Conductivity Properties of Selected Aliphatic Monocarboxylic Acid Anions in Water at 298.15 K

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The article presents the electric conductivity values of sodium salts of four selected monocarboxylic acid derivatives in aqueous solution: those with a chlorine substituent in the peripheral position, *i.e.* $ClCH(CH_2)_nCOOH$; those with a bromine substituent in the peripheral position, *i.e.* $BrCH(CH_2)_nCOOH$; as well as unsaturated sodium salts with a double bond in the peripheral position, *i.e.* $CH_2=CH(CH_2)_nCOOH$; and unsaturated sodium salts with a double bond in the second position, *i.e.* $CH_3-CH=CH(CH_2)_nCOOH$. All conductivity measurements were performed at 298.15 K in the concentration range of $0.0005 < c$ / mol $\cdot$ dm^{-3} < 0.018. The obtained values allowed the limiting molar conductivities (Λ_m^0) of the studied electrolytes to be determined using the Fuoss-Justice equation. Based on these (Λ_m^0) values, the molar limiting conductivity values (λ_A^0-) for individual anions of the tested electrolytes were calculated and analyzed as a function of carbon chain length. The work also examines the effect of substituent type (Cl or Br) and double bond location on the limiting molar conductivity values of the tested monocarboxylic acid anions and compares them with literature values.

1. INTRODUCTION

The term carboxylic acid describes a number of organic compounds with different structures and chemical properties. Structurally, carboxylic acids can be divided into monocarboxylic, dicarboxylic and unsaturated forms, and those with various substituents in the aliphatic chain. Only a few papers have, so far, described the conductometric properties of these electrolytes [1-5]; however, it

is known that the sodium salts of carboxylic acids offer extremely good solubility in water, which allows the electrical conductivity of their solutions to be studied across a wide concentration range. Nevertheless, although conductivity values have been obtained for a number of sodium salts of monocarboxylic acids, and for carboxylic acids themselves, as a function of carbon chain length and temperature [6-7],a few studies have examined the electrical conductivity of sodium salts of carboxylic acids in water at 298.15 K [8-10].

The present article determines the molar conductivity values of sodium salts of carboxylic acids containing a Cl or Br substituent, and those of unsaturated monocarboxylic acids with a double bond in the peripheral or second position; it also compares these values with those of the sodium salts of previously-studied monocarboxylic acids [7].

Halogenated acids are commonly used in organic synthesis [11]. Chloroacetic acid is stronger than acetic acid, due to the addition of a chlorine atom. The addition of more chlorine atoms causes a further increase in electronegativity, which in turn, significantly affects the physical and chemical properties of the acid. Their salts are used in cosmetic treatments, as components of anti-wrinkle peels, for removing acne scars and for reducing skin discoloration [12]. They are also used in medical analytics, the preparation of biochemicals, as well as, in molecular biology and genetics applications [13].

Acrylic acid, an unsaturated double carboxylic acid, undergoes similar reactions to aliphatic carboxylic acids and unsaturated compounds. However, its reactivity is enhanced by the presence of a $C = C - C = O$ conjugate bond system: the β-carbon atom has a strong electrophilic character, which allows acrylic acid to easily undergo nucleophilic addition. It also very readily undergoes polymerization, with a strongly exothermic and rapid course [14].

An important aspect of this work is that it examines the effect of carbon chain length on the obtained conductivity values, and is the first to compare its findings with analogous values obtained for monocarboxylic acid anions. It also assesses the effect of substituent type (Cl or Br) and the location of the double bond on the obtained conductivity values. All conductivity measurements were carried out at $T = 298.15$ K in the concentration range (*c*) $0.0005 < c \, / \, mol \cdot dm^{-3} < 0.018$ at atmospheric pressure. The obtained results were used to calculate the limiting molar conductivities (Λ^o_m) using a formula similar to the Quint-Viallard equation [15].

2. EXPERIMENTAL SECTION

2.1 Materials

Some of the studied salts were purchased from commercial companies; these were dried in a vacuum dryer to a constant mass at a temperature of $T = 373.15$ K. Other salts, which were not commercially available, were synthesized using purchased acids with high purity, and pure sodium hydroxide (pure PA micro bubbles, Avantor Performance Materials Poland SA, CAS 1310-73-2). Acetone was $\geq 99\%$ pure (Avantor Performance Materials Poland S.A). The purity of all used acids was $\geq 98\%$.

Briefly, appropriate amounts of tested acids and aqueous sodium hydroxide were mixed in a 1:1 stoichiometric ratio. The mixture was then heated and stirred to dissolve the acid and evaporate the solvent. The resulting salt was washed with high purity acetone and then dried at $T = 373.15$ K to a constant weight. The purity of the produced salts was found to be approximately 98% by weight, as determined by IR spectrum analysis using a Nicolet iS5 apparatus (Tremo Scientific). All solutions were produced using double distilled and deionized water (BEHR, Labo-Technik); after degassing, this water had a conductivity better than $0.5 \cdot 10^{-6}$ S $\cdot$ cm^{-1}.

2.2. Methods

All solutions were prepared gravimetrically using an analytical balance (Sartorius RC 210D) with an accuracy of $\pm 1 \cdot 10^{-5}$g and analyzed according to Bešter-Rogač *et. al.* [16,17], and as given elsewhere [18,19]. Electrical conductivity was measured using a Wayne-Kerr Electronics 6430B / 6440 B RLC conductivity meter (United Kingdom) with a three-electrode measuring cell, similar to that described in [20], with an uncertainty of 0.02%. The entire conductivity measurement process was carried out under an inert gas atmosphere. The measuring cell was calibrated with an aqueous solution of potassium chloride [21]. Potassium chloride (0.9999, Merck) was dried for two days at $T = 373$ K. All measured conductivity values, $\lambda = 1/R_\infty$, were obtained by extrapolation of cell resistance, $R_\infty(\nu)$, to infinite frequency $R_\infty = \lim_{\nu \to \infty} R(\nu)$ using the empirical function $R(\nu) = R_\infty + A/\nu$, where parameter A is specific for the cell. The uncertainty of the measured conductivity values was estimated at $\pm$ 0.05% based on typical sources of error, *e.g.* calibration, sample purity and measurement accuracy. The measuring cell was thermostated using a BU 20F calibration thermostat (Lauda, Germany) with a stability better than 0.005 K. In addition, the temperature was monitored using an Amarell 3000TH AD thermometer (Germany) connected to a DLK 25 flow cooler (Lauda, Germany). Conductivity measurements were carried out at different frequencies: $\nu = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 10.0$ and 20.0 kHz.

3. RESULTS AND DISCUSSION

The density, viscosity and dielectric permittivity values of water required for subsequent calculations are given in Table 1.

Table 1. Density (ρ_o), viscosity (η) and relative permittivity (ε) of pure water at temperature $T = 298.15$ K.

T/K	ρ_o/kg$\cdot$m^{-3} [a]	$10^3 \cdot \eta$ /Pa$\cdot$s [a]	ε_r [b]
298.15	997.047	0.890	78.40

[a] values for water recommended by the International Association for the Properties of Water and Steam (IAPWS) calculated on the online property calculator (https://web1.hszg.de/thermo_fpc/)
[b] values for water calculated according to the IAPWS recommendations
(http://www.iapws.org/relguide/dielec.pdf)

Molonite values were converted to molar concentrations (c), using equation Eq.1., based on independently-determined density gradient values (b).

$$c/\tilde{\tilde{m}} = \rho = \rho_o + b \cdot \tilde{m} \qquad (1)$$

where ρ is the density of the solution. Molarity (c) was needed for the conductivity equation.

