S5 Thermodynamics and Thermal Analysis
Termodinámica y Análisis Térmico (GECAT-GET)

11/07 Monday afternoon, Aula 1.2

15:30-15:45   Josefa Salgado Carballo
Thermophysical characterization of a Firefighting Foam based on eco-friendly soap compounds and bentonite clay. Effectiveness laboratory testing

15:45-16:00   Pablo Vallet Moreno
Doped Lithium Ionic Liquids as potential electrolites

16:00-16:15   Angel Manuel Fernandez Fernandez
Análisis de cristalización de hidrato de metano en un poro de sílice empleando Dinámica Molecular

16:15-16:30   J.J. Suñol Martínez
Thermal analysis of magnetic materials

16:30-16:45   Juan José Parajó Vieito
Calorimetric and electrochemical studies of lithium salt dissolved in pure ethylammonium nitrate ionic liquid

16:45-17:00   José Francisco Martinez López
Calorimetría de mezclas binarias de L-carvona con alcoholes de cadena corta C2-C3

17:00-17:15   Consolación Sánchez Sánchez
Development of real-time polymerase chain reaction methods for the quantification of Methanoculleus, Methanosarcina and Methanobacterium in anaerobic digestion

17:00-18:00   **Posters and Coffee**

Posters: **15** José Ramón Solana Quirós
Effective two-body potentials for fluid argon including three-body interactions

16 José Luis Legido Soto
Thermophysical characterization of peloids enriched with microalgae

17 José Luis Legido Soto
Study of the thermal properties of mixtures of clays and thermal waters of Latin America

18 Ângela Queirós
Density of alumina nanofluids (15 nm) in water at different temperatures

19 Fátima Muiño Blanco
Thermal analysis of Eco-Friendly Soap-Based Firefighting Foam. Effect of the bentonite addition

20 Pablo Vallet Moreno
Broad Band Dielectric Spectroscopy of nanofluids

21 Antía Santiago Alonso
Experimental characterisation of ionic gels for energy storage applications

Thermophysical characterization of a Firefighting Foam based on eco-friendly soap compounds and bentonite clay. Effectiveness laboratory testing

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The use of firefighting foams and of other natural or synthetic additives for improving the extinguishing effect of water in forest fires has been increasing in the last decades and is nowadays a widespread practice. However, due to the negative and sometimes long lasting environmental impact of several of the most used firefighting agents there is growing interest on the development of alternative "eco-friendly" formulations [1,2].

Kawahara *et al*. [2] developed a novel firefighting foam, with significantly lower environmental risk and suitable for its application in forest fires, consisting of natural soaps, methylglycinediacetic acid (MGDA) as chelating agent, propylene glycol; hexylene glycol and water.

The present work proposes an improvement of the flame retardant formulated by these researchers, based on the addition of bentonite clay. To determine the most efficient concentration of bentonite, thermophysical properties of the retardant precursors as well as of mixtures containing different clay amounts (1%, 2%, 3%, 4% and 8%) were determined. The stability of the clay into the liquid mixtures was analysed from the behaviour of the refraction index against time, while differential scanning calorimetry and thermogravimetry were used to study the thermal behaviour of these samples. Additionally, transport properties as density and viscosity against clay concentration and temperature were also determined.

Finally, the effect of the modified formulations of the retardant were tested in a soil with high organic matter content applying thermal shocks at different temperatures and exposure times and carrying out the thermal analysis of heated and unheated soils.

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Doped Lithium Ionic Liquids as potential electrolites

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Current electrolytes in Li-ion batteries are composed, mainly, by a mixture of carbonates and lithium salt, and, as it was widely reported, they have significant security and efficiency issues such as high flammability and high vapour pressure [1]. Additionally, and from an industrially point of view, liquid electrolytes present implementation problems in mass production on the assembly line due to the possibility of spillage.

To solve these industrial questions, the implementation of solid (or semi-solid) electrolytes with similar, or, if possible, better electrochemical properties than currently used is one of the objectives of 4th generation of Li-ion batteries.

