

## Accepted Manuscript

Molar conductivity and association constants of sodium salts of selected cinnamic acids in water at temperatures from 288.15 to 318.15 K

Marta Stańczyk, Agnieszka Boruń, Małgorzata Józwiak



PII: S0167-7322(19)33158-7  
DOI: <https://doi.org/10.1016/j.molliq.2019.111370>  
Article Number: 111370  
Reference: MOLLIQ 111370  
To appear in: *Journal of Molecular Liquids*  
Received date: 4 June 2019  
Revised date: 11 July 2019  
Accepted date: 13 July 2019

Please cite this article as: M. Stańczyk, A. Boruń and M. Józwiak, Molar conductivity and association constants of sodium salts of selected cinnamic acids in water at temperatures from 288.15 to 318.15 K, *Journal of Molecular Liquids*, <https://doi.org/10.1016/j.molliq.2019.111370>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Molar conductivity and association constants of sodium salts of selected cinnamic acids in water at temperatures from 288.15 to 318.15 K

Marta Stańczyk<sup>a\*</sup>, Agnieszka Boruń<sup>a</sup>, Małgorzata Józwiak<sup>a</sup>

<sup>a</sup> *University of Lodz, Faculty of Chemistry, Department of Physical Chemistry, Pomorska 165, 90-236 Lodz, Poland*

\* Corresponding author.

E-mail address: martastanczyk1@o2.pl (M.Stańczyk)

## Abstract

The electrical conductivities of aqueous solutions of sodium salts of cinnamic acid, 4-hydroxycinnamic (*p*-coumaric) acid, 3,4-dihydroxycinnamic (caffeic) acid, 4-hydroxy-5-methoxycinnamic (ferulic) acid and 3,5-dimethoxy-4-hydroxycinnamic (sinapinic) acid were measured over the temperature range (*T*) of 288.15 to 318.15 K at 5 K intervals. The limiting molar conductivity ( $\Lambda_m^0$ ) and ionic association constants ( $K_A^0$ ) were obtained using the low concentration Chemical Model (lcCM). The limiting ionic conductivity and the Eyring's activation enthalpy of charge transport of the investigated anions were determined.

**Keywords:** molar conductivity, sodium salts of phenolic acid, limiting ionic conductivity, hydrolysis

## 1. Introduction

Phenolic acids are known to have a positive effect on human health due to their antioxidant potential, which is particularly marked in the case of cinnamic acid derivatives. They are widely distributed throughout the plant kingdom, and despite being characterized by diverse chemical structures and pharmacological properties, they all share certain hydroxyl and carboxylic groups [1]. However, it is possible to distinguish between simple benzoic acids, phenylacetic acids and cinnamic acids based on the number of carbons in the side chain (Fig 1). The most common cinnamic acid derivatives are its hydroxyl derivatives, i.e. caffeic, ferulic, *p*-coumaric and synapinic acids.

Phenolic acids are commonly found in food and dietary supplements as bioactive components. However, the salts of phenolic acids, especially those formed with alkali metals, are much more water soluble than the acids themselves, and hence are better suited for use as potential disinfectants or preservatives. Recent studies describing the activities of a range of structurally-varied phenolic acid salts against food-borne pathogens indicate that both phenolic acids and their salts can be used as natural chemical agents to preserve food [2, 3]. The objects of such studies are most often *o*-, *m*- and *p*-coumaric acids, caffeic and cinnamic acid [2, 4, 5].

One well-known sodium salt of a cinnamic acid derivative containing both hydroxyl and methoxy groups is sodium ferulate (SF). It is easily synthesized and offers greater stability and water solubility than ferulic acid; as such, it is widely used in scientific research and clinical medicine, as well as in the food and cosmetics industries. For example, SF is used in foods to mask the aftertaste of acesulfame potassium, an artificial sweetener patented by Kraft Foods [6]. It is also an active agent in Chinese medicinal herbs such as *Angelica sinensis*, *Cimicifuga heracleifolia* and *Ligusticum chuangxiong*, and has been approved by the State Office of Drugs in China for treating cardiovascular and cerebrovascular diseases and for use as a prophylactic against thrombosis. In addition, clinical trials have found it to exhibit low toxicity [7], and it is regarded as safe for use in humans.

The present paper presents precise measurements of the electrical conductivity of the aqueous solutions of the sodium salts of cinnamic acid and its selected derivatives: cinnamic acid (NaCin), 4-hydroxycinnamic acid (*p*-NaCou), 3,4-dihydroxycinnamic acid (NaCaf), 4-hydroxy-5-methoxycinnamic acid (NaFer) and 3, 5-dimethoxy-4-hydroxycinnamic acid (NaSyn). All conductivities were measured at temperatures (*T*) from 288.15 K to 318.15 K in a concentration range (*c*) ranging from  $\sim 1 \cdot 10^{-4}$  to  $\sim 1.5 \cdot 10^{-2}$  mol·dm<sup>-3</sup> at atmospheric pressure. The structures of all investigated salts are presented in Fig. 2. The salts were chosen to demonstrate the influence of changes in their structure, i.e. location and number of hydroxyl or methoxy groups, on their conductometric properties. The effect of hydrolysis on the limiting molar conductivity for the investigated salts was also evaluated.

The obtained data allowed the limiting molar conductivity ( $\Lambda_m^0$ ) and the association constants ( $K_A^0$ ) for the investigated salts to be determined using the low concentration Chemical Model (lcCM). The limiting ionic conductivity, hydrodynamic radius of the anions and the values for Eyring activating enthalpy of charge transport of the anions were also calculated.