The concentrations and molar conductivities of the sodium salts (Λ_m) are presented in Table 2 (Supplementary Information) as a function of molarity of the sodium salt (m - moles of electrolyte per kilogram of solvent). The relationship between $\tilde{m}$ and c is as follows:

$$\tilde{m} = c/\rho = m/(1 + m \cdot M) \qquad (2)$$

The conductivity data were analyzed using the equation [8, 9] according to the low concentration Chemical Model (lcCM) [8,9,22]. This approach uses the following set of equations:

$$\Lambda_m = \alpha\left[\Lambda_m^0 - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + J(\alpha c) - J_{3/2}(\alpha c)^{3/2}\right] \qquad (3)$$

together with

$$K_A = \frac{1-\alpha}{\alpha^2 \cdot c \cdot y_{\pm}^2} \qquad (4)$$

and

$$\ln y_{\pm} = -\frac{A \cdot \alpha^{1/2} \cdot c^{1/2}}{1 + B \cdot r \cdot \alpha^{1/2} \cdot c^{1/2}} \qquad (5)$$

In these equations:
- Λ_m^0 is the limiting molar conductivity;
- α is the dissociation degree of the electrolyte;
- K_A is the ionic association constant;
- r is the distance parameter of the ions;
- $y_{\pm}$ is the activity coefficient of ions on the molar scale;
- A and B are the coefficients of the Debye Hückel equation.

The maximum K_A values (resulting from calculations based on Equation 3) did not exceed 0.1 - 0.2. So these are rather results resulting from iterative rounding than values that actually confirm the formation of ion pairs. Therefore, after a preliminary analysis of these observations, it was assumed that in further calculations the phenomenon of ionic association does not occur in the tested solutions, which boils down to the assumption that $\alpha = 1$.

Table 2. Molar conductances Λ_m [S·cm^2·mol^{-1}], corresponding molalites $m \cdot 10^3$ [mol·kg^{-1}] and molarity c [mol·dm^{-3}] and coefficients of hydrolysis β for studied sodium salts of carboxylic acids in water, at $T = 298.15$K and pressure $p = 0.1$ MPa.[a]

Sodium salts of chloroacetic acid (chloroetanoic)				Sodium salts 3chloropropionic acid (3-chloropropionic)			
$\dfrac{m \cdot 10^3}{mol \cdot kg^{-1}}$	$\dfrac{c}{mol \cdot dm^{-3}}$	β	$\dfrac{\Lambda_m}{S \cdot cm^2 \cdot mol^{-1}}$	$\dfrac{m \cdot 10^3}{mol \cdot kg^{-1}}$	$\dfrac{c}{mol \cdot dm^{-3}}$	β	$\dfrac{\Lambda_m}{S \cdot cm^2 \cdot mol^{-1}}$
0.5759	0.00057	0.000255	91.39	0.5963	0.00059	0.000317	88.35
1.155	0.00115	0.000182	90.64	1.177	0.00117	0.000232	87.61
2.162	0.00216	0.000133	89.73	2.199	0.00219	0.000169	86.71
3.231	0.00322	0.000111	89.00	3.207	0.00320	0.000138	86.03
4.772	0.00476	0.000090	88.17	4.660	0.00465	0.000114	85.25
6.718	0.00670	0.000076	87.32	6.661	0.00665	0.000096	84.38
8.579	0.00856	0.000067	86.64	8.515	0.00850	0.000084	83.71
10.50	0.01048	0.000060	86.04	10.34	0.01032	0.000077	83.14
12.31	0.01229	0.000056	85.53	12.15	0.01214	0.000070	82.63
14.07	0.01405	0.000052	85.08	13.95	0.01393	0.000066	82.17
15.69	0.01568	0.000049	84.70	15.58	0.01556	0.000062	81.79
17.38	0.01736	0.000046	84.33	17.26	0.01724	0.000059	81.43
Sodium salts 4-chlorobutyric acid (4-chlorobutyric)				Sodium salts of 5-chlorovaleric acid (5-chloropentanoic)			
0.5932	0.00059	0.000368	85.37	0.6162	0.00054	0.000434	82.64
1.165	0.00116	0.000269	84.65	1.149	0.00110	0.000314	81.91
2.263	0.00226	0.000199	83.69	2.181	0.00209	0.000233	81.02
3.323	0.00331	0.000162	83.00	3.170	0.00296	0.000191	80.42
4.793	0.00478	0.000135	82.23	4.561	0.00446	0.000160	79.60
6.772	0.00676	0.000112	81.39	6.564	0.00620	0.000134	78.83
8.553	0.00854	0.000099	80.76	8.359	0.00801	0.000118	78.16
10.47	0.01045	0.000089	80.16	10.25	0.00964	0.000107	77.64
12.27	0.01225	0.000083	79.67	12.02	0.01144	0.000097	77.12
13.98	0.01397	0.000077	79.24	13.68	0.01303	0.000093	76.71
15.75	0.01573	0.000073	78.83	15.38	0.01465	0.000087	76.32
17.54	0.01752	0.000069	78.45	17.07	0.01609	0.000083	76.00
Sodium salts of 6-chlorohexanoic acid (6-chlorohexanoic)				Sodium salts of bromoacetic acid (bromoetanoic)			
0.5834	0.00058	0.000522	80.74	0.5744	0.00057	0.000220	91.23
1.139	0.00114	0.000375	80.01	1.121	0.00112	0.000151	90.29
2.167	0.00216	0.000279	79.12	2.149	0.00214	0.000111	88.83
3.221	0.00321	0.000235	78.52	3.171	0.00316	0.000091	87.69
4.787	0.00478	0.000192	77.70	4.597	0.00459	0.000075	86.51
6.659	0.00665	0.000161	76.93	6.499	0.00648	0.000063	85.07
8.460	0.00846	0.000142	76.26	8.360	0.00834	0.000055	83.96
10.38	0.01038	0.000130	75.74	10.18	0.01017	0.000050	82.85
12.28	0.01229	0.000119	75.22	11.88	0.01186	0.000046	82.23
13.87	0.01389	0.000112	74.81	13.57	0.01355	0.000043	81.26

15.61	0.01564	0.000105	74.42	15.21	0.01520	0.000041	80.78
17.28	0.01732	0.000100	74.10	16.77	0.01676	0.000038	80.20

Sodium salts of 3-bromopropionic acid (3-bromopropionic)				**Sodium salts of 4-bromobutyric acid (4-bromobutyric)**			
$\dfrac{m \cdot 10^3}{mol \cdot kg^{-1}}$	$\dfrac{c}{mol \cdot dm^{-3}}$	β	$\dfrac{\Lambda_m}{S \cdot cm^2 \cdot mol^{-1}}$	$\dfrac{m \cdot 10^3}{mol \cdot kg^{-1}}$	$\dfrac{c}{mol \cdot dm^{-3}}$	β	$\dfrac{\Lambda_m}{S \cdot cm^2 \cdot mol^{-1}}$
0.5738	0.00057	0.000265	87.83	0.5783	0.00058	0.000317	84.26
1.081	0.00108	0.000192	86.89	1.084	0.00108	0.000232	83.19
2.145	0.00214	0.000143	85.43	2.148	0.00214	0.000169	81.48
3.214	0.00321	0.000121	84.29	3.233	0.00322	0.000138	80.09
4.757	0.00475	0.000100	83.11	4.817	0.00481	0.000114	78.56
6.738	0.00672	0.000086	81.67	6.773	0.00676	0.000096	77.02
8.711	0.00869	0.000077	80.56	8.800	0.00878	0.000084	75.84
10.64	0.01062	0.000070	79.45	10.72	0.01070	0.000077	74.83
12.48	0.01246	0.000066	78.83	12.58	0.01256	0.000070	73.99
14.28	0.01426	0.000062	77.86	14.38	0.01436	0.000066	73.08
15.99	0.01597	0.000059	77.38	16.12	0.01611	0.000062	72.23
17.73	0.01771	0.000056	76.80	17.86	0.01784	0.000059	71.53

Sodium salts of 5-bromovaleric acid (5-bromopentanoic)				**Sodium salts od acrilic acid (2-propenoic)**			
0.5451	0.00054	0.000378	81.31	0.5129	0.00051	0.000744	85.18
1.022	0.00102	0.000279	80.24	1.092	0.00109	0.000531	84.41
2.025	0.00202	0.000209	78.53	2.150	0.00214	0.000389	83.46
3.047	0.00304	0.000172	77.14	3.135	0.00313	0.000317	82.80
4.541	0.00453	0.000145	75.61	4.568	0.00456	0.000265	82.02
6.384	0.00637	0.000122	74.07	6.580	0.00657	0.000223	81.15
8.295	0.00828	0.000109	72.89	8.502	0.00849	0.000196	80.46
10.11	0.01009	0.000099	71.88	10.43	0.01042	0.000178	79.86
11.86	0.01184	0.000093	71.04	12.18	0.01216	0.000164	79.38
13.55	0.01353	0.000087	70.13	13.92	0.01391	0.000154	78.94
15.20	0.01518	0.000083	69.28	15.63	0.01561	0.000145	78.54
16.83	0.01682	0.000079	68.58	17.28	0.01727	0.000135	78.19