As it is well known, Ionic liquids (ILs) are characterized by amazing features like high thermal stability, negligible vapor pressure, high ionic conductivity, non-flammability, low toxicity and high electrochemical window among others [2-5] and then, they have been studied as smart electrolytes during the last decade. Furthermore, ILs and its mixtures with inorganic salts of electrochemistry interest, as lithium salts, can be encapsulated in rigid scaffolds (silica scaffolds, for example) without important changes on the main properties of the electrolytic mixture to conform a semisolid electrolyte, although before the industrial implementation further and deeper studies must be performed.

Figure 1.- Semisolid nano-encapsulated IL electrolyte in a silica scaffold.

In this work, the effect of the addition of Lithium nitrate salt to ammonium and imidazolium nitrate based ILs is studied by means of different experimental techniques such as broad band dielectric spectroscopy (BBDS), ionic conductivity, cyclic voltammetry (CV), nuclear magnetic resonance (NMR), Fourier Transform Infrared (FT-IR), density and viscosity, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Additionally, the nanoencapsulation of these mixtures in silica scaffolds was preformed and samples were analysed with the same experimental techniques and procedures and results were compared with the obtained for the bulk liquid samples.

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[4]   J.J. Parajó, P. Vallet, L.M. Varela, M. Villanueva, J. Salgado, *Environ. Sci. Pollut. Res.* **29**, 24983 (2022).
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Análisis de cristalización de hidrato de metano en un poro de sílice empleando Dinámica Molecular

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Los hidratos de gas son compuestos cristalinos de inclusión no estequiométricos formados por moléculas de agua y pequeños gases como CO_2, H_2S, N_2, gases nobles o pequeños hidrocarburos, como el CH_4, C_2H_6 o C_3H_8. Los hidratos de gas se obtienen a presiones moderadas y temperaturas en torno a 0ºC siendo el hidrato de metano el más abundante en la naturaleza y del que se estima que hay enormes cantidades en fondos marinos y bajo el permafrost continental. Estos depósitos podrían suponer una estratégica fuente de energía [1]. El metano se obtiene por descomposición de la materia orgánica que fluye verticalmente hasta encontrarse con el permafrost o el fondo oceánico, saturando el agua que se encuentra empapando los espacios intergranulares de las rocas sedimentarias. En este ambiente confinado de alta presión y baja temperatura, el gas queda atrapado en forma de hidrato.

En este trabajo se estudia el crecimiento del hidrato de metano confinado en un poro de silice empleando Dinámica Molecular (DM). Se emplean campos de fuerzas atomísticos OPLS-AA para la sílice (α-cuarzo) y el metano y el rígido no polarizable TIP4P/Ice [2] para el agua. Se diseñó un poro plano α-cuarzo de $4.022 \times 4.022 \times 9.26$ nm dejando un espacio hueco de 7nm. Se eliminaron los silicios terminales y los oxígenos se saturan con hidrógeno para obtener la neutralidad del sistema. El poro quedó formado por 1536 átomos de oxígeno, 704 de silicio y 256 de hidrógeno. En el centro del poro se situó una semilla de hidrato formada por 8 celdas unidad de la esturtura sI, que hacen un total de 368 moléculas de agua y 64 de metano. Ésta se rodeó por 2272 moléculas de agua, dejando un pequeño espacio a ambos lados del poro que se llenó con 256 moléculas de metano.

Se aplicaron condiciones periódicas de contorno, radio de corte 1.5nm y se el método de las sumas de Ewald para las correcciones electrostáticas de largo alcance. Se realizaron simulaciones NVT a 260 y 270K y en el colectivo NpT a 260K y 100bar, para lo cual se empleó el termostato de Nosé-Hoover y el barostato de Parrinello-Raman. Todas las simulaciones se llevaron a cabo con el software GROMACS/2021.1.