## 2. Materials and methods

Sodium cinnamate (AK Scientific, Inc, USA, 98%) was dried under vacuum at  $T = 373.15$  K to constant mass. The sodium salts of *p*-coumaric, caffeic, ferulic and synapinic acid were prepared using trans-*p*-coumaric acid (TCI, Tokyo, Japan, >98.0%), 3,4-dihydroxycinnamic acid, predominantly trans isomer (ACROS ORGANICS, USA, 99+%), trans-ferulic acid (Sigma Aldrich, China, 99%), 3,5-dimethoxy-4-hydroxycinnamic acid, predominantly trans isomer (ACROS ORGANIC, USA, 98%), and sodium hydroxide (micropills pure, P.A., Avantor Performance Material Poland S.A.).

The appropriate amounts of acid and aqueous sodium hydroxide were mixed in a stoichiometric ratio 1:1; the mixture was then heated and stirred to dissolve the acid and evaporate the solvent. The procedure is described in more detail elsewhere [2, 9]. The obtained salts were washed with acetone and dried at  $T = 373.15$  K to constant mass. The synthesized salts were tested by  $^1\text{H}$  NMR spectra to confirm that significant amounts of impurities were absent. The spectra for the synthesized salts were consistent with those given in the literature [10-13]. The purity of the salt obtained was 98 %.

All the solutions were prepared gravimetrically using an analytical balance (Sartorius RC 210D) with a precision of  $\pm 1 \cdot 10^{-5}$  g. Densities were measured with an Anton Paar DMA 5000 M oscillating U-tube densimeter equipped with a thermostat with temperature stability within  $\pm 0.001$  K. The densimeter was calibrated with dry air and ultrasonically-degassed extra-pure water. The estimated expanded uncertainty of the density is  $\pm 1.5 \cdot 10^{-4}$  g·cm $^{-3}$ . The density ( $\rho$ ) of the sodium salts as a function of sodium salt molality ( $m$  – moles of electrolyte per kilogram of solution) and temperature are presented in Table A1 in the Supporting Information.

Conductivity measurements were performed with a three-electrode cell and a 6430 B Precision Component Analyzer (Wayne-Kerr Electronics, UK) under an inert gas atmosphere and at frequencies ( $\nu$ ) of 0.2, 0.5, 1, 1.5, 2, 3, 5, 10 and 20 kHz. The temperature was controlled within 0.001 K by an ultrathermostat with a PD controller (Performance Digital, LABO PLUS, USA). The measurement procedure was based on the method described by Bešter-Rogač *et al.* [14, 15] and used in our previous study [8]. Considering the sources of error (calibration, purity of samples, measurements), the uncertainty of the conductivity measurements was estimated to be  $\pm 0.5$  %.

### 3. Results and discussion

The densities, viscosities and relative permittivity values of water have been described previously [8].

To convert molality  $\tilde{m}$  into molar concentration ( $c$ ), the values of density gradients ( $b$ ) were determined independently and used in the following equation  $c/\tilde{m} = \rho = \rho_o + b\tilde{m}$ , where  $\rho$  is the density of the solution. Molar concentration was needed for the conductivity equation. The density gradients and the molar conductivity of the sodium salts ( $\Lambda_m$ ) are presented in Table A2 (Supporting Information) as a function of sodium salt molality ( $m$  – moles of electrolyte per kilogram of solvent) and temperature. The relationship between  $m$ ,  $\tilde{m}$  and  $c$  is as follows  $\tilde{m} = c/\rho = m/(1 + mM)$ , where  $M$  is the molar mass of electrolyte.

The conductivity data was analyzed by the low concentration Chemical Model (lcCM) [16] using the following equations:

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

$$K_A^0 = (1 - \alpha)/(\alpha^2 c y_{\pm}^2) \quad (2)$$

$$\ln y_{\pm} = -(A\alpha^{1/2} c^{1/2})/(1 + BR\alpha^{1/2} c^{1/2}) \quad (3)$$

In these equations,  $\Lambda_m^0$  is the limiting molar conductivity;  $\alpha$  is the dissociation degree of an electrolyte;  $K_A^0$  is the ionic association constant;  $R$  is the distance parameter of ions;  $y_{\pm}$  is the activity coefficient of ions on the molar scale;  $A$  and  $B$  are the Debye–Hückel equation coefficients. The analytical form of the parameters  $S$ ,  $E$ ,  $J$  and  $J_{3/2}$  has been presented previously [16]. The calculation was performed as described by Bešter-Rogač [17, 18]. The description of the procedure for determining the distance parameter  $R$  for various types of compounds is described in literature [17–22]. In the case of our study, we assumed the distance parameter  $R = 0.820$  nm, the same as in the papers [17, 18], in which both this parameter and the method of its determination were described in detail.

Figure 3 shows the relationship between molar conductivity for the aqueous solution of NaSyn as a function of temperature. The remaining salts show a similar relationship. In the case of *p*-NaCou, NaFer and NaSyn, molar conductivity values decrease slightly with increasing concentration, while more significant changes can be observed for NaCin and NaCaf. All investigated salts demonstrated a significant increase in molar conductivity with an increase of temperature.

Figure 4 shows the molar conductivity of all salts tested at 298.15 K. The highest molar conductivity for the investigated salts were observed for the NaCin and the lowest for NaFer.

Table 1 presents the  $\Lambda_m^0$  and  $K_A^0$  values for the investigated salts. The association constants  $K_A^0$  are very low, with the maximum value obtained in the present study being only  $9.8 \text{ dm}^3 \cdot \text{mol}^{-1}$ . This finding indicates that all of the investigated salts are nearly fully dissociated in water; similar results were also obtained previously for sodium salts of benzoic acid derivatives [8].

