electrical conductivity due to reduced molecular polarity. In contrast, the introduction of cyclic and aromatic fragments, as well as an increase in the number of ester functional groups, results in an increase in electrical conductivity due to higher molecular polarizability. Based on the experimental data, the charge relaxation time (τ) and conductivity enhancement factor (K) were calculated, enabling a quantitative assessment of the antistatic efficiency of the investigated compounds. For the dicarboxylic acid esters, τ values ranged from 4.4×10^{-5} to 8.6×10^{-3} s, while K varied from 2.5×10^2 to 7.1×10^4 . For cyclohexenylsuccinic acid esters, τ was found in the range of 4.6×10^{-5} to 6.5×10^{-4} s, and K ranged from 4.8×10^3 to 6.7×10^4 . The obtained results indicate efficient dissipation of electrostatic charge in low-polarity hydrocarbon media. An inverse relationship between electrical conductivity and charge relaxation time was observed, confirming that higher conductivity corresponds to faster charge decay. The conductivity values are comparable with those of commercial antistatic additives, indicating the potential applicability of the investigated compounds as functional antistatic additives for petroleum and lubricating systems.

Keywords: electrical conductivity; surface resistivity; charge relaxation time; molecular structure; polarizability; hydrocarbon systems.

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INTRODUCTION

In modern petroleum refining and transportation systems, the accumulation of static electricity in hydrocarbon media represents a serious operational and safety issue. During technological processes such as pumping, filtration, and mixing of petroleum products, electrical charges are generated due to the triboelectric effect. In low-polarity hydrocarbon media, the relaxation of these charges is significantly limited, leading to their accumulation and the formation of high electrostatic potentials.¹⁻⁵

Highly hydrotreated and low-sulfur fuels are particularly susceptible to static charge accumulation due to the absence of naturally occurring polar components capable of charge dissipation. This significantly increases the risk of spark formation, which may result in ignition or explosion in the presence of flammable vapours. Therefore, controlling electrical conductivity is an essential requirement for the safe operation of fuel handling systems.^{6,7}

According to international standards and recommendations, antistatic protection is achieved through the introduction of specific additives that regulate charge dissipation in hydrocarbon systems.⁸⁻¹⁰ These additives are typically polar organic compounds that form weakly conductive pathways, enabling controlled charge relaxation and preventing charge accumulation.

Materials used for electrostatic protection are generally classified as conductive, dissipative, and insulating systems according to international standards such as IEC 61340 and ASTM D257.¹¹⁻¹⁴ Their performance is defined by electrical resistance or conductivity levels, which determine their ability to either conduct or gradually dissipate static charges. In addition, key requirements for antistatic materials include efficient charge dissipation capability, grounding compatibility, and long-term stability of electrophysical properties under operating conditions.¹⁵⁻¹⁸

Despite significant progress in this field, the relationship between the molecular structure of antistatic agents and their electrophysical performance remains insufficiently understood, particularly for dicarboxylic acid ester systems with variable structural features.

In this context, dicarboxylic acid esters are of particular interest due to their structural versatility, including variation in hydrocarbon chain length and the introduction of cyclic and aromatic fragments, which allow targeted tuning of their electrophysical properties. In addition, these compounds exhibit good compatibility with hydrocarbon media and high thermal-oxidative stability.

The aim of this work is to investigate the influence of molecular structure on the electrical conductivity of esters of succinic, adipic, sebacic, and cyclohexenylsuccinic acids and to evaluate their potential as antistatic additives for hydrocarbon systems.

EXPERIMENTAL

Materials

The studied dicarboxylic acid esters were synthesized according to a previously reported procedure.^{19,20} The purity of the obtained compounds was confirmed by physicochemical analysis and was not less than 99%.

Methods

The electrophysical characteristics of the investigated compounds were determined using a two-electrode method with a teraohmmeter (E6-13A), which allows measurement of electrical resistance over a wide range typical for low-conductivity media. The relative uncertainty of the measured electrophysical characteristics was estimated to be $\pm 5\%$ under the applied experimental conditions.

Prior to measurements, the electrodes were thoroughly cleaned with ethanol to remove contaminants and moisture that could affect the accuracy of the results. The sample was placed in a measuring cell ensuring a fixed distance between the electrodes and uniform contact with the tested substance. The temperature was monitored using a thermocouple. All measurements were carried out at $20 \pm 1^\circ\text{C}$.

The electrical resistivity (ρ) was calculated using the following equation (1):

$$\rho = R \cdot S / d \quad (1)$$

where R is the measured resistance, S is the electrode area, and d is the distance between the electrodes.