Sodium salts of vinylacetic acid (3-butenoic)				**Sodium sals of 3-vinylpropionic acid (4- pentenoic)**			
0.4612	0.00065	0.000854	82.44	0.5859	0.00058	0.000941	79.83
1.078	0.00119	0.000641	81.61	1.124	0.00112	0.000663	79.27
2.036	0.00219	0.000499	80.74	2.182	0.00218	0.000477	78.46
3.060	0.00317	0.000427	80.04	3.245	0.00324	0.000392	77.88
4.494	0.00465	0.000375	79.26	4.786	0.00477	0.000323	77.18
6.450	0.00665	0.000333	78.41	6.746	0.00673	0.000269	76.45
8.269	0.00850	0.000306	77.75	8.686	0.00867	0.000237	75.90
10.07	0.01034	0.000288	77.19	10.60	0.01058	0.000215	75.38
11.81	0.01209	0.000274	76.70	12.45	0.01243	0.000199	74.93
13.48	0.01382	0.000264	76.28	14.24	0.01422	0.000186	74.53
15.13	0.01547	0.000255	75.89	15.98	0.01596	0.000175	74.20

16.71	0.01710	0.000245	75.55	17.64	0.01762	0.000167	73.91

Sodium sals of 5-hexanoic acid acid (5- hexanoic)				**Sodium salts of *trans*-crotonic acid acid (*trans*-2-butenoic)**			
$\dfrac{m \cdot 10^3}{mol \cdot kg^{-1}}$	$\dfrac{c}{mol \cdot dm^{-3}}$	β	$\dfrac{\Lambda_m}{S \cdot cm^2 \cdot mol^{-1}}$	$\dfrac{m \cdot 10^3}{mol \cdot kg^{-1}}$	$\dfrac{c}{mol \cdot dm^{-3}}$	β	$\dfrac{\Lambda_m}{S \cdot cm^2 \cdot mol^{-1}}$
0.5759	0.00057	0.000956	77.93	0.6514	0.00065	0.000884	83.14
1.326	0.00132	0.000743	77.37	1.196	0.00119	0.000671	82.31
2.382	0.00238	0.000601	76.56	2.193	0.00219	0.000529	81.44
3.135	0.00313	0.000529	75.98	3.181	0.00317	0.000457	80.74
4.856	0.00484	0.000477	75.28	4.665	0.00465	0.000405	79.96
6.626	0.00661	0.000435	74.55	6.669	0.00665	0.000363	79.11
8.566	0.00855	0.000408	74.00	8.515	0.00850	0.000336	78.45
10.10	0.01008	0.000390	73.48	10.36	0.01034	0.000318	77.89
11.36	0.01134	0.000376	73.03	12.11	0.01209	0.000304	77.4
13.35	0.01333	0.000366	72.63	13.84	0.01382	0.000294	76.98
14.94	0.01493	0.000357	72.30	15.48	0.01547	0.000285	76.59
16.52	0.01651	0.000347	72.01	17.12	0.01710	0.000275	76.25

Sodium salts of *trans*-2-pentenoic acid (*trans*-2-pentenoic)				**Sodium salts of *trans* -2-hexenoic acid (*trans* -2-hexenoic)**			
0.6268	0.00063	0.000962	79.84	0.6245	0.00062	0.000974	77.92
1.122	0.00112	0.000684	79.23	1.129	0.00113	0.000761	77.3
2.133	0.00213	0.000498	78.34	2.204	0.00220	0.000619	76.37
3.204	0.00320	0.000413	77.63	3.150	0.00314	0.000547	75.75
4.634	0.00462	0.000344	76.88	4.606	0.00459	0.000495	74.99
6.523	0.00651	0.000290	76.07	6.532	0.00652	0.000453	74.17
8.381	0.00836	0.000258	75.41	8.450	0.00843	0.000426	73.5
10.31	0.01029	0.000236	74.82	10.22	0.01021	0.000408	72.96
12.07	0.01206	0.000220	74.34	12.03	0.01201	0.000394	72.46
13.69	0.01368	0.000207	73.93	13.70	0.01368	0.000384	72.05
15.47	0.01545	0.000196	73.52	15.38	0.01536	0.000375	71.67
17.10	0.01709	0.000188	73.18	16.89	0.01687	0.000365	71.34

Sodium salts of *trans* -2-octenoic acid (*trans*-2-octenoic)			
0.5031	0.00050	0.000981	74.26
1.030	0.00103	0.000768	73.57
2.026	0.00202	0.000626	72.68
3.071	0.00306	0.000554	71.98
4.559	0.00455	0.000502	71.20
6.506	0.00649	0.000460	70.39
8.389	0.00837	0.000433	69.73
10.27	0.01026	0.000415	69.16
12.05	0.01203	0.000401	68.69
13.81	0.01380	0.000391	68.26
15.46	0.01544	0.000382	67.89
17.10	0.01708	0.000372	67.54

[a] Standard uncertainties are $u(T) = 0.01$ K, $u(p) = 0.05$ MPa and the combined expanded uncertainty is $U_c(\Lambda) = 0.0005 \cdot \Lambda$ (level of confidence = 0.95).

Table 2 presents the values of the coefficients of hydrolysis β for the studied salts. As you can see, these values are very small in the tested concentration range. Thus, it can be assumed that in almost every case these differences are smaller or comparable with errors of conductivity values resulting from the experiment. The discussed effects are not able to change the values of all previously mentioned quantities, as well as the conclusions resulting from their analysis. The minimal (almost imperceptible) impact of hydrolysis effects on the limiting molar conductivity value of the tested salts has been demonstrated by the comparison of the values of the limiting molar conductivity when the hydrolysis effect is taken into account ($\Lambda^0_{m(hyd)}$) and when this effect is not taken into account (Λ^0_m). The values of these conductivities are presented in the Table 3.

Table 3. Values of limiting molar conductivity Λ^0_m [S·cm²·mol⁻¹] for sodium salts of monocarboxylic acids chlorine in the peripheral position, bromine in the peripheral position, double bond in position 2, double bond in peripheral position their anions $\lambda^0_{A^-}$ [S·cm²·mol⁻¹], values of limiting molar conductivity with effect of hydrolysis $\Lambda^0_{m(hyd)}$ [S·cm²·mol⁻¹], literature values of limiting molar conductivity for anions $\lambda^0_{A^-}$ *(lit.)* [S·cm²·mol⁻¹], standard deviations $\sigma(\Lambda)$ and diffusion coefficient for anions $D^0_{A^-}$ [cm²·s⁻¹].

