Physical and Electrochemical properties of aqueous electrolytic solutions based on sodium salt eutectic mixtures for EDLC supercapacitor application

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Abstract

The world's energy demand is increasing as a consequence of a growing and highly technological population that highly relies on fossil fuels, therefore, engaging renewable energy in the energy world supply is highly requirable. However, since most of renewable energy are intrinsically intermittent, energy harvest and distribution will largely depend on energy storage devices, namely supercapacitors. Along with this aspiring goal, is desirable that the materials used to develop these devices are not only high-performance but also the most environmentally friendly possible. In this work, mixtures of water with eutectic systems of sodium hexanoate with different carboxyl acids (hexanoic acid, octanoic acid, nonanoic acid and decanoic acid) are studied as potential electrolytes for Electrical Double Layer Supercapacitors (EDLCs).

In the first part of this study, physical characterization of these mixtures is studied through measurement and exploration of several properties, namely the conductivity, viscosity, density, surface tension and pH.

In the second part, the electrochemical performance of these mixtures is tested in EDLC cells with microporous activated carbon electrodes through Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD) and Potentiostatic Electrochemical Impedance Spectroscopy (PEIS).

From this study the eutectic system of sodium hexanoate and hexanoic acid with 60% molar composition in acid ($NaC_6:C_6(0.6)$), showed the highest conductivity, 22.3 mS/cm at 20 °C, the highest electrode specific capacitance, 71.6 F/g at 0.2 A/g, and the lowest internal resistance, 1.83 Ω, for a weight water composition of 60%.

Keywords: Electrolyte; Supercapacitor; Sodium Salt; Fatty acid; Eutectic mixture.

1. Introduction

Supercapacitors have received great attention due to their remarkable characteristics such as simple configuration, long lifetime, and their capability to charge/discharge in a short period of time [1]. In terms of specific energy and specific power, supercapacitors bridge the gap between conventional capacitors and batteries, meaning that they restore energy faster than a battery and store more energy than a conventional capacitor [1]. Additionally, electric traction, electric grid and renewable energy technology are the three main fields of study for supercapacitor application [2].

Within the different types of supercapcitors, the Electrical Double Layer Supercapacitor (EDLC) is the most mature technology and, as a consequence, the most commercialized one [3]. The operational mechanism of EDLCs relies on electrostatic interactions between the negatively polarized electrode and the cations of the electrolyte, and between the positively polarized electrode and the anions in solution, leading to a formation of an Electrical Double Layer (EDL) at the electrolyte/electrode interface.

The supercapacitor components highly influence its performance, namely the electrode, electrolyte, and the interaction between them [3]. However, compared to electrolytes, electrode materials for supercapacitors have been subject of more extensive research [4]. Despite this, a large variety of electrolytes have been tested and proposed. Supercapacitor electrolytes can be divided according to different criteria (physical state, chemical composition, pH, among others), however they are often divided into three main categories: Aqueous, Organic and Ionic Liquids [3]. Currently, organic electrolytes dominate the supercapacitor market, generally as a consequence of their higher operational voltage compared to aqueous electrolytes and their lower cost compared to ionic liquids [5].

General requirements of an electrolyte supercapacitor consist in chemical and electrochemical stability, inertness to the other supercapacitor components (electrodes, current collectors, etc), affordability, high ionic conductivity, wide temperature operational range (thermal stability), safety (low volatility and flammability), and environmental friendliness. However, it is challenging to find an electrolyte that fully satisfies all these requirements [3]. As a result, a compromise between those requirements must be made in accordance with the final supercapacitor application. Moreover, the electrolyte has an important influence in the supercapacitor performance parameters. Pivotal parameters include:

- the capacitance: the formation of the EDL and adsorption in the electrode porosity depend on the ions present in the electrolyte, namely their charge density, polarizability, size, and concentration.

- the operational voltage window is dependent on the electrolyte stability window, which will impact the energy and power densities.

- the ionic mobility in the electrolyte will affect the internal resistance of the supercapacitor which will impact its power density.

- the thermal stability of the electrolyte will determine the operational range temperature of the supercapacitor.

The role of eutectic mixtures in supercapacitor electrolytes is a relatively new subject of arising interest, being the first paper on the matter published in 2005 [6]. One of the main advantages of these mixtures is due to the fact that as they consist of a mixture of two or more compounds that through the establishment of hydrogen bonds form a new eutectic point that has a lower melting point than the ones from the pure components [7], it is possible to benefit from the properties of the pure compounds at room temperature in liquid phase. Moreover, a large amount of compounds combination can form a eutectic system, consequently a large number of systems are available to study, namely in the energy storage field.

The most studied eutectic system for supercapacitor electrolytes is Choline Chloride:Urea in a 1:2 molar ratio. This system is particularly interesting for its environmental friendliness, which is of major interest in supercapacitor as the currently commercialized cells mostly rely in organic electrolytes [8]. In this study, mixtures of water and eutectic systems of sodium hexanoate with different carboxyl acids (hexanoic, octanoic, nonanoic and decanoic) are physically and electrochemically characterized in other to explore their possible use as electrolyte for supercapacitors. Analogous to the Choline Chloride:Urea eutectic systems, the studied eutectic mixtures here presented are also constituted by environmentally compatible compounds.

1.1. Studied Eutectic Systems
Four types of eutectic solvents based on the mixture of an organic salt as HBA (sodium hexanoate) with a long alkyl chain carboxylic acid as HBD (hexanoic, octanoic, nonanoic and decanoic acids) were prepared, the respective structures are presented in **Figure 1**.
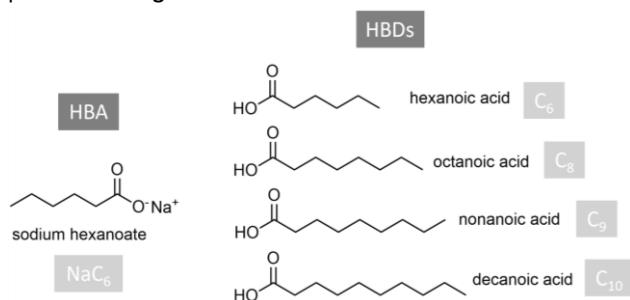

Figure 1. *Chemical structures and respective acronyms of the species used to prepare the eutectic mixtures.*

To choose the composition (acid/salt ratio) of the starting eutectic mixtures for this work two aspects were considered: At room temperature, the initial eutectic mixture is liquid, and they contain the maximum amount of salt possible to benefit from the presence of the sodium ion for ionic conductivity purposes.