The limiting molar conductivity of all investigated salts was found to increase with temperature, which is caused by a decrease in solvent viscosity. Of all the salts, the most significant increase in limiting molar conductivity, together with the highest values, were observed for NaCin. An increase in the number of substituents, as well as their type, significantly reduced the limiting molar conductivity of studied salts. Much smaller differences in limiting molar conductivity were observed between NaBen and the salts *o*-NaSal, *m*-NaSal, *p*-NaSal, NaPro, NaVal and NaSyr [8]. In the case of NaCin salts, such a significant difference may be due to the elongation of the carbon chain at the carboxyl group, as well as the presence of a double bond in this chain.

The limiting molar conductivity of the salts investigated in the present study follows the sequence NaCin > NaSyn > *p*-NaCou > NaCaf > NaFer at temperatures of 288.15 K and 293.15 K; however, at the other tested temperatures, the sequence becomes NaCin > NaSyn > NaCaf > *p*-NaCou > NaFer, with *p*-NaCou and NaCaf changing places. These two salts, both of which contain one or two hydroxyl groups with the maximum difference between them being two units, were found to have similar values; hence, in this case, an increase in the number of hydroxyl groups in the molecule does not appear to significantly affect the limiting molar conductivity value.

This finding contradicts those observed for the sodium salts of certain benzoic acid derivatives (*p*-NaSal and NaPro): for these, the presence of higher numbers of hydroxyl groups was found to be associated with a significant decrease in conductivity [8]. The difference between the limiting molar conductivity for those salts increased linearly with increasing temperature, with the greatest difference observed at 318.15 K [8]. However, in the present study, the greatest difference between the cinnamic acid salts *p*-NaCou and NaCaf was observed at 298.15 K. Much greater differences in limiting molar conductivity were

observed for the salts containing methoxy groups (i.e. NaFer and NaSyn), but this difference was found to decrease with increasing temperature; surprisingly, the limiting molar conductivity of each salt increases with the number of methoxy groups in the molecule.

The next stage of our study examined the limiting molar conductivity values of the anions  $\lambda_{A^-}^0$  in water using the appropriate literature value for the sodium cation [23].

$$\lambda_{A^-}^0(T) = \Lambda_{m, NaA}^0(T) - \lambda_{Na^+}^0(T) \quad (4)$$

The results for all investigated anions are presented in Table 2.

Using Walden's rule, the Stokes (hydrodynamic) radii  $r_s$  was calculated for the investigated anions

$$\eta \lambda_{A^-}^0 = 8.204 z_i / r_s \quad (5)$$

where  $z_i$  is the charge number of the ion,  $\eta$  is the dynamic viscosity of water.

The results of these calculations were collected in Table 3.

The hydrodynamic radius of the studied anions increases in the following order:  $Cin^- < Syn^- < p-Cou^- < Caf^- < Fer^-$  for the two lowest studied temperatures (288.15 K and 293.15 K) and  $Cin^- < Syn^- < Caf^- < p-Cou^- < Fer^-$  for the remaining temperatures (from 298.15 K to 318.15 K). The hydrodynamic radius for  $Cin^-$  changes slightly with increasing temperature. For the  $Fer^-$  anion, the hydrodynamic radius was found to decrease as the temperature increased, with an exception being observed at 313.15 K. Interestingly, while very little change in hydrodynamic radius was observed for both  $p-Cou^-$  and  $Syn^-$  below 298.15 K, the radius of the former was found to decrease slightly above this temperature while that of the latter only increased slightly. For the  $Caf^-$  anion, the hydrodynamic radius did not change between 288.15 K and 293.15 K. If we know van der Waals radii we can compare them with the hydrodynamic radii to obtain information about the hydration of the ions. However, as the van der Waals radius for the above ions are unknown, we can only assume that the  $Cin^-$  anion is subject to slight hydration, resulting in a greater effect on mobility and ionic conductivity than for the other studied anions. Of the studied anions,  $Fer^-$  probably possesses the largest hydration shell.

The Eyring activation enthalpy of charge transport  $\Delta H_{\lambda}^{\ddagger}$  for the investigated anions was obtained using the dependence:

$$\ln \lambda_{A^-}^0 + 2/3 \ln \rho_o = -\Delta H_{\lambda}^{\ddagger} / RT + D \quad (6)$$

where  $D$  is an empirical constant.

Comparing the slope of the linear dependencies of  $\ln \lambda_{A-}^0 + 2/3 \ln \rho_0$  against the inverse of the temperature ( $1/T$ ) yielded the following  $\Delta H_{\lambda}^{\ddagger}$  values: 18.33 kJ·mol<sup>-1</sup> for Cin<sup>-</sup>, 18.43 kJ·mol<sup>-1</sup> for *p*-Cou<sup>-</sup>, 21.08 kJ·mol<sup>-1</sup> for Caf<sup>-</sup>, 23.54 kJ·mol<sup>-1</sup> for Fer<sup>-</sup> and 14.97 kJ·mol<sup>-1</sup> for Syn<sup>-</sup> (Fig 5).

Regarding the activation enthalpy of charge transfer, greater differences were observed between the cinnamic acid salts tested in the present study than the sodium salts of benzoic acid derivatives studied previously [8]. Those differences were small and higher than those related to the viscous flow of pure water. While the  $\Delta H_{\lambda}^{\ddagger}$  value of the Syn<sup>-</sup> anion was almost identical to that of pure water, those of the other studied anions were higher; this indicates that the charge transport in these solutions requires ion desolvation and rearrangement of the solvent molecule around the ion to a certain extent. These processes are slightly more pronounced for the Caf<sup>-</sup> and Fer<sup>-</sup> anions, for which the difference is much larger.