Anion	Λ^0_m	$\Lambda^0_{m(hyd)}$	$\lambda^0_{A^-}$	$D^0_{A^-}$	$\sigma(\Lambda)$	$\lambda^0_{A^-}$ *(lit.)*
Sodium salts of monocarboxylic acids (chlorine in the peripheral position)						
ClCH₂COO⁻	91.79	91.78	41.64±0.02	1.11·10⁻⁵	0.04	42.43 [23]
ClCH₂CH₂COO⁻	88.46	88.45	38.31±0.01	1.02·10⁻⁵	0.03	38.05 [23]
ClCH₂CH₂CH₂COO⁻	85.75	85.74	35.61±0.01	9.48·10⁻⁶	0.03	-
ClCH₂CH₂CH₂CH₂COO⁻	82.93	82.93	32.78±0.02	8.73·10⁻⁶	0.02	-
ClCH₂CH₂CH₂CH₂CH₂COO⁻	80.90	80.90	30.75±0.01	8.19·10⁻⁶	0.02	-
Sodium salts of monocarboxylic acids (bromine in the peripheral position)						
BrCH₂COO⁻	91.27	91.26	41.12±0.01	1.09·10⁻⁵	0.02	42.43 [23]
BrCH₂CH₂COO⁻	88.00	87.99	37.85±0.01	1.01·10⁻⁵	0.02	38.05 [23]
BrCH₂CH₂CH₂COO⁻	84.40	84.39	34.25±0.02	9.12·10⁻⁶	0.01	-
BrCH₂CH₂CH₂CH₂COO⁻	81.25	81.23	31.10±0.02	8.28·10⁻⁶	0.02	-
Sodium salts of monocarboxylic acids (double bond in position 2)						
CH₂=CHCOO⁻	85.44	85.43	35.29±0.02	9.39·10⁻⁶	0.02	35.89 [24]
CH₃CH=CHCOO⁻	83.74	83.73	33.59±0.01	8.94·10⁻⁶	0.01	36.04 [25]

	Λ_m^0	$\Lambda_{m(hyd)}^0$	$\lambda_{A^-}^0$	$D_{A^-}^0$	$\sigma(\Lambda)$	$\lambda_{A^-}^0 \, (lit.)$
$CH_3CH_2CH=CHCOO^-$	80.02	80.00	30.05±0.01	$8.20\cdot10^{-6}$	0.02	29.77 [23]
$CH_3CH_2CH_2CH=CHCOO^-$	78.21	78.20	28.06±0.02	$7.47\cdot10^{-6}$	0.01	-
$CH_3CH_2CH_2CH_2CH_2CH=CHCOO^-$	74.54	74.52	24.39±0.02	$6.09\cdot10^{-6}$	0.02	-

Sodium salts of monocarboxylic acids (double bond in peripheral position)

Anion	Λ_m^0	$\Lambda_{m(hyd)}^0$	$\lambda_{A^-}^0$	$D_{A^-}^0$	$\sigma(\Lambda)$	$\lambda_{A^-}^0 \, (lit.)$
$CH_2=CHCOO^-$	85.44	85.42	35.29±0.02	$9.39\cdot10^{-6}$	0.02	35.89 [24]
$CH_2=CHCH_2COO^-$	82.80	82.79	32.65±0.02	$8.69\cdot10^{-6}$	0.01	33.15 [26]
$CH_2=CHCH_2CH_2COO^-$	80.10	80.09	29.95±0.01	$7.97\cdot10^{-6}$	0.03	-
$CH_2=CHCH_2CH_2CH_2COO^-$	78.15	78.13	27.85±0.01	$7.41\cdot10^{-6}$	0.02	-

The molar conductivity values of the tested salts (Table 2) are linear and perfectly correlate with carbon chain length.

The calculations were carried out as described by Bešter-Rogač [27, 28]. The R distance parameter was determined for the test compounds as described previously [27-33]. The calculations were carried out assuming that $R = q$ (q - Bjerrum distance [32]).The analytical form of the parameters $S, E, J,$ and $J_{3/2}$ has been presented previously [19, 20] (Table 4.).

Table 4. The analytical form of parameters S, E, J_1 and J_2 for studied monocarboxylic anions $ClCH(CH_2)_nCOO^-$, $BrCH(CH_2)_nCOO^-$, $CH_2=CH(CH_2)_nCOO^-$, $CH_3\text{-}CH=CH(CH_2)_nCOO^-$ in the water, at 298.15K.

Anions	S	E	J_1	J_2
$ClCH_2COO^-$	70.24	8.237	79.34	245.38
$ClCH_2CH_2COO^-$	69.47	9.007	75.58	245.38
$ClCH_2CH_2CH_2COO^-$	68.85	9.631	72.52	245.38
$ClCH_2CH_2CH_2CH_2COO^-$	68.20	10.285	69.32	245.38
$ClCH_2CH_2CH_2CH_2COO^-$	67.74	10.755	67.03	245.38
Anions	S	E	J_1	J_2
$BrCH_2COO^-$	70.12	8.357	78.76	245.38
$BrCH_2CH_2COO^-$	69.37	9.113	75.06	245.38
$BrCH_2CH_2CH_2COO^-$	68.54	9.945	70.98	245.38
$BrCH_2CH_2CH_2CH_2COO^-$	67.82	10.674	67.42	245.38
Anions	S	E	J_1	J_2
$CH_2=CHCOO^-$	68.78	9.705	72.16	245.38
$CH_2=CHCH_2COO^-$	68.17	10.315	69.17	245.38

	S	E	J1	J2
$CH_2=CHCH_2CH_2COO^-$	67.55	10.940	66.12	245.38
$CH_2=CHCH_2CH_2CH_2COO$	67.07	11.425	63.75	245.38
Anions	S	E	J1	J2
$CH_2=CHCOO^-$	68.78	9.705	72.16	245.38
$CH_3CH=CHCOO^-$	68.39	10.098	70.24	245.38
$CH_3CH_2CH=CHCOO^-$	67.58	10.916	66.23	245.38
$CH_3CH_2CH_2CH=CHCOO^-$	67.12	11.377	63.98	245.38
$CH_3CH_2CH_2CH_2CH_2CH=CHCOO^-$	66.27	12.225	59.83	245.38

Initially, the conductivities were first determined for the solutions of the sodium salts of the halogenated monocarboxylic acids, i.e. with chlorine in the peripheral position. The limiting molar conductivity values of these salts were determined at 298.15 K using the equations of conductivity which were presented in papers [34, 35] (Table 2). The limiting molar conductivity values of the anions of the tested acids were determined from the following relationship, assuming the literature value of the limiting molar conductivity of the sodium cation in water at $T = 298.15$ K [36]:

$$\lambda^0_{A^-} = \Lambda^o_m - \lambda^o_{Na^+} \qquad (6)$$

where: Λ^0_m - represents the limiting molar conductivity values of the sodium salts of the studied carboxylic acids.

Table 3 presents our calculations and literature values of limiting molar conductivities for the anions of these acids and values of diffusion coefficients. The values of the diffusion coefficients $D^0_{A^-}$ [cm^2·s^{-1}] for the examined anions were calculated from the equation:

$$D^0_{A^-} = \frac{R \cdot T \cdot \lambda^0_{A^-}}{F^2} \qquad (7)$$

where: R is the gas constant, k and F is the Faraday constant. The values of $D^0_{A^-}$ calculated from Equation 7 are presented in Table 2.

The courses of changes in the values of diffusion coefficient $D^0_{A^-}$, as the function of the carbon chain length of the anions of the tested monocarboxylic acids, are linear (see Table 3).

The analysis of the $D^0_{A^-}$ values for all types of tested acid anions is very interesting. Theoretically, the diffusion coefficient at a given temperature should decrease as the particle size increases. In the groups studied by us, electrolyte, the unsaturated anions of carboxylic acids have a lower diffusion coefficient than anions with large substituents such as Cl or Br. Most likely, this effect is caused by the influence of E and Z geometric isomerism in the studied unsaturated anions of the

acids. It should also be noted that the lowest $D_{A^-}^0$ values have acid anions with a double bond in the peripheral position.