From a previous study [9] developed with my collaboration, sodium hexanoate (NaC_6) with long chain fatty acids eutectic solvents, namely, octanoic acid (C_8), nonanoic acid (C_9) and decanoic acid (C_{10}), where characterized. The solid-liquid phase diagrams of these mixtures were built at ambient pressure allowing to determine the composition window in which these mixtures were homogeneous liquids at ambient temperature. It was possible to conclude that for these mixtures the eutectic point occurs between 0.6 and 0.7 molar of acid, occurring by order of length of acid chain (octanoic, nonanoic and decanoic), being the corresponding temperature as lower as smaller the acid chain. Therefore, the eutectic point does not change greatly with the carboxylic acid (HBD), being the effect of the sodium hexanoate (HBA) predominant as stated in [9]. Considering that the length of the acid chain does not have a major effect on the eutectic composition occurrence and that, as previously stated, the size of the electrolyte ions can have a major effect in the overall supercapacitor performance, the combination of sodium hexanoate with hexanoic acid (NaC_6:C_6) was also studied for 0.6 and 0.7 molar composition in acid. Taking this into account, the starting mixtures used where NaC_6:C_6 with x_{acid}=0.6 and x_{acid}=0.7, NaC_6:C_8 with x_{acid}=0.6 and x_{acid}=0.7, NaC_6:C_9 with x_{acid}=0.7 and NaC_6:C_{10} with x_{acid}=0.7. The eutectic mixtures used, and their respective acronyms are summarized in **Table 1**.

Table 1. *Eutectic mixtures acronyms and respective description.*

Eutectic mixture acronyms	Description
NaC_6:C_6(0.6)	Sodium hexanoate with hexanoic acid with 60% molar in acid
NaC_6:C_6(0.7)	Sodium hexanoate with hexanoic acid with 70% molar in acid
NaC_6:C_8(0.6)	Sodium hexanoate with octanoic acid with 60% molar in acid
NaC_6:C_8(0.7)	Sodium hexanoate with octanoic acid with 70% molar in acid
NaC_6:C_9(0.7)	Sodium hexanoate with nonanoic acid with 70% molar in acid
NaC_6:C_{10}(0.7)	Sodium hexanoate with decanoic acid with 70% molar in acid

For each eutectic system nine mixtures with different water composition where prepared, varying the water content from 10% to 90% in weight.

2. Experimental Section
2.1. Chemical compounds
The sodium hexanoate ($C_6H_{11}NaO_2$) used to prepare the eutectic mixtures was synthetized through a saponification reaction using a sodium hydroxide in methanol solution and hexanoic acid also in methanol. The sodium hydroxide (NaOH) (CAS 1310-73-2) used in the sodium hexanoate synthesis was purchased from Eka and the methanol (CH_3OH) (CAS 67-56-1) with 99.8% of purity was purchased from Sigma-Aldrich. The hexanoic acid ($C_6H_{12}O_2$) (CAS 142-62-1) with 99% of purity was purchased from Aldrich, the octanoic acid ($C_8H_{16}O_2$) (CAS 124-07-2) with 99% purity was purchased from Acros Organics, the nonanoic acid ($C_9H_{18}O_2$) (CAS 607-197-00-8) with 97% of purity was purchased from Sigma and decanoic acid ($C_{10}H_{20}O_2$) (CAS 334-48-5) with 99% of purity was purchased from Alpha Aesar.

2.2. Eutectic mixtures preparation

The eutectic mixtures of sodium hexanoate with long alkyl chain carboxylic acids where prepared adding the acid to the sodium hexanoate in a glass vial. Each compound was weighted in an analytical high precision Mettler Toledo (MS205DU) balance with an uncertainty of $\pm 10^{-4}$ g. Each mixture was slowly heated up with constant stirring using a Heidolph MR Hei-Tec heating-stirring plate, until a clear liquid phase was obtained. Then the heating was turned off allowing the mixtures to rest and slowly cool down to ambient temperature.

2.3. Eutectic-water mixtures preparation

The mixtures of eutectic and water were also prepared in glass vials adding water to the eutectic mixture and weighted in the above mentioned balance. Then using a Labnet vortex mixer each water-eutectic combination was agitated. The water used to prepare these mixtures was ultrapure, double distilled water passed through a reverse osmosis system and further treated with a Milli-Q plus water purification apparatus.

2.4. Physico-Chemical Characterization

The phase diagrams, viscosity, density, surface tension, conductivity and pH data were collected for each sample, the technical aspects, equipment, and experimental conditions used for each technique will be described in the respective subsection.

2.4.1. Phase diagrams

Using a VWR thermostatic bath, the physical aspect of the samples was registered between -10°C and 60°C (± 0.01°C).

2.4.2. Centrifuge

The centrifugation of the gel mixtures was carried out in a VWR CompactStar CS 4 centrifuge at 4500 rpm.

2.4.3. pH

The pH data was collected at 20 °C using a *Consort SP28X* pH electrode connected to a *Consort multiparameter C3010 analyser*.

2.4.4. Viscosity

The viscosity measurements were carried out between 10°C and 60°C (± 0.02°C) using an automatic *Anton Paar*® rolling-ball viscometer (*Lovis 2000 M/ME*). The viscometer was pre-calibrated with ultra-pure water. The uncertainty of the measurements was 2%.

2.4.5. Density

The density measurements were carried out between 10°C and 60°C (± 0.02°C) using an *Anton Paar*® densimeter equipped with a digital vibrating tube densimeter. The densimeter was pre-calibrated with ultra-pure water. The uncertainty of the measurements was 2×10^{-5} g.cm^{-3}.

2.4.6. Surface Tension

Surface tension measurements were carried out by Du Noüy method using a K10ST Krüss digital tensiometer at ambient temperature with an 0.1 mN/m accuracy.