Las simulaciones fueron del orden de 500ns, hasta que se alcanzó el equilibrio y después se estableció un periodo de producción de 200ns más. Al final de la simulación, las celdas del hidrato se observan desplazadas y ligeramente deformadas con respecto a la posición inicial de la semilla, por lo que para caracterizar la estructura obtenida se obtuvieron los perfiles de densidad y se calcularon los parámetros de orden F_3 [3] y F_4 [4] así como el ángulo del enlace de hidrógeno promediados durante el periodo de producción y a lo largo del eje Z. Todos ellos muestran como el metano, inicialmente situado junto a las paredes de sílice, es sustituido por moléculas de agua que quedan fuertemente adsorbidas por puentes de hidrógeno. Los parámetros de orden muestran que esta capa adsorbida se trata de un fluido y que el metano queda atrapado como hidrato en el interior del poro. Las deformaciones que se observan en el cristal se deben posiblemente a la imposición del confinamiento al que se ve sometido el cristal que no puede crecer con total libertad en las tres direcciones.

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Thermal analysis of magnetic materials

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Microstructural changes in soft and hard magnetic materials can provoke the loss or the improvement of the desired magnetic behaviour. Thermal analysis techniques are useful to provide information about the characteristic temperatures at which these structural transformations (as well as the magnetic transformations: Curie or Néel) occurs. Likewise, thermodynamic parameters as the enthalpy and entropy changes and, the specific heat can also be obtained from calorimetry.

In this work, we analyse some soft magnetic Fe, Ni, Fe-Co and Fe-Mn rich alloys produced by mechanical alloying (powdered particles). At low temperatures, differential scanning calorimetry (DSC) scans show broad exothermic processes linked to the release of the mechanically induced microstrain. At higher temperatures (> 600 K), exothermic peaks linked to the grain growth of the nanocrystalline alloys are found. The activation energy of the crystallization process can be determined by analysing (Kissinger linear method) the DSC scans at different heating rates. Fig. 1. Show the linear fitting of the main crystallization process of some Fe-rich alloys. Higher transition temperature and activation energy indicate higher thermal stability.

The optimized design of annealing temperature-time conditions favour the development of alloys with improved soft magnetic behaviour: high magnetization of saturation, high remanence and low coercivity [1]. Furthermore, the controlled addition of magnetic and non-magnetic elements shifts the functional magnetic response and the working temperature interval. The production of these magnetic materials with the desired nanocrystalline microstructure is a field of continuous research [2]. Temperature diagrams can be obtained. Fig. 2. shows the transformation temperatures of Ni rich (Heusler) alloys with a martensitic transformation.

The enthalpy and entropy changes are determined by the integration of the DSC signal. Furthermore, in multi-component alloys the mixing enthalpy is a key parameter. Mechanical alloying favour the extension of the solubility limits and a minor effect of the mixing enthalpy constraints.
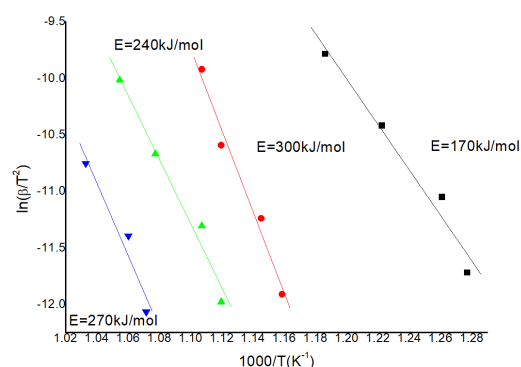

Figure 1. Activation energy of the main crystallization processes of some Fe rich alloys (Kissinger linear fitting method).
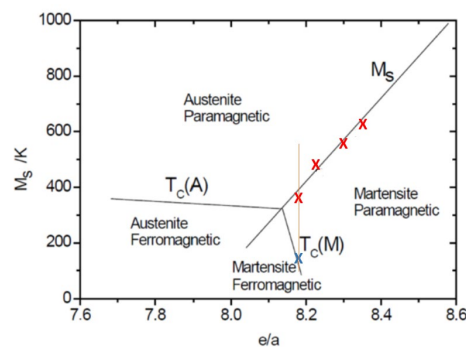

Figure 2. Transformation temperatures diagram: some Heusler alloys with martensitic transformation.

