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Molten salts as engineering fluids – A review
Part I. Molten alkali nitrates

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HIGHLIGHTS

- Thermophysical property data for molten alkali nitrates were reviewed.
- Influence of accurate data for these properties are discussed.
- Its use as heat transfer/storage fluids in CSP technologies is analyzed.
- The review includes pure nitrates and relevant mixtures.

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ABSTRACT

Molten salts constitute an important class of fluids for high temperature applications, like catalytic medium for coal gasification, molten salt oxidation of wastes or for latent or sensible heat storage. In particular, molten alkali nitrates are being used as heat transfer/storage fluids in concentrated solar power (CSP) technologies. These kind of technologies operate in ranges of temperature for which molten salts are particularly adequate, due to its main characteristics: stability at high temperatures, low vapor pressure, liquid state in a large range of temperatures, ability to dissolve many inorganic and organic compounds, viscosity generally low (as ions are mutually independent) and high heat capacity per unit volume. For the proper design and dimensioning of heat exchangers and other ancillary equipment's it is decisive to have accurate data for the thermophysical properties of the employed fluids. This paper reviews the available data for the relevant properties that are important to a salt system for storage and heat transfer applications. Those are the melting point, density, viscosity, heat capacity and thermal conductivity. The chosen fluids were the pure molten lithium, sodium and potassium nitrates and relevant mixtures, like the solar salt ($NaNO_3/KNO_3$: 60/40), HITEC® (a ternary mixture of $NaNO_3$, KNO_3 and $NaNO_2$) and some new quaternary mixtures. Review reveals that there are still large discrepancies between different sets of data for the same salt systems and that it is impossible currently to recommend reference data/measuring methods that can guide the reader for a selection of the best systems. The impact of that and the potential applications are briefly discussed. The reviewed fluids have great potential for actual and future applications in renewable processes for energy storage and transformation.

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Nomenclature

E_η	activation energy for fluid flow	A	pre-exponential factor
a, b	constants in Eq. (2)	T	temperature
ρ	density	λ	thermal conductivity
C_P	heat capacity at constant pressure	E	thermal energy storage capacity
x_i	molar fraction of substance i in a mixture	η	viscosity
M	molar mass of mixture	R	universal gas constant
M_i	molar mass of substance i in a mixture		

1. Introduction

Molten salts are engineering fluids with a large range of applications (Fig. 1). The term "molten salt" is commonly used to designate a liquid obtained from the fusion of an inorganic salt. Some examples include sodium chloride ("table salt") or salts containing oxoanions like potassium nitrate. The main characteristics of this kind of fluids are: stability at high temperatures; low vapor pressure; liquid state in a large range of temperatures; ability to dissolve many inorganic and organic compounds; viscosity is generally low (as ions are mutually independent); high heat capacity per unit volume [1,2]. The concept of high temperatures is assumed to be greater than 200 °C, and therefore molten salts containing organic cations or anions, like the ionic liquids are excluded from the current review.

In this paper, and in a companion one, we will review some of the recent progresses in molten salts formulations and characterization, with special emphasis on the utilization of molten salts as heat storage/heat transfer fluids or molten baths. Energy and environment are key issues in every modern society and the search for renewable sources of energy and environmental protection have direct impact on economy.

Among other technologies, using molten salts, concentrated solar power plants (CSP) or molten salt oxidation (MSO) received special attention in recent years [3–6]. This kind of technologies uses molten salts as heat transfer or heat storage fluids. An important aspect is the selection of the working fluids. Available data on the thermophysical and thermal properties of some selected molten salts will be reported and critically evaluated, since accuracy of data can have a severe impact in the dimensioning of equipment's [7].

2. A glimpse into the history of molten salt technologies

Molten salt based technologies can be traced back to Humphrey Davy who, in the dawn of the nineteen century, isolated alkali metals from the corresponding fused salts [8–10]. Growing needs of metals and alloys pushed to the establishment of large scale plants, notably for the production of aluminum based on the Hall-Héroult process. In the 50s of the last century emerges the utilization of molten salts in nuclear reactors [11]. The first molten salt reactor (MSR) was built at Oak Ridge National Laboratory (ONRL). During the next decades ORNL successfully operated the MSR, designing a new Molten Salt Breeder Reactor (MSBR) which used thorium as the fertile component of the liquid fuel, containing as carrier salts mixtures of lithium fluoride and beryllium fluoride called "FLiBe". At the same time, molten salts were envisaged in the chemical industry as synthetic or catalytic medium for processes like coal gasification (Kellogg-Pullman molten salt process and Rockwell molten salt gasification) dehydration and others [12,13]. More recently and facing the nowadays urgent problems (renewable energy and environmental protection) molten salts have been used as heat transfer fluids (HTF) or molten bath for new and sustainable technologies like CSP and MSO. MSO was first utilized on a pilot scale at ORNL and Rockwell to effectively destroy hazardous organic compounds [14,15]. CSP plants produce electricity utilizing conventional technologies, but using solar radiation as energy input and molten salts, such as mixtures of nitrates/nitrites, as energy storage and energy transfer fluids. Although the CSP technologies date back to 1970s, most of the commercial plants have been developed in the last decade [16,17]. This brief overview on the molten salts technologies history can be complemented with the analysis of the evolution of the number of publications dedicated to molten salts. Fig. 2 shows the number of publications for each decade, since the 40s, as retrieved on the ISI web of science (www.isiknowledge.com). The

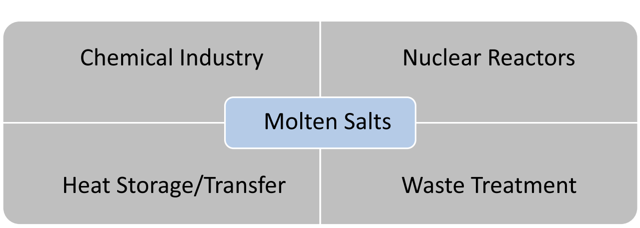

Fig. 1. Some applications of molten salts.

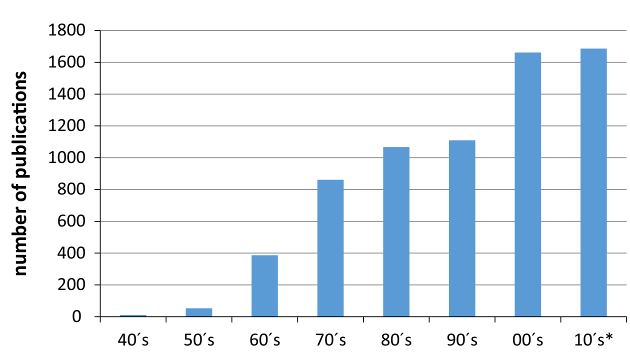

Fig. 2. Publications on "molten salts" or "molten salt" indexed in the Web of Science on December 2015 (*this data in a five years period only).