The final stage of the study examined the effect of hydrolysis on molar conductivity. The degree of hydrolysis ( $\beta$ ) and the limiting molar conductivity were evaluated as described previously [8]. The  $\beta$  values of the sodium salts of *p*-coumaric, caffeic, ferulic and sinapinic acid (Table A3) were determined based on the literature values for their dissociation constant ( $K_a$ ) [24] at 298.15 K (Table A4): the obtained values were very small, ranging from 0.0001442 to 0.0012803. In the case of NaCin (Table A5),  $K_a$  is known for a wide range of temperatures [25] (Table A6) and therefore  $\beta$  could be assessed across the entire temperature range: it was found to range from 0.0001464 (318.15 K) to 0.0009232 (288.15 K). The differences between the degree of hydrolysis ( $\beta$ ) the highest and lowest temperatures are very small at any given concentration.

For NaCin, at each of the temperatures studied, the limiting molar conductivity value calculated excluding the effect of hydrolysis ( $\Lambda_m^0$ ) was practically identical to that calculated accounting for hydrolysis ( $\Lambda_{m,h}^0$ ) (Table 4). The largest differences between these values (0.18 S·cm<sup>2</sup>·mol<sup>-1</sup>) were observed in the case of NaSyn and NaFer (Table 5). The smallest differences were obtained for NaCaf (0.08 S·cm<sup>2</sup>·mol<sup>-1</sup>). However, the values of  $\Lambda_{m,h}^0$  are always slightly lower than these of  $\Lambda_m^0$  because  $\Lambda_m^0$  also includes the conductivity contributed by NaOH. As in the case of benzoic acids salts, the differences in limiting molar conductivity of all the studied cinnamic acid salts are much smaller than the estimated uncertainty regarding conductivity measurements ( $\pm 0.5\%$ ); as such, it appears that the hydrolysis of the salt has no significant effect on the analysis of conductometric data. If the hydrolysis would



have a greater impact, it would be visible already in the behavior presented in figures 3 and 4, respectively (as described in Ref. 26).

#### 4. Conclusions

The obtained values of association constants are insignificant, which indicates that the investigated salts are completely dissociated in aqueous solution. For the two lowest of the studied temperatures (i.e. 288.15 K and 293.15 K), the limiting ionic conductivity of the salts decreases in the following order:  $\text{Cin}^- > \text{Syn}^- > p\text{-Cou}^- > \text{Caf}^- > \text{Fer}^-$ , while the hydrodynamic radius increases in the opposite direction:  $\text{Cin}^- < \text{Syn}^- < p\text{-Cou}^- < \text{Caf}^- < \text{Fer}^-$ . For the remaining studied temperatures (from 298.15 K to 318.15 K), the order is as follows:  $\text{Cin}^- > \text{Syn}^- > \text{Caf}^- > p\text{-Cou}^- > \text{Fer}^-$ , with the hydrodynamic radius again increasing in the opposite direction:  $\text{Cin}^- < \text{Syn}^- < \text{Caf}^- < p\text{-Cou}^- < \text{Fer}^-$ . Although a change in the number of hydroxyl groups in the molecules of the studied salts does not significantly affect the limiting molar conductivity, the number of methoxy groups does. Among the investigated salts, phenomenon of hydrolysis does not affect the analysis of conductometric data.

#### Acknowledgment

This work is part of the research program for young scientists “Thermodynamic studies of selected macromolecules in terms of their application in industry, environmental protection and medicine” with project number B1711100001600.02, is financed by the University of Lodz.

#### References

- [1] G. Granata, G.M.L. Consoli, R. Lo Nigro, C. Geraci, Hydroxycinnamic acids loaded in lipid-core nanocapsules, *Food Chem* 245 (2018) 551–556.
- [2] M.A. Stachlewska, Inhibitory properties of lithium, sodium and potassium *o*-, *m*- and *p*-coumarates against *Escherichia coli* O157:H7, *Acta Sci. Technol. Aliment.* 14 (2015) 77–84.
- [3] J. Cabezas-Pizarro, M. Redondo-Solano, C. Umaña-Gamboa, M.L. Arias-Eschandi, Antimicrobial activity of different sodium and potassium salts of carboxylic acid against