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Calorimetric and electrochemical studies of lithium salt dissolved in pure ethylammonium nitrate ionic liquid

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The most relevant properties of Ionic Liquids (ILs) are their wide electrochemical windows, high thermal stabilities, non-flammability, and the possibility of tuning their conductivities by adding stable inorganic salts. The interfacial phenomena associated to electrochemical processes will depend not only on the properties of the two phases involved as well as the interfacial properties, which are distinct from the bulk adjacent phase.

The importance of calorimetric studies and the inexistence of a model that allows the systematic prediction of the effect of adding salts on the electric double layer (EDL) structure, imposes complex challenges for the formulation of the IL + inorganic salt electrolyte mixtures. The addition of lithium salts is highly reported due to their importance for energy storage applications and the need to work at high concentration levels (0.5 or 1 M lithium salts concentrations are commonly used) [1].

Differential scanning calorimetry (DSC) and termogravimetry (TGA) were used in this work to determine the liquid window, which is essential to get a useful operation temperature range for a selected electrolyte. The lowest limit of liquid range of the fluids, associated to melting or glass transition temperatures, was determined using differential scanning calorimetry (DSC), whereas the upper limit, which is given by degradation or boiling temperatures, was stablished by means of thermogravimetric analysis (TGA). The main conclusion of this study was that salt addition induces melting-point depressions, but no boiling point elevations were detected. [2]

The electrochemical properties of the Hg/ethylammonium nitrate interface were followed through the interpretation of differential capacity curves and potential of zero charge values based on an acceptable model that accurately describes the effect of chemical nature of ions in the EDL thickness [3]. The selection of non-structured mercury electrode allowed to decouple the template effect of the surface in defining the anatomy of the double layer structure. The model followed to estimate the thickness of the charge plane of the adjacent layer to the electrode by the EAN was based on a simple Helmholtz model and its applicability was validated with the ions size obtained independently using informatic tools. After the method validation, the EAN was mixed with different molalities of $LiNO_3$, focussing on concentrations below 0.1 m and extending the study to the saturation range (2 m).

The correlation between differential capacitance, pzc and charge density curves vs. the mixture composition was obtained. The asymmetric U-shaped of the C(E) curves measured at the Hg/pure EAN are not affected by the presence of the inorganic ions from the salt, however, the values of thickness of the double layer estimated from the integral capacities' present non-monotonic behaviour (e.g., the thickness of the charge plane at rational negative potentials increase for a specific range of lithium molalities).

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Calorimetría de mezclas binarias de L-carvona con alcoholes de cadena corta C₂-C₃.

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La determinación experimental de propiedades termofísicas de mezclas de compuestos presentes en aceites esenciales de plantas con alcoholes es importante de cara al diseño de instalaciones y procesos de extracción. El compuesto R-carvona o L-carvona, designado según IUPAQ) como (5R)-5-Isopropenil-2-metil-2-ciclohexen-1-ona, (Figura1), es una cetona quiral, terpenoide monocíclico, que está presente en los aceites volátiles de la hierbabuena (*Mentha spicata*). Usado en la industria alimentaria y en productos ambientadores y aromaterapia, su importante bioactividad y propiedades ha sido recientemente revisada [1].
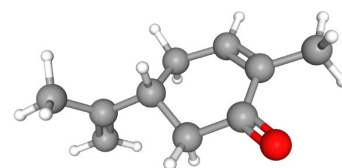
Figura 1. L-carvona

En este trabajo se presenta un estudio de las capacidades caloríficas molares a presión atmosférica ($C_{P,m}$) para mezclas binarias formadas por L-carvona con etanol y con propanol. Las capacidades caloríficas de estas mezclas se han medido entre 298.15 y 328.15 K, cada 10 grados, en todo el rango de composición. Las medidas se han realizado mediante un calorímetro de tipo Calvet de la firma Setaram, modelo C80. El procedimiento experimental y los cálculos implicados han sido descritos en un trabajo previo [2].