They are also presented as a course of function $\lambda_{A^-}^o = f(n)$, with *n* indicating the number of carbon atoms in the aliphatic chain (Figure 1). The data in Table 3 and Figure 2 indicate that the values given in available literature differ slightly from those obtained in this work, especially for $n = 1$. It should be noted that it is difficult to determine the nature of the relationship $\lambda_{A^-}^o = f(n)$ based on earlier literature data due to its paucity; however, the results obtained in the present study for the five studied acid salts with Cl as a substituent in the aliphatic chain indicate that the analyzed relationship $\lambda_{A^-}^o = f(n)$ is a monotonically decreasing function.
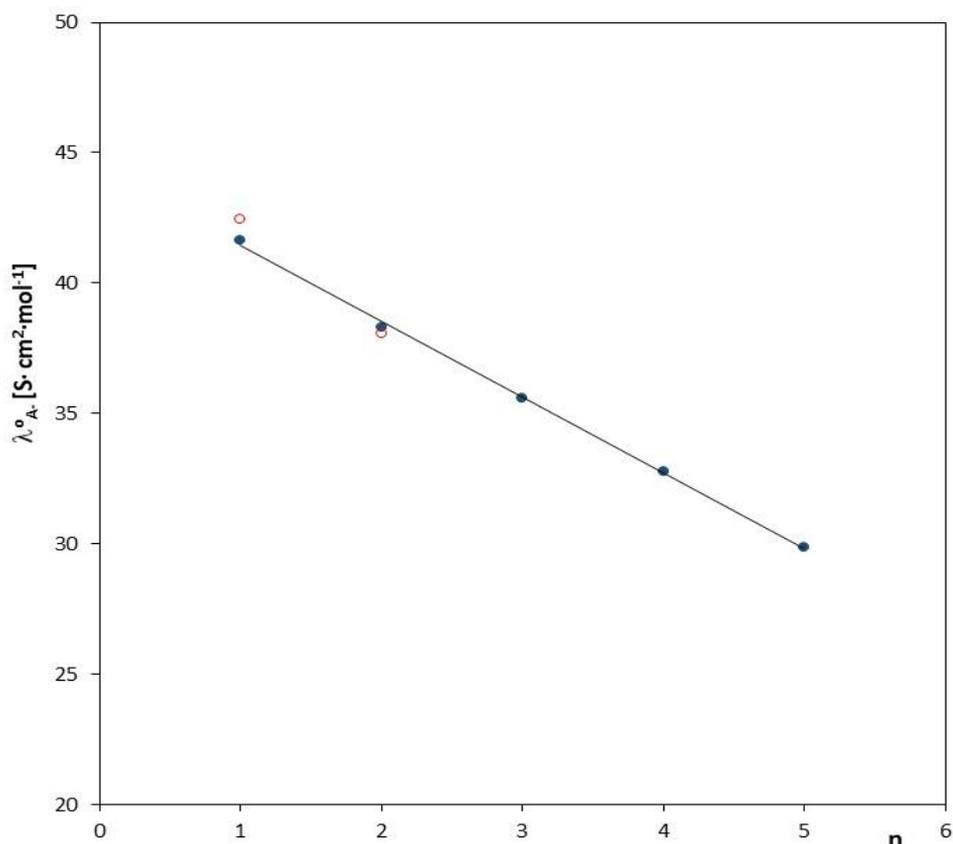
Figure 1. The plot of dependence of the $\lambda_{A^-}^0$ [S·cm^2·mol^{-1}] *v*alues as a function of carbon chain length (*n*) for the studied chloro-monocarboxylic anions (chlorine in the peripheral position) at 298.15 K.   ● experimental values, and ○ literature values [23].
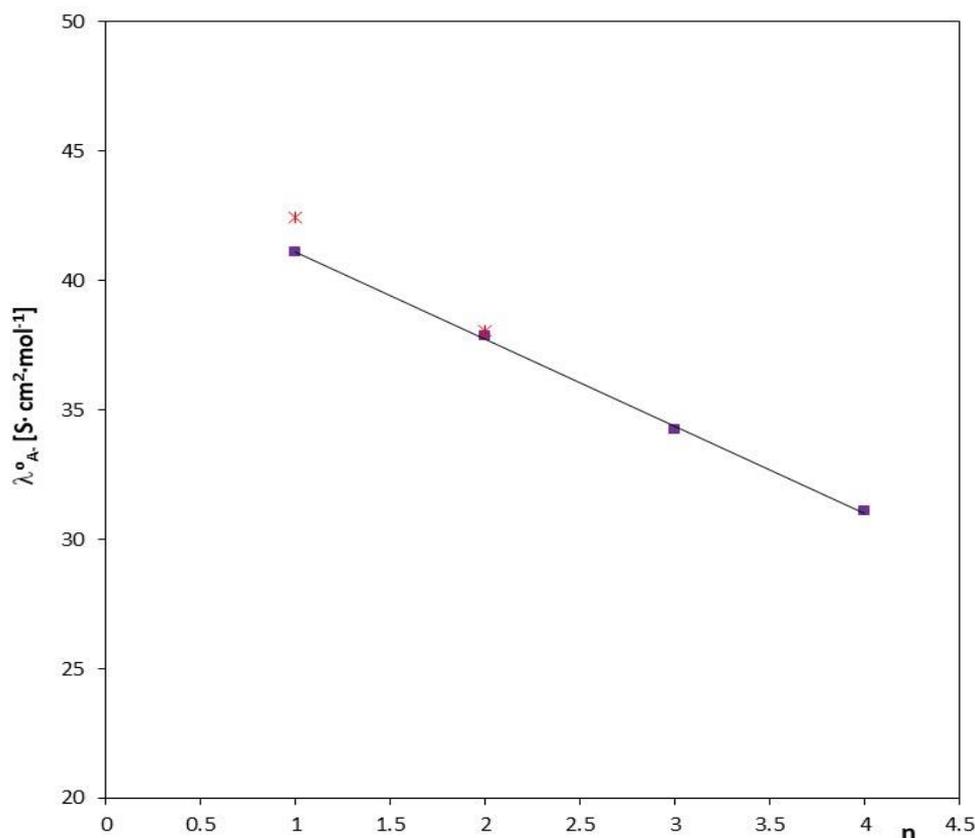
Figure 2. The plot of dependence of the $\lambda_{A^-}^0$ [S·cm²·mol⁻¹] *v*alues as a function of carbon chain length (*n*) for the studied bromo-monocarboxylic acid anions (bromine in the peripheral position) at 298.15 K. ■ experimental values, and * literature values [23].

In order to more fully analyze this relationship, we have attempted to test Eq. 8 for its description.

$$\lambda_{A^-}^0 = a \cdot e^{-bn} + c \tag{8}$$

The values of coefficients *a* and *c* were determined using multi-parameter methods (Table 5),

Table 5. Values of *a*, *b* and *c* parameters for the studied monocarboxylic organic anions (chlorine in the peripheral position)

Anion	*a*	*b*	*c*
$ClCH_2COO^-$	28.132	0.151[6]	17.477
$ClCH_2CH_2COO^-$	28.132	0.151[6]	17.477
$ClCH_2CH_2CH_2COO^-$	28.132	0.151[6]	17.477
$ClCH_2CH_2CH_2CH_2COO^-$	28.132	0.151[6]	17.477
$ClCH_2CH_2CH_2CH_2COO^-$	28.132	0.151[6]	17.477

assuming the value of coefficient *b* as 0.151 [6], *i.e.* the main value obtained for the studied monocarboxylic acid anions. The relationship described by the equation $\ln(\lambda_{A^-} - c) = a - bn$ is given in Figure 3.
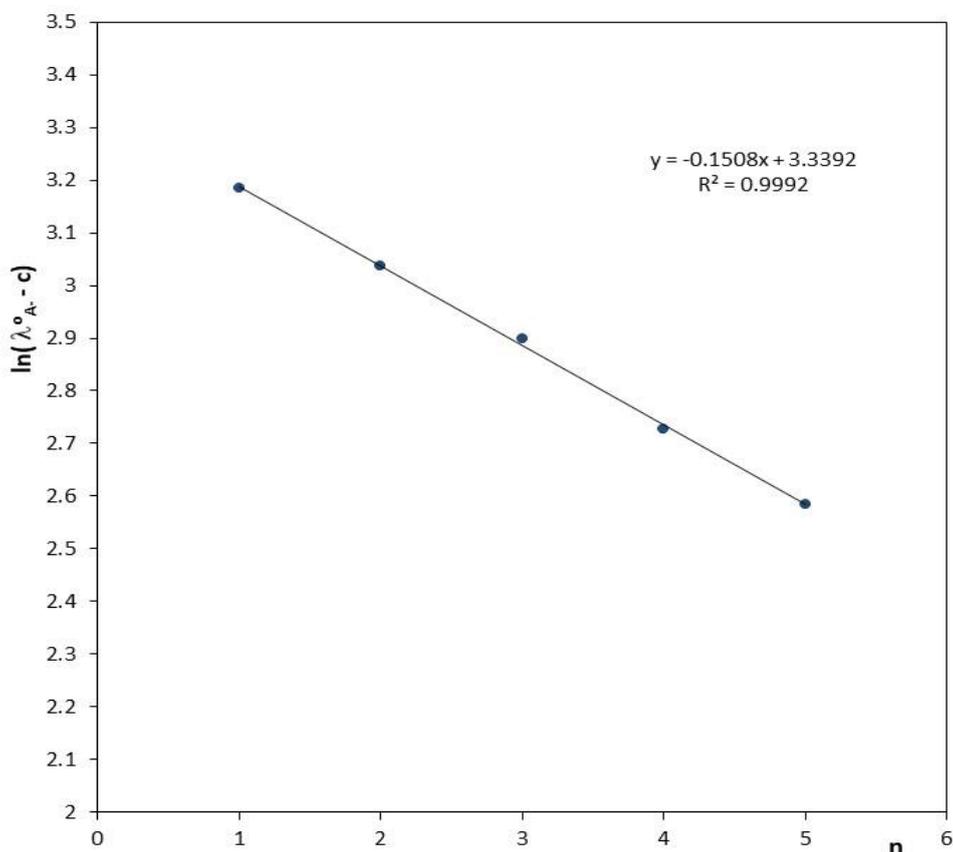

Figure 3. The course of changes in the function $\ln(\lambda_{A^-}^0 - c) = f(n)$ (*n* - number of carbon atoms in the carbon chain) for halogenated anions of studied monocarboxylic acids in which Cl is in the peripheral position.