- some common foodborne pathogens and spoilage-associated bacteria, *Rev. Avgent Microbiol.* 50 (2018) 56-61.
- [4] S. Marković, J. Tošovic, Comparative study of the antioxidative activities of caffeoylquinic and caffeic acids, *Food Chem* 210 (2016) 585–592.
- [5] L. Dorantesa, G. Apariciob, A. Ramirez, Improving water solubility of natural antibacterials to inhibit important bacteria in meat products, *Procedia Food Sci* 1 (2011) 173 – 177.
- [6] J. A Riemer, US patent 5336513, "Bitterness Inhibitors", issued 1994-08-09, assigned to Kraft General Foods.
- [7] B.-H.Wang, J.-P. Ou-Yang, Pharmacological actions of sodium ferulate in cardiovascular system, *Cardiovasc. Drug Rev.* 23 (2005)161–172.
- [8] M. Stańczyk, A. Boruń, M. Jóźwiak, Conductance studies of aqueous solutions of sodium salts of selected benzoic acid derivatives at temperatures from (288.15 to 318.15) K, *J. Mol. Liquids* 278 (2019) 247-252.
- [9] M. Matejczyk, R. Świsłocka, A. Golonko, W. Lewandowski, E. Hawrylik, Cytotoxic, genotoxic and antimicrobial activity of caffeic and rosmarinic acids and their lithium, sodium and potassium salts as potential anticancer compounds, *ADV MED SCI-POLAND* 63 (2018) 14–21.
- [10] R. Świsłocka, Spectroscopic (FT-IR, FT-Raman, UV absorption,  $^1\text{H}$  and  $^{13}\text{C}$  NMR) and theoretical (in B3LYP/6-311++G\*\* level) studies on alkali metal salts of caffeic acid, *Spectrochim Acta A* 100 (2013) 21–30.
- [11] R. Świsłocka, M. Kowczyk-Sadowy, M. Kalinowska, W. Lewandowski, Spectroscopic (FT-IR, FT-Raman,  $^1\text{H}$  and  $^{13}\text{C}$  NMR) and theoretical studies of *p*-coumaric acid and alkali metal *p*-coumarates, *Spectroscopy* 27 (2012) 35–48.
- [12] A. M. Khvan, E. L. Kristallovich, Kh. A. Abduazimov, Complexation of caffeic and ferulic acids by transition-metal ions, *Chem Nat Compd.* 37 ( 2001) 72-75
- [13] S. Woranuch, R. Yoksan, Preparation, characterization and antioxidant property of water-soluble ferulic acid grafted chitosan, *Carbohydr Polym.* 96 (2013) 495– 502.
- [14] M. Bešter-Rogač, J. Hunger, A. Stoppa, R. Buchner, 1-Ethyl-3-methylimidazolium ethylsulfate in water, acetonitrile, and dichloromethane: molar conductivities and association constants, *J. Chem. Eng. Data* 56 (2011) 1261–1267.
- [15] M. Bešter-Rogač, D. Habe, Modern advances in electrical conductivity measurements of solutions, *Acta Chim. Slov.* 53 (2006) 391–395.

- [16] J.M.G. Barthel, H. Krienke, W. Kunz, Physical chemistry of electrolyte solutions: modern aspects, Springer, New York 1998.
- [17] M. Bešter-Rogač, Nonsteroidal anti-inflammatory drugs ion mobility: a conductometric study of salicylate, naproxen, diclofenac and ibuprofen dilute aqueous solutions, *Acta Chim. Slov.* 56 (2009) 70–77.
- [18] M. Bešter-Rogač, Sodium salts of benzoic, *m*-salicylic, and *p*-salicylic acid: a conductivity study of diluted aqueous solutions, *J. Chem. Eng. Data* 56 (2011) 4965–4971.
- [19] D. Rudan-Tasič, C. Klofutar, M. Bešter-Rogač, The electric conductivities of aqueous solutions of rubidium and cesium cyclohexylsulfamates, potassium acesulfame and sodium saccharin, *Acta Chim. Slov.* 53 (2006) 324–330.
- [20] M. Tomšič, M. Bešter-Rogač, A. Jamnik, R. Neueder, J. Barthel, Conductivity of magnesium sulfate in water from 5 to 35°C and from infinite dilution to saturation, *J. Solution Chem.* 31 (2002) 19–31.
- [21] J. Gujta, M. Bešter-Rogač, B. Hribar-Lee, An investigation of ion-pairing of alkali metal halides in aqueous solutions using the electrical conductivity and the monte carlo computer simulation methods, *J. Mol. Liquids* 190 (2014) 34–41.
- [22] M. Bešter-Rogač, M. V. Fedotova, S. E. Kruchinin, M. Klähn, Mobility and association of ions in aqueous solutions: the case of imidazolium based ionic liquids, *Phys. Chem. Chem. Phys.* 18 (2016) 28594–28605.
- [23] H.S. Harned, B.B. Owen, The physical chemistry of electrolyte solutions, 3<sup>rd</sup> edn., Reinhold, New York, 1958.
- [24] S.P. Ozkorucuklu, J.L. Beltrán, G. Fonrodona, D. Barrón, G. Alsancak, J. Barbosa, Determination of dissociation constants of some hydroxylated benzoic and cinnamic acids in water from mobility and spectroscopic data obtained by CE-DAD, *J. Chem. Eng. Data* 54 (2009) 807–811.
- [25] R.C. Das, U.N. Dash, K.N. Panda, Thermodynamics of the dissociation of *trans*-cinnamic acid, *Can. J. Chem.* 54 (1976) 1916–1917.
- [26] A. Krofič, A. Apelbalt, M. Bešter-Rogač, Dissociation constants of parabens and limiting conductances of their ions in water, *J. Phys. Chem. B* 16 (2012) 1385–1392.

**Table 1.** Limiting molar conductivity  $\Lambda_m^0$ , association constants  $K_A^0$  and standard deviations  $\sigma(\Lambda)$  for the investigated salts in water over the temperature range from 288.15 K to 318.15 K.