Las capacidades caloríficas molares de exceso, $C^E_{P,m}$ obtenidas de los datos experimentales se han comparado con las calculadas mediante el método *COSMO-RS* y mediante *UNIFAQ*. En todas las mezclas los resultados obtenidos mediante *COSMO-RS* presentan mejores resultados que los obtenidos mediante *UNIFAQ*.

En la figura 2, se muestran los resultados obtenidos para las mezclas de L-carvona (1) + etanol (2).
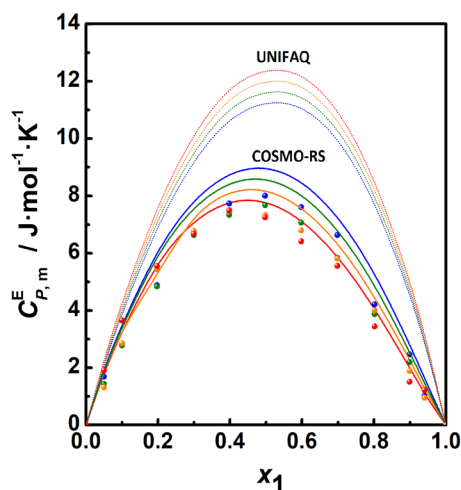

Figura 2. Capacidades caloríficas molares de exceso para las mezclas: L-carvona(1) + etanol(2) a las temperaturas de 298,15 K (●); 308,15 K (■); 318,15 K (■) y 328,15 (●)

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Development of real-time polymerase chain reaction methods for the quantification of Methanoculleus, Methanosarcina and Methanobacterium in anaerobic digestion

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Due to the great environmental impacts generated by the processes of obtaining conventional energy, in recent years, more and more companies are betting on other sources of renewable energy such as Anaerobic Digestion (AD) technology. To promote this technology, it is essential to know at the molecular level the dynamics of microbial communities, the correlations between environmental variables and methanogenic community structure.

In the present study, three primer pairs were selected from seven primer pairs which were designed and tested with different concentrations and conditions to detect Methanosarcina, Methanoculleus and Methanobacterium by real-time polymerase chain reaction (PCR) based on the SYBR Green System.

The functionality of the developed methods was demonstrated by the high linear relationship of the standard curves, and the specificity of each primer was empirically verified by testing DNA isolated from methane-producing and non-producing strains. These assays also exhibited good repeatability and reproducibility, which indicates the robustness of the methods.

The described primers were successfully used to investigate the methanogenic communities of 10 samples from an anaerobic co-digestion of tomato industry. Ct values below 28 were obtained for each of the primer pairs designed. The genus Methanosarcina was the dominant methanogenic group.

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Effective two-body potentials for fluid argon including three-body interactions

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Sadus et al. [1,2] proposed the following simple relationship between the three-body E_3 and two-body E_2 contributions to the configurational energy of Ar, Kr and Xe

$$\frac{E_3}{E_2} = \lambda \frac{\nu\rho}{\varepsilon\sigma^6},$$

where $\rho = N/V$ is the number density, ν is the nonadditive parameter, ε is the potential depth and σ the distance at which the pair potential $u(r) = 0$. This relationship, which was derived on the basis of computer simulations in the liquid phase at subcritical temperatures considering the Barker-Fisher-Watts (BFW) potential for the two-body (2B) interactions and the Axilrod-Teller (AT) approximation for thre three-body (3B) interactions, allows to incorporate the 3B interactions into an effective 2B potential, which simplifies the calculations either from theory or from computer simulations. A value $\lambda = -2/3$ was reported in [1], but from further simulations a value $\lambda = -0.85$ was recommended [2].