2.4.7. Conductivity

The ionic conductivity measurements were performed with a multichannel conductivity meter (*BioLogic*®, France) based on a frequency response analyzer (MCM 10) connected to a Peltier-based temperature control unit with ten slots (WTSH 10, Biologic). The measurements were conducted between -20°C and 50°C (±0.02°C) in sealed cells with Pt parallel-plate electrodes protecting the samples from air exposure.

2.5. Electrochemical Tests

The electrodes used in the electrochemical tests were prepared with activated carbon (AC) from *Blue solution, France,* coated on aluminum, having a composition of AC/polyvinylidene difluoride/carbon black with an 80/10/10 wt ratio (wt: weight). The AC (Blue Solution, France) has a specific area of 1500 m^2 g^{-1} (BET) with an average pore size 1.17 nm. The average loading of AC per unit area is 5 mg cm^{-2} and the bulk density reaches 0.7 cm^3 g^{-1}.

The cells were assembled in *Swagelok*® cells comprising two AC electrodes (diameter: 10 mm) and a *Whatman*® GF/C glass microfiber filter (thickness of 0.67 mm) as the separator as illustrated in **Figure 2**. The quantity of electrolyte added to each cell was approximately 150 µL.

Cyclic voltammetry (CV), Galvanostatic charge-discharge cycling (GCD), and potentiostatic impedance spectroscopy (PEIS) were conducted in cells by a computer-controlled multichannel potentiostat/galvanostat (VMP3, *Biologic*®, France).
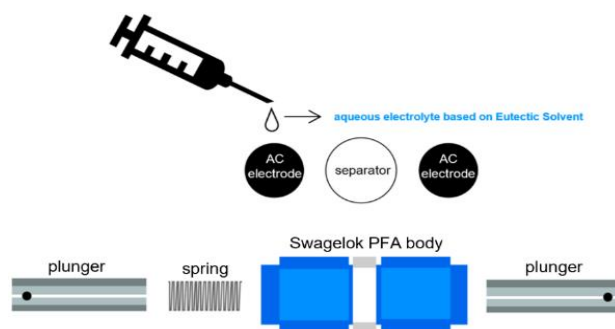

Figure 2. *Schematic illustration of the Swagelock® cell used in the electrochemical tests.*

The long-term cycling protocol by GCD cycles was performed at a normalized current density of 0.2 A g^{-1} or 0.1 A g^{-1} (normalized with respect to the mass of the activated carbon, 5.0 mg per electrode) for 5000 cycles. The CV was performed at 1, 5, 10 and 20 mV/s scan rates. PEIS was conducted between 500 kHz and 5 mHz (ten points per decade) at open-circuit voltage with an oscillating amplitude fixed at 5 mV. All EDLC devices were cycled under ambient conditions.

3. Results and Discussion

3.1. Sample Selection: Water composition and temperature seep

As previously indicated, a supercapacitor's electrolyte has a significant impact in the operating temperature, and thus it is critical to monitor any changes, namely phase changes, occurring in the studied mixtures. Taking into consideration the

hydrophobic nature of the initial eutectic systems, the water composition and temperature are crucial variables to consider ensuring the presence of a homogeneous media. The physical aspect of each mixture was investigated as a function of temperature from -10 °C to 60 °C with a sweep rate of 5 °C. The observed physical aspect was registered at each temperature step after mixing and after about 10 minutes of resting at the corresponding temperature. With the collected observations it was possible to build drafts of sol-gel diagrams, **Figure 3** to **Figure 8 ,** in which different physical state areas are proposed (1 phase, 2 phases, 3 phases, turbid gel and solid).
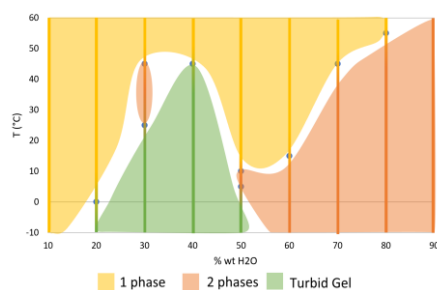
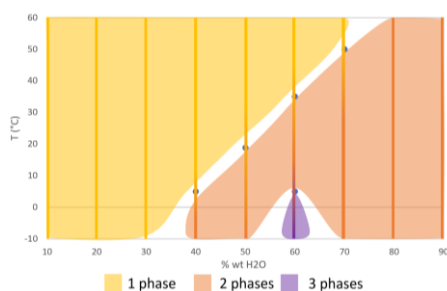**Figure 3.** *Phase diagram for the NaC$_6$:C$_6$(0.6) eutectic-water group.*

Figure 4. *Phase diagram for the NaC$_6$:C$_6$(0.7) eutectic-water group.*
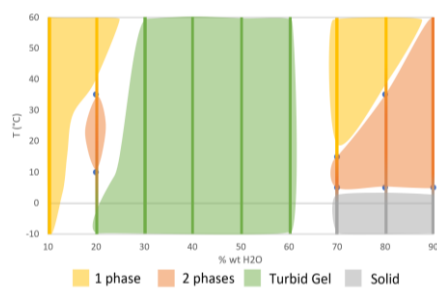
Figure 5. *Phase diagram for the NaC$_6$:C$_8$(0.6) eutectic-water group.*
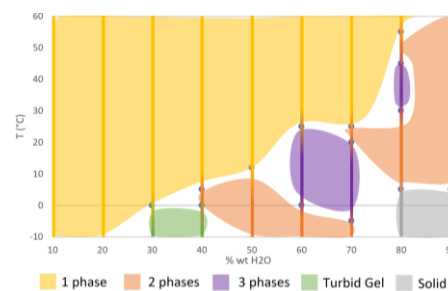
Figure 6. *Phase diagram for the NaC$_6$:C$_8$(0.7) eutectic-water group.*
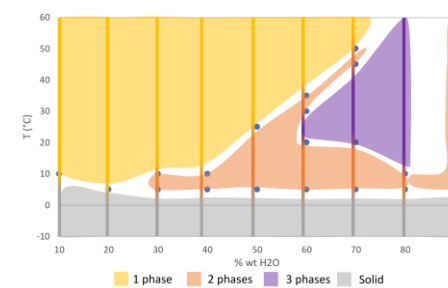
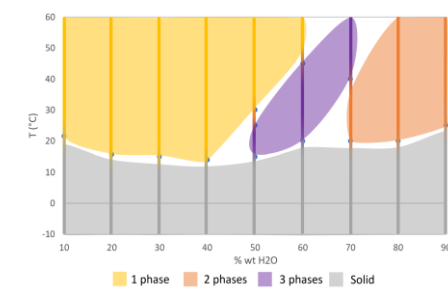**Figure 7.** *Phase diagram for the NaC$_6$:C$_9$(0.7) eutectic-water group.*