The correlation coefficient for parameters *a* and *b* was found to be high, which suggests that the relationship $\lambda_{A^-}^o = f(n)$ can be accurately described by an equation of the type $\lambda_{A^-}^0 = a \cdot e^{-bn} + c$ (Eq. 8). Therefore, it appears that the discussed relationships can be described by an appropriate mathematical formula, but only if the number of carbon atoms in the hydrophobic groups is included in the calculation, i.e. not the carbon atom of the carboxyl group. An analysis of the presented results suggests that they can be described by means of exponential functions.

To examine the effect of the electronegativity of the substituent on the analyzed relationships, the salts with a Cl atom in the peripheral position were compared with those with a Br atom. The molar conductivity values (Λ_m) for selected sodium salts of monocarboxylic acids in water at 298.15 K, with Br in the peripheral position, are collected in Table 3; their limiting conductivity values are presented in Table 3 and Figure 2, together with literature values. Few full descriptions of homologous series of the studied anions are available in the literature.

The next stage of the study examined whether Equation 8 could be used to describe the relationship $\lambda_{A^-}^o = f(n)$ for the sodium salts of Br substituted acids, as performed previously for Cl. Again, the values of parameters a and c were calculated for the anions of monocarboxylic acids with Br in the peripheral position, assuming b to be 0.150, as before (Table 6).

Table 6. Values of a, b and c parameters for studied monocarboxylic organic anions (bromine in the peripheral position)

Anion	a	b	c
BrCH$_2$COO$^-$	32.271	0.151[6]	13.587
BrCH$_2$CH$_2$COO$^-$	32.271	0.151[6]	13.587
BrCH$_2$CH$_2$CH$_2$COO$^-$	32.271	0.151[6]	13.587
BrCH$_2$CH$_2$CH$_2$CH$_2$COO$^-$	32.271	0.151[6]	13.587

As observed for the Cl substituted acids, the a and c coefficients again demonstrated highly satisfactory values for the Br anions. Figure 4 shows the course of changes in function $\ln(\lambda_{A^-}^0 - c) = a - bn$ for these anions.
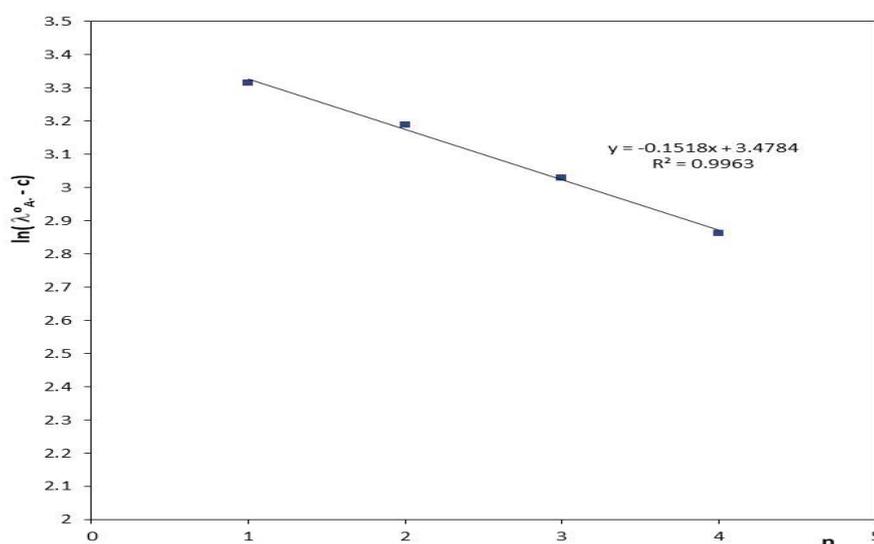
Figure 4. The course of changes in the function $\ln(\lambda_{A^-}^0 - c) = f(n)$ (n - number of carbon atoms in the carbon chain) for anions of studied monocarboxylic acids in which Br is in the peripheral position.

The next stage of the study examined the conductivity of two sets of sodium salts of unsaturated monocarboxylic acids with a double bond: one group with the bond in position 2, and another with the bond in the peripheral position. The molar conductivity values of the salts (Λ_m) in water at T = 298.15 K are collected in Table 2. The molar conductivity values of the anions were determined as above (Tables 3), based on the literature values of the molar conductivity of the sodium

cation [36]. The change in conductivity as a function of the number of carbon atoms in the aliphatic chain is illustrated in Figures 5 and 6.
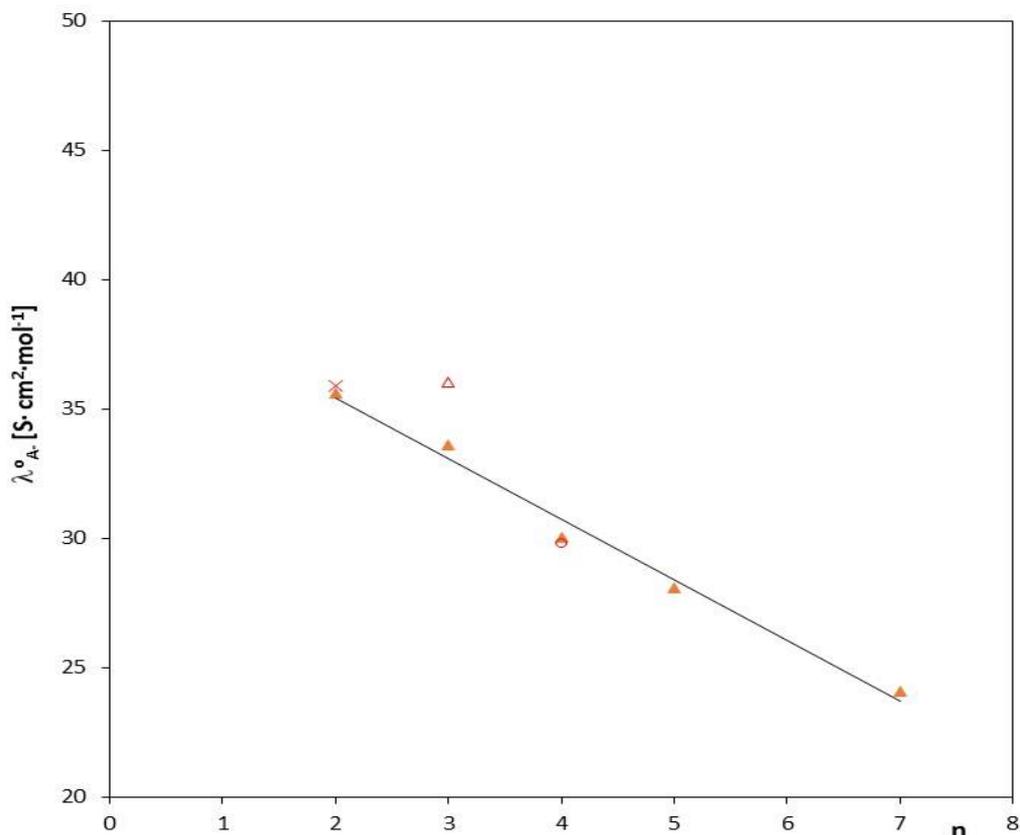

Figure 5. The plot of dependence of the $\lambda^0_{A^-}$ [S·cm^2·mol^{-1}] values as a function of carbon chain length (*n*) for the studied unsaturated monocarboxylic acid anions (double bond is in position 2) at 298.15 K. ▲ experimental values, **x** literature values [24], △ literature values [25] and ○ literature values [23].