The aim of this work is twofold. On the one hand, to analyze whether a similar relationship holds for the Lennard-Jones potential. On the other hand, to see whether the relationship still holds for spercritical temperatures and wider density ranges.

Figure 1: Ratio of the three-body to two-body energies for argon at $T = 140\,\mathrm{K}$ with the LJ (circles) and BFW (squares) potentials as a function of the reduced density ρ^*. The solid lines are linear fittings.

To this end, first we have carried out Monte Carlo NVT computer simulations to obtain the 2B and 3B contributions to the configurational energy for Ar with the LJ and BFW potentials at tempertature $T = 140\,\mathrm{K}$, that corresponds to reduced temperatures $T^* = kT/\varepsilon = 0.9853$ and $T^* = 1.1686$ for BFW and LJ potentials, respectively, and reduced densities in the liquid range $0.5 \leq \rho^* \leq 0.7$, with $\rho^* = \rho\sigma^3$. The results, shown in Fig. 1, are consitent with the roughly constant value of λ reported in [1,2]. Our results provide $\lambda = -0.77$ for LJ and $\lambda = -0.88$ for BFW.

Next, we have carried out simulations for wide ranges of temperatures and densities, including supercritical temperatures. The results are shown in Fig. 2, from which it is clear that the parameter λ must have a more complex dependence on temperature and density than reported in refs. [1,2].
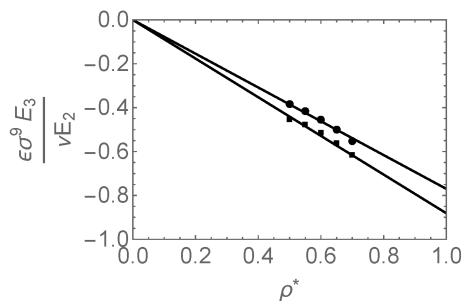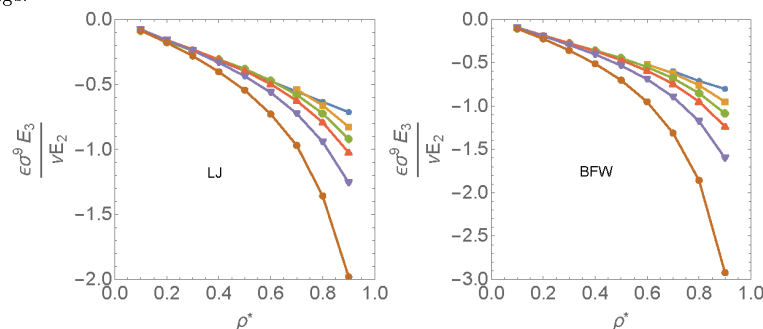

Figure 2: Ratio of the 3B to 2B energies for argon with the LJ (left) and BFW (right) potentials as a function of the reduced density ρ^* for reduced temperatures $T^* = 0.7, 1.0, 1.5, 2.0, 3.0$, and 5.0, respectively, from top down. (Note that the reduced temperatures are not equivalent for both potentials because the values of ε are different). The curves are guides for the eye.

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Thermophysical characterization of peloids enriched with microalgae

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In this work, the thermophysical properties of mixtures of a clay, mineral water and the microalgae are presented. These types of mixtures are called peloids [1]. Peloids are thermotherapeutic agents that are used in numerous spas and thermal centres, their behaviour depends on their physical properties and these properties will determine its form of application.

The properties studied are density, specific heat, thermal conductivity, and thermal diffusivity as a function of the concentration of the water, at atmospheric pressure and a temperature of 308.15 K.

The specific heat has been determined using a CALVET microcalorimeter [2]. The density of the mixtures was carried out by a pycnometric method [3]. A Decagon KD2 Pro conductivity meter was used to measure thermal conductivity [4]. Thermal diffusivity was calculated from the data obtained on thermal conductivity, density and specific heat [5].

The properties studied will help in choosing the most suitable type of application for each mixture for the different applications in the field of cosmetics, thermalism and wellness [6,7].