The electrical conductivity (σ) was determined as the reciprocal of the resistivity.

Based on the experimentally obtained conductivity values, additional electrophysical parameters characterizing the antistatic properties of the investigated compounds were calculated.

The charge relaxation time (τ) was determined according to the relation:

$$\tau = \varepsilon \varepsilon_0 / \sigma \quad (2)$$

where ε is the relative dielectric permittivity of the medium and ε_0 is the vacuum permittivity. For comparative calculations, a relative dielectric permittivity of $\varepsilon = 3.5$ was adopted as a representative value for the investigated series of weakly polar organic ester compounds. The adopted value was used as a calculation parameter and was not considered an experimentally determined individual dielectric permittivity for each compound.

The conductivity enhancement factor (K) was calculated as the ratio of the electrical conductivity of the investigated compound to that of the base hydrocarbon medium:

$$K = \sigma / \sigma_0 \quad (3)$$

where $\sigma_0 = 1 \times 10^{-11} \text{ S m}^{-1}$ is a typical conductivity value for low-polar hydrocarbon systems.

RESULTS AND DISCUSSION

Experimental data on the electrophysical characteristics of the studied dicarboxylic acid esters are summarized in Table I.

TABLE I. Electrophysical characteristics of dicarboxylic acid esters

Ester	R / Ω	$\rho / \Omega \text{ m}$	$\sigma / \text{S m}^{-1}$	τ / s	K
Dioctyl succinate	1.4×10^7	2.8×10^6	3.6×10^{-7}	8.6×10^{-5}	3.6×10^4
Dinonyl succinate	6.2×10^8	1.44×10^7	6.9×10^{-8}	4.5×10^{-4}	6.9×10^3
Butyl octyl succinate	7.0×10^8	1.4×10^7	7.1×10^{-8}	4.4×10^{-4}	7.1×10^3
2-Hydroxyethyl octyl succinate	1.6×10^7	3.2×10^6	3.1×10^{-7}	1.0×10^{-4}	3.1×10^4
2-(Hexanoyloxy)ethyl octyl succinate	2.0×10^7	4.0×10^6	2.5×10^{-7}	1.2×10^{-4}	2.5×10^4
Bis[2-(hexanoyloxy)ethyl] succinate	7.0×10^7	1.4×10^6	7.1×10^{-7}	4.4×10^{-5}	7.1×10^4
Dioctyl adipate	3.0×10^6	6.0×10^7	1.6×10^{-8}	1.9×10^{-3}	1.6×10^3
Butyl octyl adipate	1.1×10^8	2.2×10^7	4.5×10^{-8}	6.9×10^{-4}	4.5×10^3
2-(Hexanoyloxy)ethyl octyl adipate	4.5×10^7	9.0×10^6	1.1×10^{-7}	2.8×10^{-4}	1.1×10^4
Bis[2-(hexanoyloxy)ethyl] adipate	8.0×10^7	1.6×10^7	6.2×10^{-8}	5.0×10^{-4}	6.2×10^3
Bis(4-methylcyclohexyl) adipate	1.2×10^8	2.4×10^7	4.1×10^{-8}	7.6×10^{-4}	4.1×10^3
Heptyl 4-methylcyclohexyl adipate	1.4×10^9	2.8×10^8	3.6×10^{-9}	8.6×10^{-3}	3.6×10^2
Bis(4-methylcyclohexyl) sebacate	9.9×10^7	1.9×10^7	5.3×10^{-8}	5.8×10^{-4}	5.3×10^3
Dibenzyl sebacate	3.0×10^7	6.0×10^6	1.7×10^{-7}	1.8×10^{-4}	1.7×10^4
2-Hydroxyethyl octyl sebacate	1.5×10^8	3.0×10^7	3.3×10^{-8}	9.4×10^{-4}	3.3×10^3
Bis[2-(hexanoyloxy)ethyl] sebacate	2.0×10^9	4.0×10^8	2.5×10^{-9}	1.2×10^{-3}	2.5×10^2

Based on the obtained conductivity data, the charge relaxation time (τ) and conductivity enhancement factor (K) were calculated.

The investigated esters exhibited charge relaxation times in the range of $4.4 \times 10^{-5} - 8.6 \times 10^{-3}$ s, indicating their ability to promote efficient dissipation of accumulated electrical charges in low-polar hydrocarbon media. Compounds characterized by higher conductivity values consistently displayed shorter relaxation times, confirming the expected inverse relationship between charge transport capability and the rate of electrostatic charge decay.