Figure 8. *Phase diagram for the NaC$_6$:C$_{10}$(0.7) eutectic-water group.*

After the temperature sweeping for each water composition is possible to conclude that for groups in which the eutectic composition is 0.7 molar in acid, the occurrence of one liquid phase (yellow region) is wider. Moreover, for those eutectic compositions, 3 phases are observed when the water content ranges from 50% to 80%. On the other hand, the occurrence of a gel phase (green region) has a predominance in mixtures where the eutectic has a larger quantity of salt (0.6 molar composition in acid). Also, the longer the acid chain is, the larger is the solid phase (grey region) which compromises the possibility to have an electrolytic solution at low temperatures. In general, the larger the water content and the lower the temperature, the greater is the probability to have phase separation and the use of these mixtures as electrolytes is compromised. Considering the aforementioned considerations, the mixtures chosen to be studied were those that exhibited a homogenous phase (liquid or gel) in a high range of temperature. For gel mixtures, it was important to centrifuge them (4500 rmp for 30 minutes) to test their stability, between the gel mixtures, only NaC$_6$:C$_8$(0.6) + 30%H$_2$O showed phase separation. The following table gives a

summary of the mixtures that were selected to proceed with physical and electrochemical characterization.

Table 2. *Selected mixtures for further characterization.*

Eutectic Combination	water wt%	water molar%	Physical aspect at 20 °C
NaC₆:C₆(0.6)	10	43.6	One liquid phase
	20	63.5	One liquid phase
	40	82.2	Turbid gel
	50	87.4	One liquid phase
	60	91.2	One liquid phase
NaC₆:C₆(0.7)	10	43.3	One liquid phase
	20	63.2	One liquid phase
	30	74.6	One liquid phase
	40	82.1	One liquid phase
	50	87.2	One liquid phase
NaC₆:C₈(0.6)	10	46.3	One liquid phase
	40	83.7	Turbid gel
	50	88.5	Turbid gel
	60	92.0	Turbid gel
NaC₆:C₈(0.7)	10	46.7	One liquid phase
	20	66.3	One liquid phase
	30	77.3	One liquid phase
	40	84.0	One liquid phase
	50	88.7	One liquid phase
NaC₆:C₉(0.7)	10	48.7	One liquid phase
	20	68.0	One liquid phase
	30	78.4	One liquid phase
	40	84.9	One liquid phase
NaC₆:C₁₀(0.7)	10	50.6	One liquid phase
	20	69.6	One liquid phase
	30	79.6	One liquid phase
	40	85.9	One liquid phase

3.2. Physical Characterization
3.2.1. Ionic Conductivity

Ionic conductivity, σ, is a property that allows to evaluate the capacity of an electrolyte to conduct electricity through the presence of ions. For this reason, ionic conductivity can be used as a first test to evaluate the potential application of a solution as electrolyte. Taking this into account ionic conductivity is highly dependent on ion dissociation and mobility, thus it can depend on the size of ions and on the interaction between them. In **Figure 9**, a summary of the conductivity results for all aqueous eutectic mixtures at 20 °C is presented.
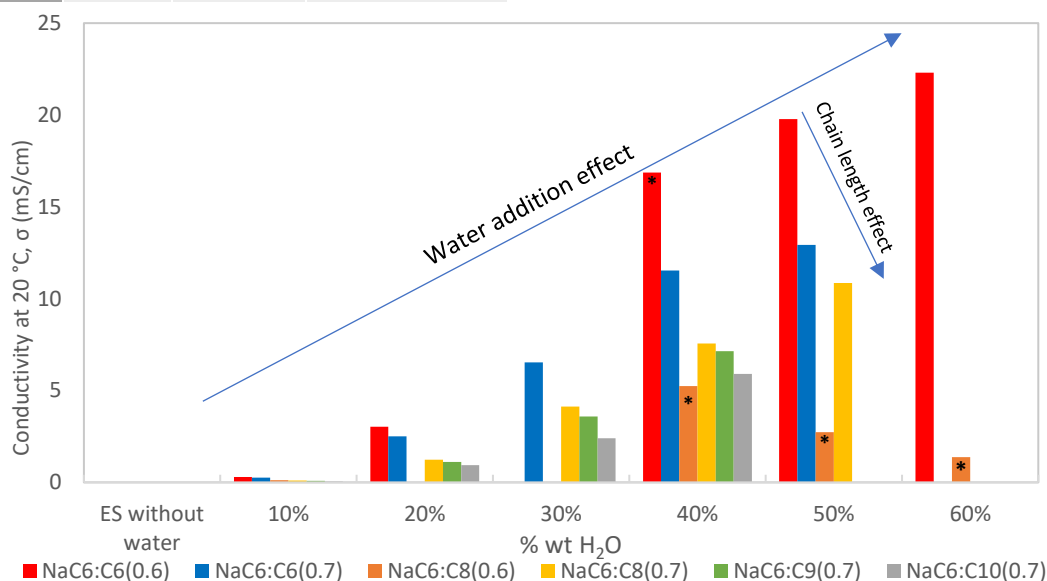

Figure 9. *Conductivity data at 20 °C organized by water massic %. "*" identifies mixtures in gel form.*

In general, conductivity increases with the water content and decreases with the acid chain length. This is related to the fact that the water addition to the eutectic mixture affects the eutectic original H-bond network, improving the mobility of the species. Additionally, the size of the ions compromises their mobility, and therefore the conductivity is smaller for the mixtures with the larger acid chain. However, for mixtures containing the same acid (i.e. NaC₆:C₆(0.6) and NaC₆:C₆(0.7)) and with similar molar water composition, for example NaC₆:C₆(0.6) + 50 wt%H₂O (87.4 molar% H₂O) and NaC₆:C₆(0.7) + 50 wt%H₂O

(87.2 molar% H_2O), the conductivity for the NaC₆:C₆(0.6) mixture is much higher than it is for NaC₆:C₆(0.7) (19.8 mS/cm and 12.9 mS/cm, respectively). Therefore, the amount of salt present in the mixture has a significant effect on the conductivity, which can be associated with the presence of a larger amount of sodium cation (Na⁺) that due to its smaller size, shows greater mobility.