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Study of the thermal properties of mixtures of clays and thermal waters of Latin America

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In most Latin American countries there are places where mixtures of clay and thermal water are used for therapeutic and cosmetic purposes. In Argentina, in the Copahue thermal complex in the state of Neuquén, a peloid is used therapeutically [1]. In Brazil, the so-called Peruíbe Black Mud is well known [2]. Other mixtures are the Chilca salt mines in Peru [3], the San Vicente Hot Springs in Ecuador [4], Cubagua in the Margarita Islands in Venezuela [5], and in Colombia in the Totumo volcano in Cartagena [6].

In Central America we can also find different types of peloids, such as in the Arenal volcano in the area of Fortuna in Costa Rica [7], and in the Caribbean islands, the mixtures of Cuba stand out in the Baños de San Diego and Pinar del Rio [8].

In this work, the thermal properties (specific heat, thermal conductivity, density and thermal diffusivity) of mixtures of clays with thermal waters from Latin America are studied.

The thermal conductivity has been measured with the Decagon KD2 Pro probe [9], the specific heat has been determined using a CALVET microcalorimeter [10], the density of the mixtures was determined by a pycnometric method [11]. Thermal diffusivity was calculated from the data obtained on thermal conductivity, specific heat and density [12].

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Density of alumina nanofluids (15 nm) in water at different temperatures

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Following our study about thermophysical properties of nanofluid [1-5] in this work the density of alumina (15 nm) nanoparticles in water is presented. The density of the mixtures was carried out by a pycnometric method. The measurements were carried out at various concentrations (up to 2% in volume) at atmospheric pressure and at twelve temperatures (from 288.15 K to 343.15 K).

The study shows the influence of the volume fraction and temperature on this quantity showing a linear increment as the volume fraction increases. This linear behaviour is described empirically by Pak and Cho [6] equation.

The enhancement of density, defined as the ratio of the nanofluid density and that of the base fluid, was calculated and its behaviour was analysed. It is discussed whether their positive values can be considered greater than what would be expected. The contributions to density of these nanofluids from water and nanoparticles are separated.

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codes of the symposium and of this communication

Thermal analysis of Eco-Friendly Soap-Based Firefighting Foam. Effect of the bentonite addition

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Flame retardant agents are natural or synthetics additives used for improving the effectiveness of water in extinction fire. Their effectiveness mainly depends on its ability to increase water retention and prolong the isolation time of the fuel from the source of ignition and/or oxygen by including foaming agents, moisturizers and/or superabsorbents in its composition. However, currently the most used fire extinguishing agent is still water, essentially because of the side-effects of phosphorous, nitrogen, sulphur, fluorine and aluminium contents of extinguishing agents that can cause the pollution into rivers and forest surroundings after their application.

The concern about the environmental effects of these flame retardant agents has led to the search for alternative formulations with less impact or "eco-friendly" increased during the last years [1]. Thus, firefighting foams involving naturally derived fatty acid salts (soap) as the main component have recently been developed. In particular, Kawahara and collaborators [2] proposed a mixture of potassium laurate, potassium oleate and sodium oleate, as the soap components, with methylglycinediacetic acid (MGDA), propylene glycol, hexylene glycol and water. So far, these efforts on searching short-term firefighting foams have been focussed on their toxicity towards aquatic and/or semiaquatic environments, although their effect on terrestrial ecosystems is still unknown [3].

In the present work, an optimization of the flame retardant of Kawahara *et al*. [2] is proposed by the addition of bentonite clay (with weight concentrations of 1%, 2%, 3%, 4% and 8%), which can retain water longer during exposure to the heat source. Thermal behaviour of these samples by means of differential scanning calorimetry and thermogravimetry was studied obtaining that the evaporation peak of water showed a shift towards higher temperatures with the intermediate concentrations (2% and 3%) of bentonite.

Finally, the effect of the retardant was checked, in laboratory, in a soil exposed to thermal shocks at different temperatures in terms of carbon content reduction.