$T/K$	NaCin			<i>p</i> -NaCou			NaCaf		
	$\Lambda_m^0$	$K_A^0$	$\sigma(\Lambda)$	$\Lambda_m^0$	$K_A^0$	$\sigma(\Lambda)$	$\Lambda_m^0$	$K_A^0$	$\sigma(\Lambda)$
	$S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$\text{dm}^3 \cdot \text{mol}^{-1}$		$S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$\text{dm}^3 \cdot \text{mol}^{-1}$		$S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$\text{dm}^3 \cdot \text{mol}^{-1}$	
288.15	$81.57 \pm 0.17$	$9.11 \pm 0.01$	0.57	$59.30 \pm 0.02$	$0.90 \pm 0.01$	0.05	$57.86 \pm 0.01$	$2.01 \pm 0.01$	0.05
293.15	$92.87 \pm 0.16$	$9.77 \pm 0.01$	0.55	$66.81 \pm 0.03$	0.00	0.12	$65.35 \pm 0.02$	$1.97 \pm 0.01$	0.06
298.15	$104.59 \pm 0.16$	$9.68 \pm 0.01$	0.55	$74.95 \pm 0.05$	0.00	0.16	$76.86 \pm 0.02$	$3.56 \pm 0.01$	0.06
303.15	$116.88 \pm 0.15$	$9.47 \pm 0.01$	0.52	$83.76 \pm 0.04$	0.00	0.13	$84.68 \pm 0.01$	$4.08 \pm 0.01$	0.05
308.15	$129.78 \pm 0.15$	$9.34 \pm 0.01$	0.52	$92.70 \pm 0.05$	0.00	0.16	$94.57 \pm 0.02$	$2.59 \pm 0.01$	0.09
313.15	$143.06 \pm 0.17$	$9.13 \pm 0.01$	0.58	$101.95 \pm 0.05$	0.00	0.18	$102.75 \pm 0.02$	$3.07 \pm 0.01$	0.06
318.15	$156.93 \pm 0.20$	$9.06 \pm 0.01$	0.69	$111.78 \pm 0.05$	$0.05 \pm 0.01$	0.18	$112.86 \pm 0.03$	$2.18 \pm 0.01$	0.10

**Table 1.** continued

$T/K$	NaFer			NaSyn		
	$\Lambda_m^0$	$K_A^0$	$\sigma(\Lambda)$	$\Lambda_m^0$	$K_A^0$	$\sigma(\Lambda)$
	$S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$\text{dm}^3 \cdot \text{mol}^{-1}$		$S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$\text{dm}^3 \cdot \text{mol}^{-1}$	
288.15	$55.31 \pm 0.03$	0.00	0.10	$63.00 \pm 0.05$	0.00	0.16
293.15	$62.74 \pm 0.04$	0.00	0.13	$71.63 \pm 0.04$	0.00	0.15
298.15	$70.49 \pm 0.04$	0.00	0.15	$80.60 \pm 0.05$	$0.05 \pm 0.01$	0.18
303.15	$82.52 \pm 0.05$	0.00	0.19	$89.22 \pm 0.05$	$0.68 \pm 0.01$	0.18
308.15	$91.51 \pm 0.05$	0.00	0.16	$98.13 \pm 0.05$	$1.52 \pm 0.01$	0.19
313.15	$99.74 \pm 0.04$	0.00	0.15	$105.83 \pm 0.07$	$0.13 \pm 0.01$	0.27
318.15	$109.34 \pm 0.05$	0.00	0.19	$113.13 \pm 0.11$	0.00	0.39

**Table 2.** Limiting ionic conductivity  $\lambda_{A^-}^0$  of anions of investigated salts in water at different temperatures.

$T/K$	Cin <sup>-</sup>	<i>p</i> -Cou <sup>-</sup>	Caf <sup>-</sup>	Fer <sup>-</sup>	Syn <sup>-</sup>
	$\lambda_{A^-}^0/S \cdot cm^2 \cdot mol^{-1}$				
288.15	41.85	19.58	18.14	15.59	23.28
293.15	48.06	22.00	20.54	17.93	26.82
298.15	54.44	24.80	26.71	20.34	30.45
303.15	61.16	28.04	28.96	26.80	33.50
308.15	68.25	31.17	33.04	29.98	36.60
313.15	75.51	34.40	35.20	32.19	38.28
318.15	85.57	40.42	41.50	37.98	41.77

**Table 3.** Hydrodynamic radii  $r_s$  of the investigated anions at different temperatures.

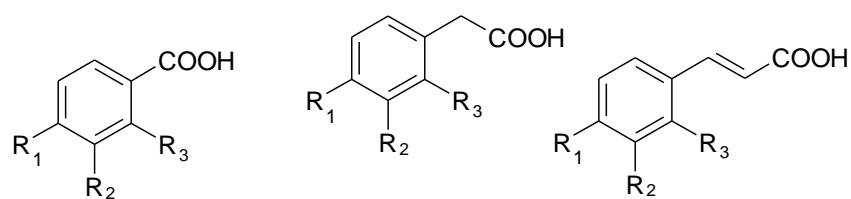
$T/K$	Cin <sup>-</sup>	<i>p</i> -Cou <sup>-</sup>	Caf <sup>-</sup>	Fer <sup>-</sup>	Syn <sup>-</sup>
	$r_s/nm$				
288.15	0.172	0.368	0.397	0.462	0.310
293.15	0.170	0.372	0.399	0.457	0.305
298.15	0.169	0.372	0.345	0.453	0.303
303.15	0.168	0.367	0.355	0.384	0.307
308.15	0.167	0.366	0.345	0.381	0.312
313.15	0.166	0.365	0.357	0.391	0.328
318.15	0.161	0.341	0.332	0.362	0.330

**Table 4.** Limiting molar conductivity of sodium cinnamate in water at different temperatures excluding and including the effect of hydrolysis.