As demonstrated in Table 3 and Figures 5 and 6 the values obtained in the present paper differ slightly from those given in the literature. Such differences were also observed for the halogenated anions of monocarboxylic acids. However, it should be remembered that most literature data were obtained in the 1930s, using equipment and solution preparation methods that differ greatly from those used in the present study.

The possibility of describing the relationship $\lambda^o_{A^-} = f(n)$ with Eq. 7 was tested for both tested sets of monocarboxylic acid anions, i.e. those with a Cl or a Br substituent. Assuming $b = 0.150$, the values of parameters *a* and *c* were obtained for the anions with a double bond in position 2 and for those with a double bond in the peripheral position (Tables 7 and 8).
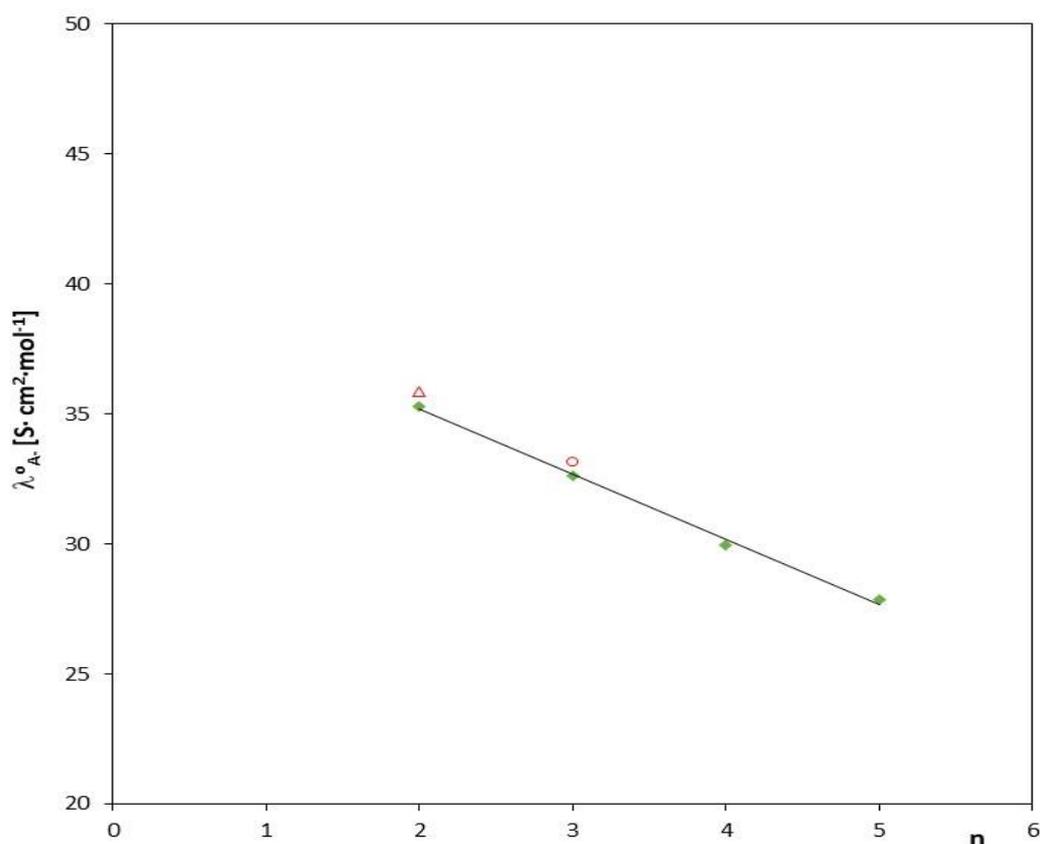
Figure 6. The plot of dependence of the $\lambda^0_{A^-}$ [S·cm^2·mol^{-1}] values as a function of carbon chain length (*n*) for the studied anions of unsaturated monocarboxylic acids (double bond in the peripheral position) at 298.15 K. ♦ experimental values, △ literature values [24] and ○ literature values [26].

Table 7. Values of *a*, *b* and *c* parameters for studied anions of unsaturated monocarboxylic acids (double bond in position 2)

Anions	*a*	*b*	*c*
CH$_2$=CHCOO$^-$	27.738	0.151[6]	14.806
CH$_3$CH=CHCOO$^-$	27.738	0.151 [6]	14.806
CH$_3$CH$_2$CH=CHCOO$^-$	27.738	0.151[6]	14.806
CH$_3$CH$_2$CH$_2$CH=CHCOO$^-$	27.738	0.151[6]	14.806
CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH=CHCOO$^-$	27.738	0.151[6]	14.806

Table 8. Values of *a*, *b* and *c* parameters for studied anions of unsaturated monocarboxylic acids (double bond in the peripheral position)

Anions	*a*	*b*	*c*
CH$_2$=CHCOO$^-$	27.751	0.151[6]	14.802
CH$_2$=CHCH$_2$COO$^-$	27.751	0.151[6]	14.802

$CH_2=CHCH_2CH_2COO^-$	27.751	0.151[6]	14.802
$CH_2=CHCH_2CH_2CH_2COO^-$	27.751	0.151[6]	14.802

Despite the fact that only four or five samples were used for the analysis, the *a* and *c* coefficients nevertheless demonstrated highly satisfactory agreement for both types of anions. The relationships $\ln(\lambda_{A^-}^0 - c) = a - bn$ are given for both types of anions in Figures 7 and 8.


$$y = -0.151x + 3.3283$$
$$R^2 = 0.9992$$
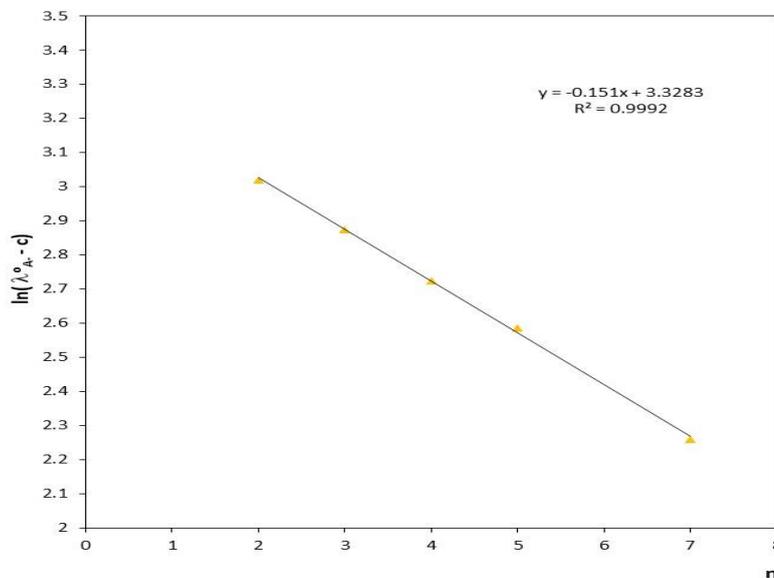
Figure 7. The course of changes in the function $\ln(\lambda_{A^-}^0 - c) = f\,(n)$ (*n* - number of carbon atoms in the carbon chain) for the studied anions of unsaturated monocarboxylic acids with double bond in position 2.