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Broad Band Dielectric Spectroscopy of nanofluids

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Nanofluids are composed by a mixture of, at least, a base lubricant and dispersed nano additives particles, as Choi defined in 1995 [1]. Usually, nanofluids are studied with the aim to obtain the best equilibrium between increase in thermal conductivity (positive effect) and viscosity (negative effect) and many bibliographic studies can be found in this field.

Since the global economy is moving to a decarbonized system of production to reduce the CO_2 emissions, electric vehicles (EVs) are increasing rapidly in manufacturing and attention [2]. Hence, the lubricants need to comply new safety requirements, since many EVs are built alternating permanent magnet synchronous motor and current induction motors [3]. Here, the dielectric constant and the electrical conductivity, obtained by electrochemical impedance spectroscopy (EIS), are critical parameters to ensure the proper operation inside the electrical motor (EM). As the last authors pointed out [3], the electrical conductivity should be in the specific range between 10^{-6} and 10^{-12} $S \cdot cm^{-1}$. An electrical shock, compromising user safety, due to current leaks can appears if the conductivity is higher than 10^{-6} $S \cdot cm^{-1}$. On the other hand, if the lubricant is a complete insulator (conductivity below 10^{-12} $S \cdot m^{-1}$), a static current may appear and may lead to a damage to the EV. Furthermore, and obviously, electronic conductivity and short circuit should be completely avoided.

In this work, nanolubricants based on Matic VI transmission fluid (supplied by Repsol), dopped with different nano additive particles (graphene nanoplaquets, graphene oxide and titanate oxide) at different concentrations (0.5% and 1% in weight proportions) are analysed to obtain the electrical conductivity. To ensure that this property is correctly determined, dielectric spectroscopy is measured. To ensure that the Ohmic regime is achieved, he electrical conductivity is evaluated analysing the imaginary part of the electrical permittivity following the well-known criterion that the slope in a logarithm base of $log\varepsilon''$ vs $\log\omega$ should be -1.00 ± 0.02 [4].

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Experimental characterisation of ionic gels for energy storage applications.

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In recent years, the fast growth of the technology market created the need to develop better energy storage systems. Current batteries still have shortcomings in terms of efficiency and safety, especially at high temperatures. In addition, electrolytes that make up the batteries are based on flammable and volatile mixtures that can put the safety of the operator at risk [1]. Ionic liquids (ILs) appear as an alternative to conventional electrolytes in the development of new batteries trying to solve these disadvantages.

ILs are organic salts consisting of a cation and an anion whose melting point is below than 100 ºC [2]. Among their main characteristics, it is important to highlight the (practically) unlimited combinations that can be formed; the large number of cations and anions with different properties (i.e., alkyl chain length, functional group present in the alkyl chain length, functional group present in the compound) make it possible to obtain the most suitable compound for each application [3].

For the optimisation of ILs as electrolytes, mixtures of these fluids are made with inorganic salts of a common cation, lithium in the most cases [4,5] (but also multivalent salts) [6]. However, these ILs and mixtures with inorganic salts must be immobilised in a matrix for use in electrochemical devices such as batteries (superconductors or fuel cells) [7,8]. The resulting material from this confinement of IL (or mixtures with inorganic salts) in a matrix

Figure 1. Ionogel formed by [Chol][TFSI] in PVDF matrix.

(silica, polymeric, etc.) are known as ionogels or ionic gels (Fig- 1), that have electrical conductivities similar (or even higher) to those at the liquid state and are mechanically stable, so they are very easily manipulated.

In this work we study the physicochemical and electric properties of ionogels formed by dissolutions of ILs and [Li][TFSI] in silica and polymeric matrix (PVDF) by experimental characterisation techniques such as differential scanning calorimetry (DSC), thermogravimetry (TGA), nuclear magnetic resonance (NMR) and dielectric relaxation spectroscopy (BBDS). The selected ILs are [Chol][TFSI] and [BMPyrr][TFSI].

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