Moreover, for the NaC₆:C₈(0.6) group the gel formation greatly decreases the conductivity. However, for the NaC₆:C₆(0.6), the gel formation does not seem to have affect the

tendency of conductivity to rise with the water content. Thus, mixtures with small acid chains, high water content and high amount of salt, namely $NaC_6:C_6(0.6) + 60\%H_2O$, gather the best conditions to achieve the highest conductivity 22.3 mS/cm at 20 °C.

3.2.2. Viscosity

Especially in the study of electrolytes, viscosity reveals to be an important parameter once it is related to the mobility of ionic species and, therefore, it has an influence in the performance of the supercapacitor. For this reason, the viscosity can provide information on a molecular basis, since it is a direct consequence of the intermolecular interactions, and it is an important parameter to establish the operational conditions of the electrolyte/supercapacitor [10]. **Figure 10** illustrates the viscosity evolution with the water content and temperature.
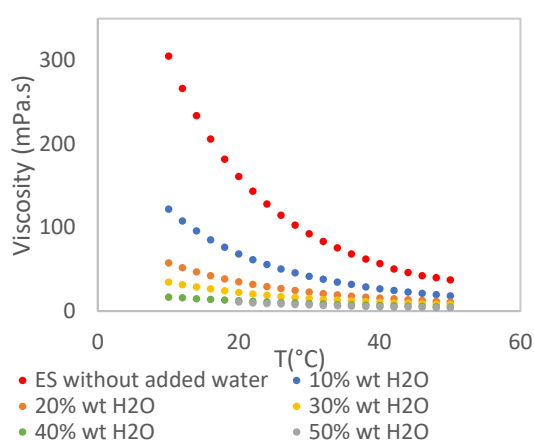

Figure 10. *Viscosity data as function of temperature for the $NaC_6:C_6(0.7)$-water mixtures.*

For all mixtures it was observed that the viscosity greatly decreases with the water content and with temperature. Moreover, the effect on viscosity is more prominent at lower water content and lower temperature than it is at high water content and high temperature. The addiction of water in eutectic mixtures interferes with the pre-established hydrogen bonding between the eutectic system compounds resulting in higher mobility of the species and therefore decreasing the viscosity and increasing conductivity as discussed above.

3.2.3. Surface Tension

The sodium hexanoate and fatty acids have amphiphilic nature once the polar carboxyl group will have water affinity and, in contrast, the apolar long alkyl chain is hydrophobic. For this reason, in presence of water these compounds will self-assemble forming aggregates, where the carboxyl group will orient to the water molecules and the carbon chain will avoid it.

As expected, the surface tension decreased with the concentration of the eutectic mixture until the critical aggregation concentration (CAC) was reached, after the CAC a plateau region was observed. The CAC value decreases as the carbon acid chain increases once the hydrophobicity rises with the hydrocarbon chain. Moreover, it is possible to say that the water-eutectic mixtures under study are likely to have a high level of organization since they have considerably larger

concentrations than their corresponding determined CACs. The values of the CAC according to the number of carbons in the alkyl acid chain are presented in **Table 3**.

Table 3. *Critical Aggregation Concentration (CAC) in mol/L according to the number of carbons in the alkyl acid chain.*

Number of carbons in the acid chain	CAC (mol/L)
6	2.75×10^{-2}
8	9.24×10^{-3}
9	1.96×10^{-3}
10	9.65×10^{-4}

3.2.4. Walden Plot

Walden plot is a qualitative/semi-qualitative method to study the ionicity (fraction of ions that participate in conduction) of electrolytic solutions. The bisector represented in Walden plot is used as a reference and it represents the theoretical behaviour of 0.01 mol/L KCl aqueous solution, in which ions are known to be fully dissociated having equal mobility [7]. **Figure 11** illustrates the distribution of the studied mixtures in the Walden plot.
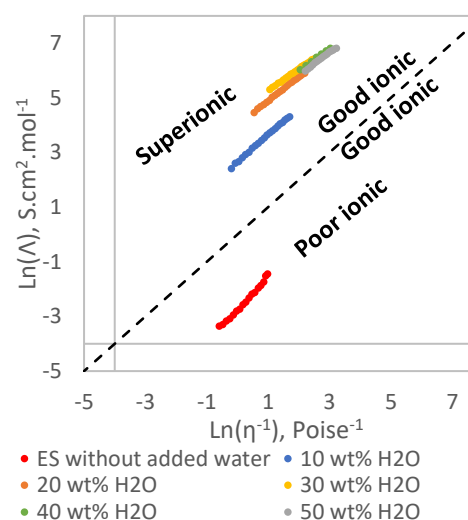

Figure 11. *Walden plot representation for $NaC_6:C_6(0.7)$ mixtures.*

It was observed that for all NaC_6:Acid mixtures, the water addition turns the original poorly ionic eutectic mixture into a good ionic liquid and superionic liquid.

3.2.5. pH

The pH measurements for each studied mixture exceeded the pK_a of the corresponding acids meaning that the deprotonated form of the acid predominates. For each eutectic-water group, the pH was constant with the addition of water, therefore the number of free protons in solution was not considerably altered. As was earlier observed, the presence of water significantly affects each group's conductivity, however since the number of free protons was not affected by the water content, this means that the increase of conductivity with the water content is not due to a larger amount of free protons in solution.

3.3. Electrochemical Study
3.3.1. Cyclic Voltammetry

Cyclic voltammetry tests were performed for each mixture at four different scan rates, 1 mV, 5 mV/s; 10 mV/s and 20 mV/s and for a voltage range from 0 to 1 Volt, all at room temperature (~20 °C).