$$y = -0.151x + 3.3262$$
$$R^2 = 0.9975$$
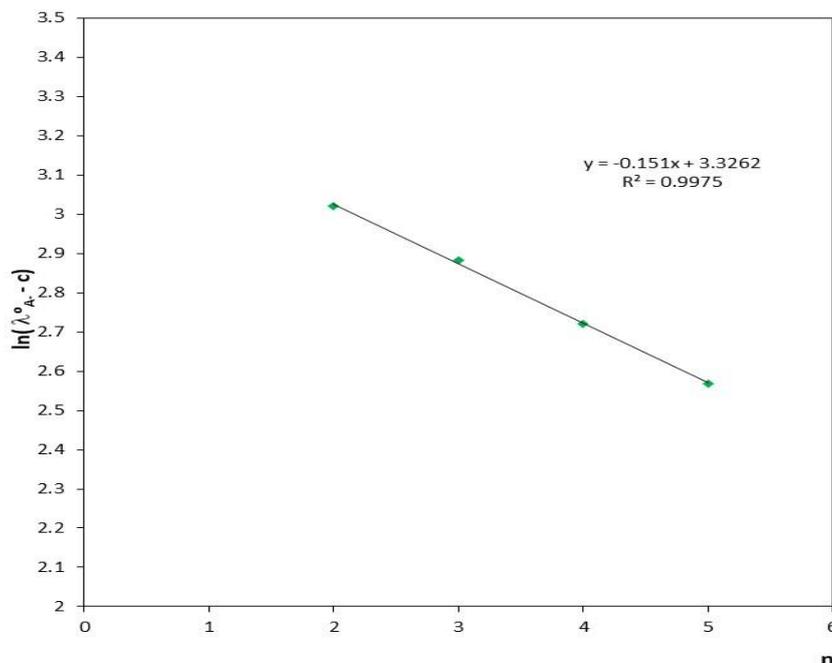
Figure 8. The course of changes in the function $\ln(\lambda_{A^-}^0 - c) = f\,(n)$ (*n* - number of carbon atoms in the carbon chain) for the studied anions of unsaturated monocarboxylic acids with double bond in peripheral position.

Equation 8 was found to adequately describe the relationship $\lambda_{A^-}^o = f(n)$, as indicated by its high correlation coefficients.

Figure 9 presents the relationships between limiting molar conductivities and carbon chain length (*n*) for all anions of unsaturated acids analyzed in the present paper, as well as previously-obtained values for the anions of saturated monocarboxylic acids [6, 7]. It can be seen that similar relationships exist for both the saturated and unsaturated monocarboxylic acid anions; it may be possible that they belong to the same group of dependencies. This similarity suggests that the presence of a double bond in the carbon chain does not significantly affect the mobility of the tested anion.

A closer analysis of the $\lambda_{A^-}^o$ values indicates that anions with a double bond demonstrated slightly lower conductivity. It appears that the loss of two hydrogen atoms, associated with the presence of the double bond, seemingly reduces the volume of the anion. However, it should be noted that the presence of two carbon atoms with sp^2 hybridization stiffens the anion structure: it becomes less "flexible". Due to this lack of flexibility, the carbon chain is less able to rotate and adapt to the direction of electric field force lines compared to one characterized by sp^3 hybridization; hence, steric obstacles to movement observed under the influence of the field are as small as possible. In this case, hydrophobic effects have a much smaller impact, as indicated by the apparent molar volumes (see: [1]), again indicating that the appearance of a double bond slightly changes the apparent molar volumes of an anion.

As the molar volume may only slightly increase or decrease depending on the position of the double bond, i.e. position 2 or peripheral, it does not appear possible to determine the effect of the location of the double bond on the conductivity of the anion based on our present findings. This is confirmed by the analysis of the $\lambda_{A^-}^o$ values for anions characterized by *n* = 2 or *n* = 4. Unfortunately, carboxylic acids with different values of *n*, which can be used to synthesize further sodium salts and thus allow a more complete interpretation of changes in $\lambda_{A^-}^o$, are not commercially available.

In contrast, significant differences in limiting molar conductivity can be seen between the anions of monocarboxylic acids with a halogen atom in the peripheral position and those without it (Figure 9).

If the hydrogen atom is replaced by a halogen atom, the $\lambda_{A^-}^o$ values are clearly higher. It is difficult to reconcile this fact with the change in size of the anion, bearing in mind the large size of the chlorine or bromine atoms. All hydrodynamic models of ion conductivity indicate that anions containing halogen atoms should have lower conductivity. It appears that the reason for the increase in electrical conductivity observed following halogen atom substitution may lie in the nature of the interaction between these anions and the solvent.
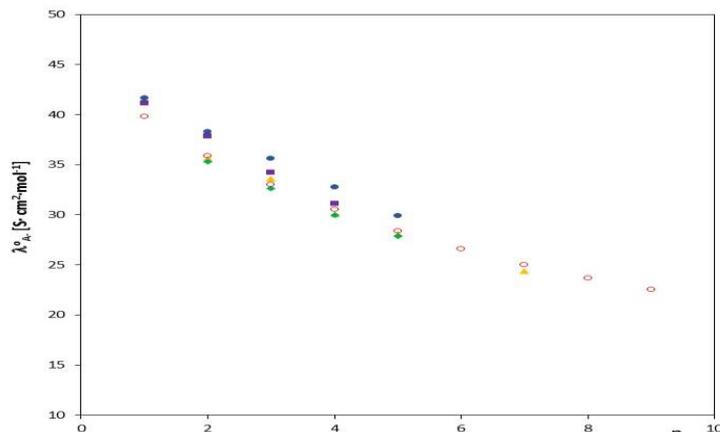
Figure 9. The plot of dependence of the $\lambda_{A^-}^0$ [S·cm^2·mol^{-1}] values as a function of the length of the carbon chain (*n*) for anions of unsaturated monocarboxylic acids (bind in peripheral position) ♦; anions of unsaturated monocarboxylic acids (double bond in position 2) ▲; monocarboxylic acid halogenated anions (chlorine in the peripheral position), monocarboxylic acid halogenated anions (bromine in the peripheral position) ■ and monocarboxylic acid anions ○ from the number of carbon atoms (*n*) in the carbon chain of the studied anion at 298.15 K.

4. CONCLUSION

The introduction of a chlorine atom into a carbon chain has previously been found to increase the apparent volume of the anion by as much as about 28 cm^3·mol^{-1} [1]. However, the presence of a double bond in the carbon chain resulted in changes in apparent volume less than 0.5 cm^3·mol^{-1}. These findings suggest that the presence of a chlorine atom weakens the effects associated with hydrophobic hydration of the carbon chain, making the environment of the ion less "rigid" and forcing the structure of its environment to undergo some "loosening". In this way, the ions gain greater mobility, and their molar limiting conductivity, associated only with their interaction with the solvent, increases.

A similar situation can be observed for bromine atoms but with a few differences. Bromine atoms have a lower electronegativity value as substituents than chlorine atoms and thus also affect the polarization of the O-H bond in the carboxyl group to a lesser extent than chlorine atoms. Bromide monocarboxylic acids are weaker acids than chloride monocarboxylic acids. It can be assumed that as the length of carbon chain increases, the difference in conductivity values between Br-substituted monocarboxylic acid anions and the unsubstituted ones will reduce (Figure 9). This is due to the weakening influence of the carboxyl group on the substituent. The analysis of the limiting conductivity values of the examined anions ($\lambda_{A^-}^0$) as well as the diffusion coefficient values for these anions ($D_{A^-}^0$) indicates that:

• these values for anions with a double bond are slightly lower than for anions with a Cl or Br substituent. It appears that the loss of two hydrogen atoms, associated with the presence of the double bond, seemingly reduces the volume of the anion. However, it should be noted that the

presence of two carbon atoms with sp^2 hybridization stiffens the anion structure: it becomes less "flexible".

- the obtained results also indicate that the values of limiting conductivity of the examined anions ($\lambda_{A^-}^0$) as well as the values of diffusion coefficients for these anions ($D_{A^-}^0$) slightly differ from the discussed values for saturated (see literature) and unsubstituted monocarboxylic acids.

- The values of coefficient *b* affect the nature of the changes in dependence described by Equation 8 and determine the value of changes ($\Delta\lambda$) caused by the appearance of the next group -CH$_2$- in the anion (CH$_2$)$_n$COO$^-$. These can be described by Eq. 8:

$$\Delta\lambda^0 = \lambda_{n+1}^0 - \lambda_n^0 = A_2 \cdot A_1^n \tag{8}$$

where: $A_1 = e^{-b}$ and $A_2 = a \cdot (e^{-b}-1)$

Therefore, it seems that the value of coefficient b is strictly responsible for the influence of the -CH$_2$- group on the conductivity of the anion.

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