The conductivity enhancement factor varied from 2.5×10^2 to 7.1×10^4 , demonstrating a substantial increase in electrical conductivity relative to the base hydrocarbon medium. These findings suggest that the synthesized esters are capable of significantly improving the electrostatic dissipation properties of low-conductivity hydrocarbon systems.

Analysis of the experimental results revealed that the electrical conductivity of the investigated dicarboxylic acid esters is strongly dependent on molecular structure. In general, elongation of the hydrocarbon chains in both the alcohol and acid fragments resulted in decreased conductivity, which may be attributed to reduced molecular polarity and diminished mobility of charge carriers.

Molecular symmetry was also found to exert a pronounced influence on conductivity. Unsymmetrical esters exhibited higher conductivity values than their symmetrical counterparts, likely due to an increase in molecular dipole moment arising from structural asymmetry, which facilitates charge transfer processes.

An increase in the number of ester functional groups led to enhanced conductivity. In particular, complex esters containing multiple ester moieties

demonstrated higher conductivity values compared with simple diesters, which can be associated with the greater number of polar centers participating in charge transport.

The incorporation of cyclic and aromatic fragments produced a significant effect on the electrical conductivity of the investigated compounds. Aromatic substituents promoted conductivity enhancement owing to the high polarizability of π -electron systems and partial electron delocalization, whereas cyclic structures influenced molecular rigidity and electron density distribution, thereby facilitating charge mobility within the system.

Comparable structure-conductivity relationships were also identified for the cyclohexenylsuccinic acid esters summarized in Table II.

TABLE II. Electrophysical characteristics of cyclohexenylsuccinic acid esters

Ester	R / Ω	$\rho / \Omega \text{ m}$	$\sigma, \text{S m}^{-1}$	τ / s	K
Dibutyl 2-(cyclohex-1-en-1-yl)succinate	1.8×10^8	1.8×10^7	5.6×10^{-8}	5.5×10^{-4}	5.6×10^3
Butyl isobutyl 2-(cyclohex-1-en-1-yl)succinate	1.5×10^7	1.5×10^6	6.7×10^{-7}	4.6×10^{-5}	6.7×10^4
Butyl nonyl 2-(cyclohex-1-en-1-yl)succinate					
Dibenzyl 2-(cyclohex-1-en-1-yl)succinate					
Dinonyl 2-(cyclohex-1-en-1-yl)succinate	5.0×10^7	5.0×10^6	2.0×10^{-7}	1.6×10^{-4}	2.0×10^4
Benzyl cyclohexyl 2-(cyclohex-1-en-1-yl)succinate	7.5×10^7	7.5×10^6	1.3×10^{-7}	2.4×10^{-4}	1.3×10^4

For the investigated compounds, the charge relaxation time was found to vary within the range of $4.6 \times 10^{-5} - 6.5 \times 10^{-4} \text{ s}$, whereas the conductivity enhancement factor ranged from 4.8×10^3 to 6.7×10^4 . Compounds exhibiting higher electrical conductivity consistently demonstrated shorter relaxation times, confirming the inverse relationship between charge transport efficiency and electrostatic charge dissipation rate, which is indicative of enhanced antistatic performance.

The experimental results demonstrate that the electrical conductivity of cyclohexenylsuccinic acid esters is governed by the combined influence of several structural factors. Symmetrical aliphatic esters containing relatively short hydrocarbon chains exhibited lower conductivity values, which can be attributed to their lower polarity and reduced mobility of charge carriers.

In contrast, disruption of molecular symmetry, particularly through the introduction of branched alkyl substituents, resulted in a pronounced increase in conductivity due to the enhancement of molecular dipole moment and redistribution of electron density. The incorporation of cyclic and aromatic fragments also contributed significantly to conductivity enhancement as a

consequence of increased electronic polarizability and stronger intermolecular interactions facilitating charge transport.

Overall, the obtained results indicate that the electrostatic properties of cyclohexenylsuccinic acid esters can be effectively regulated through targeted modification of molecular architecture, including variation of alkyl chain structure, molecular symmetry, and incorporation of polarizable cyclic or aromatic moieties.

To evaluate the practical relevance of the obtained results, the electrical conductivity of the synthesized esters was compared with that of commercially used antistatic additives (Tables III and IV).