Inside each eutectic-water system, the water content influence was clearly seen, as the higher the water content the more pronounced is the quasi-rectangular shape. Cyclic Voltammetry was performed for all the mixtures summarized in **Table 1**, excepting the gel mixtures. For these mixtures it was not possible to perform cyclic voltammetry adequately. **Figure 12** and **Figure 13** illustrate the water addition effect in the voltammograms.
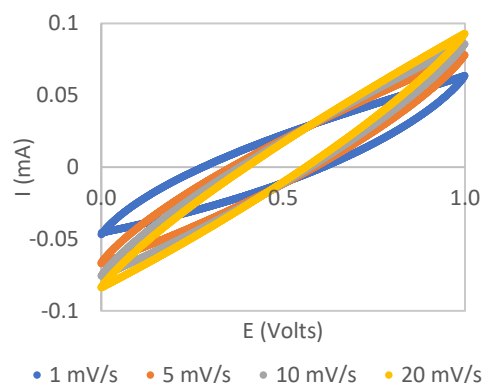

● 1 mV/s ● 5 mV/s ● 10 mV/s ● 20 mV/s

Figure 12. *Cyclic voltammograms performed at 1 mV/s, 5 mV/s, 10 mV/s and 20 mV/s scan rates for a voltage limit of 1 volt for the NaC$_6$:C$_6$(0.7).*
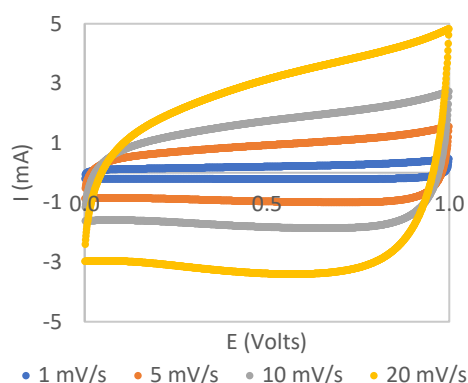

● 1 mV/s ● 5 mV/s ● 10 mV/s ● 20 mV/s

Figure 13. *Cyclic voltammograms performed at 1 mV/s, 5 mV/s, 10 mV/s and 20 mV/s scan rates for a voltage limit of 1 volt for the NaC$_6$:C$_6$(0.7) + 50% H$_2$O mixture.*

This effect of the water content on the voltammograms shape is an indication that the presence of water lowers the electrolyte resistance (by improving the ionic mobility) and allows the ions to have a faster response to the applied voltage, and therefore establish in the electrode pores and surface faster. **Figure 14** reunites voltammograms of mixtures with the same water content but different acid chain lengths.
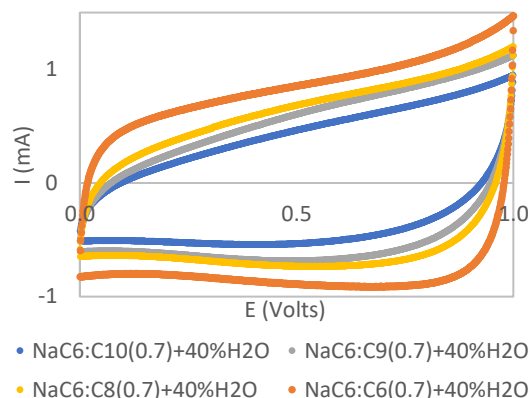

● NaC6:C10(0.7)+40%H2O   ● NaC6:C9(0.7)+40%H2O
● NaC6:C8(0.7)+40%H2O   ● NaC6:C6(0.7)+40%H2O

Figure 14. *Cyclic Voltammetry curves plotted at 5 mV/s potential scan rate for NaC$_6$:C$_6$(0.7), NaC$_6$:C$_8$(0,7), NaC$_6$:C$_9$(0,7), NaC$_6$:C$_{10}$(0.7) with 40%wt H$_2$O.*

This superposition of voltammograms allows to conclude that lower acid chain leads to a voltammogram that as more rectangular shape. This can be related to the fact that smaller molecules have greater mobility and as a consequence, their time scale to establish at the electrode surface to form the EDL is smaller. Moreover, smaller ions can introduce easily in the microporosity (less resistance).

3.3.2. Galvanostatic Charge-Discharge

Based on CV results, the mixtures demonstrating better performance (quasi-rectangular shape voltammograms) were selected to perform Galvanostatic Charge-Discharge (GCD) tests. The operational conditions to perform GCD method were based in the results of CV, namely the applied current in GCD corresponded, approximately, to the current obtained in CV at the plateau zone (current supported by the system). **Figure 15** is an example of GCD data collected for over 5000 cycles.
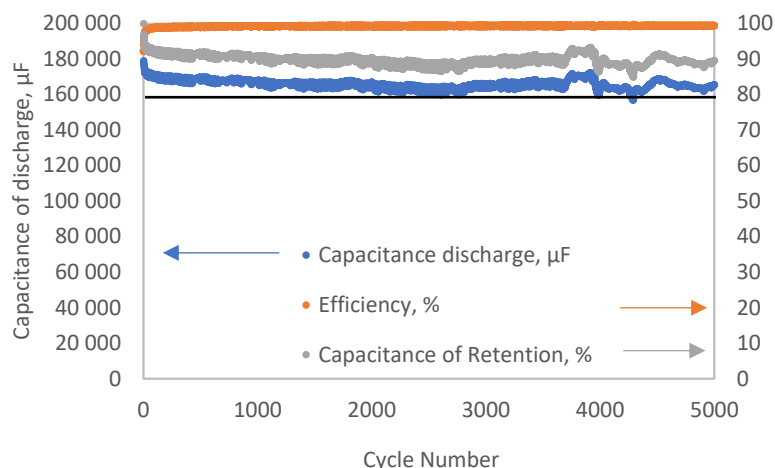
Figure 15. *Capacitance, Capacitance of retention, and efficiency as function of cycle number for NaC$_6$:C$_6$(0.6) + 60%H$_2$O mixture.*

In all tests the efficiency of charge and discharge was maintained closed to 100%. To evaluate the life cycle of each mixture the capacitance loss between the initial capacitance and the capacitance at the 5000 cycle was quantified ($\frac{C_i - C_{5000}}{C_i} \times 100$) and is presented in **Table 4** as well as the capacitance retained after 5000 cycles.