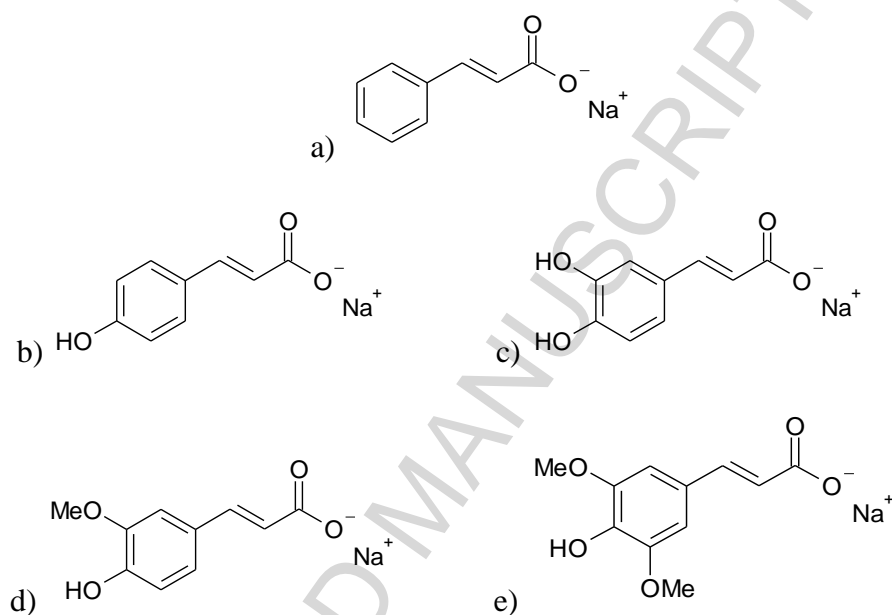
	NaCin						
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
$\Lambda_m^0/S \cdot cm^2 \cdot mol^{-1}$	81.57	92.87	104.59	116.88	129.78	143.06	156.93
$\Lambda_{m,h}^0/S \cdot cm^2 \cdot mol^{-1}$	81.54	92.86	104.58	116.87	129.77	143.05	156.93

**Table 5.** Limiting molar conductivity of the investigated salts in water at 298.15 K excluding and including the effect of hydrolysis.

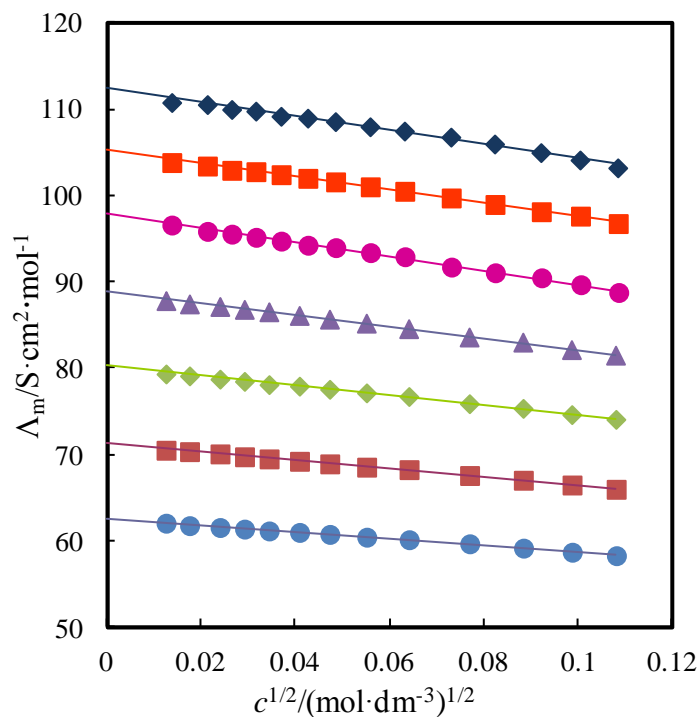
	<i>p</i> -NaCou	NaCaf	NaFer	NaSyn
	298.15 K			
$\Lambda_m^0/S \cdot cm^2 \cdot mol^{-1}$	74.95	76.86	70.49	80.60
$\Lambda_{m,h}^0/S \cdot cm^2 \cdot mol^{-1}$	74.81	76.78	70.31	80.42



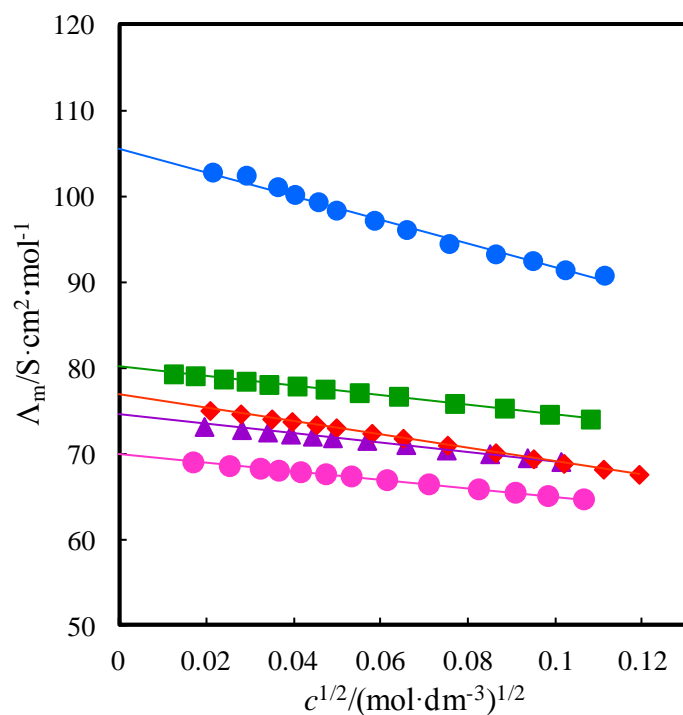
**Fig.1.** Division and structure of phenolic acids