TABLE III. Electrophysical characteristics of commercial antistatic additives

Additive	Typical concentration / ppm	σ / S m ⁻¹
STADIS 450	1-5	$(1-5) \times 10^{-7}$
ASA-3	1-3	$\sim 10^{-7}$
INTRON 500	1-5	$(1-5) \times 10^{-7}$
Antis DF3	1-2	$\geq 2 \times 10^{-7}$

TABLE IV. Comparative conductivity analysis

System	Range of σ / S m ⁻¹
Dicarboxylic acid esters	$2.5 \times 10^{-9} - 7.1 \times 10^{-7}$
Cyclohexenylsuccinic acid esters	$4.8 \times 10^{-8} - 6.7 \times 10^{-7}$
Commercial antistatic additives	$1 \times 10^{-7} - 5 \times 10^{-7}$
Base hydrocarbon media	$\sim 10^{-12} - 10^{-10}$

The conductivity of the investigated esters is higher than that of the base hydrocarbon medium and, in several cases, comparable to the range of commercial antistatic additives. In particular, unsymmetrical and polar-functionalized esters exhibit conductivity values up to 7.1×10^{-7} S m⁻¹, approaching those of widely used commercial formulations.

It should be noted that commercial antistatic additives are effective at very low concentrations (ppm level), whereas the synthesized esters exhibit relatively high electrical conductivity, which may enable the achievement of antistatic performance at reduced additive dosages.

Overall, the comparative analysis indicates that the investigated dicarboxylic acid esters and cyclohexenylsuccinic acid esters demonstrate electrophysical characteristics comparable to conventional antistatic additives, confirming their potential applicability as functional antistatic agents in hydrocarbon systems.

CONCLUSION

The results of the present study demonstrate that dicarboxylic acid esters and cyclohexenylsuccinic acid esters exhibit an enhanced ability to facilitate charge transport in low-polar hydrocarbon media, leading to an increase in electrical conductivity relative to the base hydrocarbon system.

It was established that the electrical conductivity of the investigated compounds is governed by molecular structure and depends on hydrocarbon chain length, molecular symmetry, and the presence of polarizable functional fragments, confirming the possibility of targeted tuning of their electrophysical properties.

A clear correlation between electrical conductivity, charge relaxation time and conductivity enhancement factor was observed, whereby an increase in conductivity is accompanied by a decrease in τ and an increase in K , indicating improved charge dissipation efficiency.

Overall, the obtained conductivity values indicate effective electrostatic charge dissipation in hydrocarbon media. The studied esters of dicarboxylic acids and cyclohexenylsuccinic acid esters exhibit conductivity values comparable to those of commercially available antistatic additives, suggesting their potential applicability as functional antistatic agents for fuels and lubricating systems.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/13983>, or from the corresponding author on request.

ИЗВОД

АНТИСТАТИЧКА СВОЈСТВА ЕСТАРА ДИКАРБОКСИЛНИХ КИСЕЛИНА

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У овом раду испитивана су електрофизичка својства естара дикарбоксилних киселина и естара циклохексенилхилибарне киселине. Површинска отпорност и електрична проводљивост мерене су методом две електроде помоћу тераомметра (Е6-13А). Успостављена је зависност између молекулске структуре и електричне проводљивости. Показано је да повећање дужине угљоводоничног ланца, како у алкохолном тако и у киселинском фрагменту, доводи до смањења електричне проводљивости услед смањене поларности молекула. Насупрот томе, увођење цикличних и ароматичних фрагмената, као и повећање броја естарских функционалних група, доводи до повећања електричне проводљивости услед веће поларизабилности молекула. На основу експерименталних података израчунати су време релаксације наелектрисања (τ) и фактор повећања проводљивости (K), што је омогућило квантитативну процену антистатичке ефикасности испитиваних једињења. За естре дикарбоксилних киселина вредности τ кретале су се у распону од $4,4 \times 10^{-5}$ до $8,6 \times 10^{-3}$ s, док је K варирао од $2,5 \times 10^2$ до $7,1 \times 10^4$. За естре циклохексенилхилибарне киселине, τ је био у опсегу од $4,6 \times 10^{-5}$ до $6,5 \times 10^{-4}$ s, а K се кретао од $4,8 \times 10^3$ до $6,7 \times 10^4$. Добијени резултати указују на ефикасну дисипацију електростатичког наелектрисања у нискополарним угљоводоничним срединама. Уочена је обрнуто пропорционална зависност између електричне проводљивости и времена релаксације наелектрисања, што потврђује да већа проводљивост одговара бржем опадању наелектрисања. Вредности проводљивости су упоредиве са вредностима комерцијалних

антистатичких адитива, што указује на потенцијалну применљивост испитиваних једињења као функционалних антистатичких адитива за нафтне и мазивне системе.

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