Table 4. *Specific Capacitance at the beginning of cycling and at the 5000th cycle, % of capacitance loss and % of retained capacitance.*

Mixture	wt% H$_2$O	C$_{initial}$ (F/g)	C$_{5000}$ (F/g)	$\frac{\Delta C}{C_i}$	% Retained Capacitance (Ci/C$_{5000}$)
NaC$_6$:C$_6$(0.6)	50	64.6	56.3	12.8	**87**
	60	71.6	66.2	7.5	**92**
NaC$_6$:C$_6$(0.7)	30	62.1	53.4	14.0	**86**
	40	67.2	61.8	8.0	**92**
	50	52	35.4	31.9	68
NaC$_6$:C$_8$(0.7)	20	47.1	39.3	16.6	**83**
	30	44	27.3	38.0	62
	40	-	-	-	-
	50	56.8	54	4.9	**95**
NaC$_6$:C$_9$(0.7)	20	42.5	33.6	20.9	79
	30	38.5	30.4	21.0	79
	40	47.3	36	23.9	76
NaC$_6$:C$_{10}$(0.7)	20	28.6	17.6	38.5	62
	30	22.8	19.1	16.2	**84**
	40	24.9	15.9	36.1	64

Often in literature, a value of 80% retained capacitance is given as a reference to evaluate the life cycle. Therefore, the greater the number of cycles with a capacitance retention higher than 80%, the better the cycling stability. From the above presented table, it is seen that a great number of electrolytes fulfil this parameter after 5000 cycles. Only four samples have much lower capacitance retention than 80%, namely NaC$_6$:C$_{10}$(0.7) with 20% and 40% of water, NaC$_6$:C$_8$(0.7) +30%H$_2$O and NaC$_6$:C$_6$(0.7) +50%H$_2$O. Moreover, the life cycle, here evaluated by the specific capacitance decay, does not seem to be related to the water content or the acid chain, but to a more complex phenomenon.
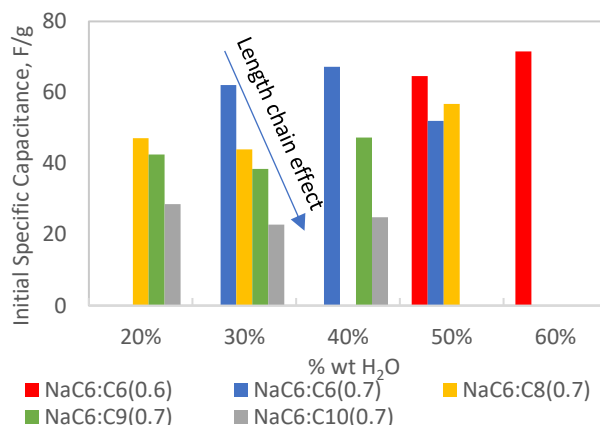

Figure 16. *Initial specific capacitance per electrode displayed by massic water content.*

From **Figure 16**, it can be seen that the acid chain length has an important effect in the obtained specific capacitance. This may reflect the difficulty of the ionic species to insert in the microporosity of the carbon electrodes (and even to establish at the surface) as their sizes increases. The highest capacitance, 71.6 F/g, is obtained for the mixture containing the acid with the smallest alkyl chain and with the highest water content, NaC$_6$:C$_6$(0.6) + 60%H$_2$O. This is promising value that can be enhanced through the optimization of the electrode used (for example, testing these systems in mesoporous carbon).

3.3.3. Potentiostatic Electrochemical Impedance Spectroscopy

Potentiostatic Electrochemical Impedance Spectroscopy was performed for the same mixtures used in GCD, before ("fresh" cell) and after cycling (100 charge/discharging cycles at the same conditions of GCD). For all mixtures it was observed a spectrum shape characteristic of EDLC, in which three main regions can be highlighted: A semi-circle at high

frequencies, a 45° line at middle frequencies and a straighter line at lower frequencies. In **Figure 17** these regions are delimited by R_A, R_B and R_C.
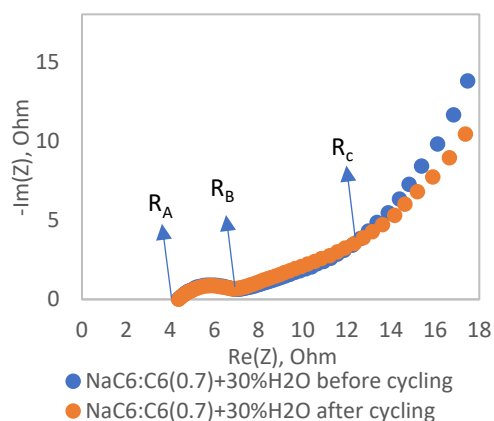

Figure 17. Nyquist plot for NaC6:C6(0.7) + 30%H2O with identification of the different zone limits.

For all cases for the low frequency zone, has a straighter shape before cycling than after cycling which reflects the decrease of the capacitive behaviour with the usage as expected, being in accordance with the GCD results in which it is observed a decrease of the capacitance with the number of performed cycles.

The values of R_A are associated with the internal resistance (ESR) of the cell, which is greatly influenced by the electrolyte resistance, the determined values for each mixture are presented in **Figure 18**.
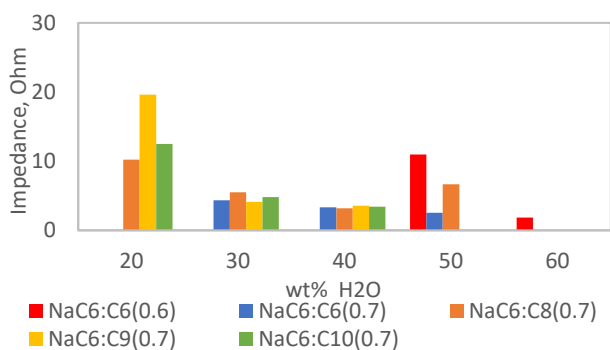

Figure 18. R_A values before cycling displayed by water content.