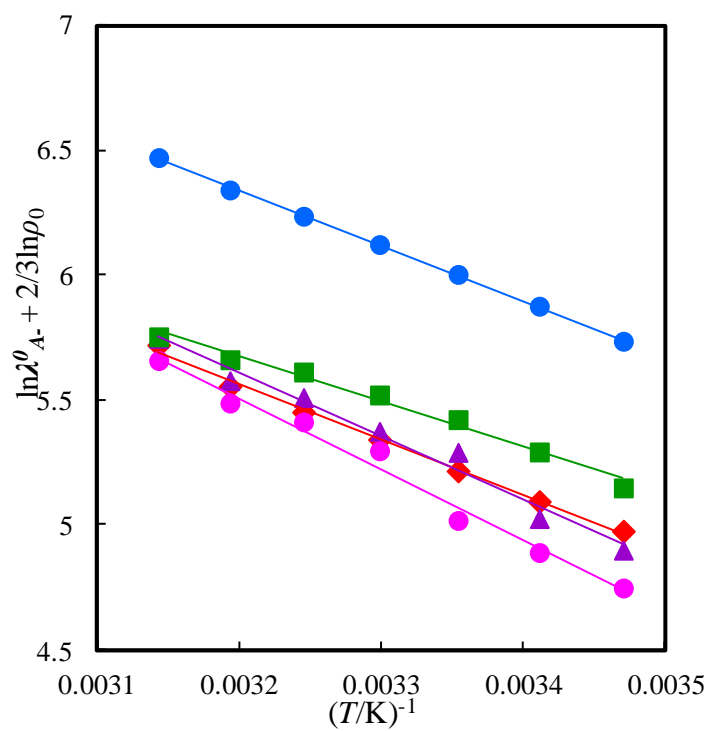
**Fig. 2.** The structures of the investigated salts; a) sodium cinnamate, b) sodium *p*-coumarate, c) sodium caffeate, d) sodium ferulate, e) sodium synapinate



**Fig. 3.** Molar conductivity  $\Lambda_m$  of aqueous solution of NaSyn versus  $c^{1/2}$  at experimental temperatures • 288.15 K; ■ 293.15 K; ♦ 298.15 K; ▲ 303.15 K; ● 308.15 K; ■ 313.15 K; ♦ 318.15 K. The lines represent the lcCM calculations.



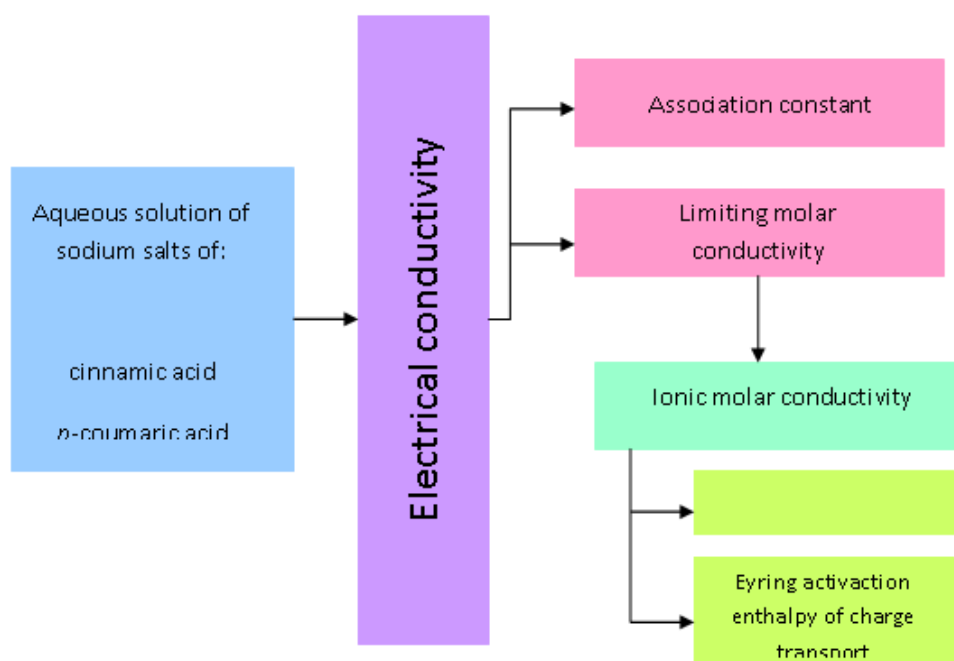
**Fig. 4.** Molar conductivity  $\Lambda_m$  of • NaCin; ▲ *p*-NaCou; ♦ NaCaf; ● NaFer; ■ NaSyn versus  $c^{1/2}$  in water at 298.15 K. The lines represent the lcCM calculations.



**Fig. 5.** Plot of  $\ln\lambda_{A^-}^0 + 2/3\ln\rho_0$  as a function of  $1/T$  for  $\bullet$  Cin $^-$ ;  $\blacktriangle$  *p*-Cou $^-$ ;  $\blacklozenge$  Caf $^-$ ;  $\bullet$  Fer $^-$  and  $\blacksquare$  Syn $^-$  in water.



## Graphical abstract



## Highlights

- Conductivity of sodium cinnamate, sodium *p*-coumarate, sodium caffeinate, sodium ferulate and sodium synapinate in water.
- The sodium salts of cinnamic acid and its derivatives are completely dissociated in aqueous solution.
- The limiting molar conductivity and ionic molar conductivity were determined.
- The hydrolysis of the salts has no significance in the analysis of conductometric data.