As can be seen from the previous figure, the R_A values present higher values for 20% water content, decreasing until 40%. This reflects the higher resistance of the electrolytes with lower water content, which is associated with higher viscosity and lower conductivity. However, the NaC_6:C_6(0.6) and NaC_6:C_8(0.7) at 50% H_2O the electrolyte resistance increases, which was not expected. Despite this, it is important to point that these compositions are "limit" compositions, in a sense that the NaC_6:C_6(0.6) + 50%H_2O is the composition after the gel formation, and the NaC_6:C_8(0.7) + 50%H_2O is the composition close to the limit of miscibility of the water/eutectic. The NaC_6:C_6(0.6) + 60%H_2O is the mixture that has the lowest internal resistance (ESR), 1.83 Ω.

The decrease of the ESR values with water content for eutectic-based electrolytes was also observed for the Choline Chloride:Urea systems [8]. Moreover, the cells using Choline Chloride:Urea systems present an internal resistance of approximately 10 Ω for a 5 wt% of water content which is equivalent to the 20 wt% of the studied systems.

The R_c values delimit the Warburg region which is related to the ion's diffusion in the microporosity of the electrodes. The determined R_c values for each mixture are presented in **Figure 19**.
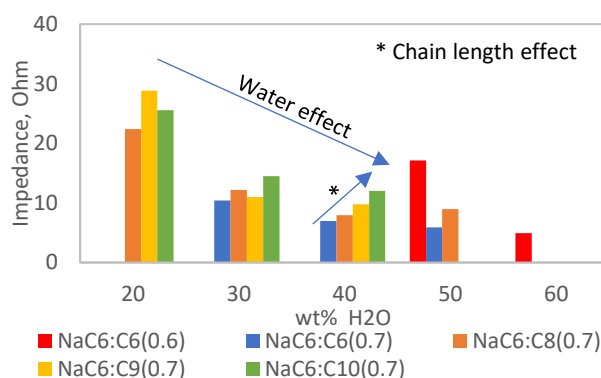

Figure 19. R_C values before cycling displayed by water content.

As can be seen in the previous figure, the values of R_c generally increase with the acid alkyl chain and decrease with water content, for a water composition ranging between 20% and 40%. These results are in accordance with the previous results from CV in which more resistive voltammograms (deviating from the quasi-rectangular shape) were obtained for mixtures containing longer chains, and with the GCD results showing lower capacitance for higher alkyl chains. All these findings are a reflex of a more difficult diffusion of the anions in the microporosity and to form the EDL. The NaC_6:C_6(0.6) + 60% H_2O has the lowest resistance associated to the ion's diffusion in the microporosity.

4. Conclusions

Mixing water with eutectic mixtures of sodium hexanoate with fatty acids (hexanoic, octanoic, nonanoic, decanoic) leads to a complex variety of physical states for different concentrations of each compound. Those physical states include clear homogeneous liquid phase, two phases, three phases and, even, turbid gel mixtures. These observations are clear evidence of the variety of interactions established between the different compounds in solution. On one hand, this limits the operational temperature range of this mixtures as electrolytes. On the other hand, it allows the preparation of stable gel media without the need to use an additional supporting matrix, making these mixtures potential candidates for quasi-solid electrolytes, which are advantageous to prevent the electrolyte leakage.

In the conductivity study, three parameters highly influence the results: the water content, the acid chain length, and the amount of salt in the mixture. Generally, it was observed that the conductivity increased with the water content and decreased with the acid chain length, reflecting the higher mobility of the species triggered by the presence of water and the

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intrinsic higher capability of diffusion of smaller species. Moreover, it was observed that for mixtures with the same acid chain length and containing similar molar water composition, the conductivity was higher for those with higher amount of salt. Overall, $NaC_6:C_6(0.6) + 60\%H_2O$ presented the highest conductivity, 22.3 mS/cm at 20 °C. The viscosity results showed that the water addiction decreases the viscosity of the mixtures resulting in higher mobility of the species, in accordance with the conductivity observations.

In Cyclic Voltammetry tests, the water content influence was clearly seen, as the higher the water content the more pronounced is the quasi-rectangular shape, indicating that the presence of water lowers the electrolyte resistance allowing the ions to have a faster response to the applied voltage, and therefore establish in the electrode pores and surface faster. Comparing voltammograms of mixtures with same water content but different acid chain lengths, it was observed a more rectangular shape voltammogram for lower acid chain, which is associated with their higher mobility and ability to form the Electrical Double Layer (EDL) and absorb in the electrode microporosity.

Galvanostatic Charge-Discharge tests, allowed to test the life cycle of the cells using the studied mixtures has electrolytes, as well as the electrode specific capacitance. About half of the tested mixtures presented a capacitance retention higher than 80% after 5000 charge-discharge cycle, although a clear evolution of the life-cycling with the water content or the acid chain was not found. The specific capacitance obtained showed a clear decrease with the increase of the acid chain, which was in accordance with the CV results, proving that larger anions have more difficulty in forming the EDL and adsorbing at the electrode microporosity. The highest specific capacitance was obtained for the $NaC_6:C_6(0.6) + 60\%H_2O$ mixture, 71.6 F/g at 0.2 A/g.

In Potentiostatic Electrochemical Impedance Spectroscopy experiments, a spectrum shape characteristic of EDLC was observed for all mixtures: a semi-circle at high frequencies, a 45° line at middle frequencies and a straighter line at lower frequencies. The equivalent series resistance (ESR) presented higher values for a smaller water content, which reflects the higher resistance of the electrolytes with lower water content, which are associated with higher viscosity and lower conductivity. The $NaC_6:C_6(0.6) + 60\%H_2O$ electrolyte presented the lowest resistance, 1.83 Ω. The resistance related to the ion's diffusion in the microporosity, generally showed to decrease with the water content and with acid chain length. Such behaviour is in accordance with the CV and GCD results. Once more, the $NaC_6:C_6(0.6) + 60\% H_2O$ presented the best result, having the lowest resistance associated to the ions diffusion in the microporosity.

To conclude, this study showed that mixtures of water with eutectic mixtures of sodium hexanoate and long alkyl chain fatty acids have a promising role has electrolytes, being the $NaC_6:C_6(0.6) + 60\% H_2O$ the electrolyte with more promising results. However, further optimization of the performance of these mixtures can still be done, namely studying these mixtures in different electrode materials, for example mesoporous carbon.

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