Importance of Accurate Data on Viscosity and Thermal Conductivity in Molten Salts Applications†

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The transport properties of molten salts at high temperatures are crucial for the efficient design of industrial equipment and chemical processes involving these materials. However, large discrepancies among the data published by different authors and different laboratories still exist, mostly caused by the difficulties in accurate measurements. This situation with regard to thermal conductivity and viscosity is especially serious for plant design. The aim of this paper is to demonstrate the implications of the uncertainty of molten salt thermophysical properties, such as thermal conductivity and viscosity, on the design of heat exchangers and other equipment. Some of the recent applications of ionic liquids at high temperatures, both as heat-transfer and chemical-reaction media, will be presented in order to illustrate how the knowledge of thermophysical properties is important for proper and optimal technological design, using two examples (thermal storage in solar plants and molten salt oxidation of wastes) among the many possible. The results obtained support that the implementation of those applications needs a careful selection of experimental data; otherwise, equipment will be either under- or overdimensioned, with the consequent poor operation or increased capital costs.

Introduction

The transport properties of molten materials such as thermal conductivity, electrical conductance, and viscosity at high temperatures are crucial for the efficient design of industrial equipment and chemical processes, like high-temperature batteries, thermal storage devices, waste treatment by molten salts, metals and alloys production in molten salt beds, and others. The accuracy of experimental data is then very important. However, the available literature on the subject shows that there are large discrepancies among different authors in different laboratories. In addition, the accuracy statements are nonexistent or ill defined. The aim of this paper is to evaluate the importance of the accuracy of data on viscosity and thermal conductivity in some of the molten salts applications at high temperature.

Molten Salts and Their Thermophysical Properties

Molten salts are ionic liquids obtained by the fusion of a salt. The number of these systems is incredible high, and they range from relatively low temperatures (room temperature ionic liquids) to very high temperatures. Sodium chloride (NaCl), for instance, melts at 1074 K and boils at 1686 K, at atmospheric pressure. The general characteristics of molten salts are as follows: (a) liquid state over a large range of temperature, (b) ability to dissolve a relatively large amount of many inorganic and organic compounds, (c) low vapor pressure and stability at normal pressures, (d) low viscosity, as the ions are mutually independent, for most of the cases, (e) chemical inertness (no reaction with air or water), (f) high heat capacity per unit volume. These and other characteristics allow their utilization in many processes not possible with normal solvents. The major applications can be classified as heat-transfer or chemical-reaction media, and we will deal with those applications.

The importance of the knowledge of accurate data for thermophysical properties is self-evident. However, the practical determination of these properties at high temperatures is difficult. Among others, we can refer to the following problems: (a) samples can react with cell walls or atmosphere, giving rise to secondary reactions; (b) the accurate measurement of temperature is difficult, as special thermocouples or calibrated pyrometers have to be used; (c) convection and radiation are very important and their contribution to heat transfer increases with temperature; (d) non-Newtonian flows can degrade experimental results.[1] On the other hand, when data are available, the differences among different laboratories are sometimes dramatic. As an example, Figure 1 shows the thermal conductivity of KNO_3 as a function of temperature.[3−11] The differences among different sets of data can be as high as 25%. Also $d\lambda/dT$ is either positive or negative. For KCl the deviation between different sets of data reaches 300% at 1000 K.[2]

For viscosity the situation is similar. Figure 2 shows the variation of the viscosity of molten Na_2CO_3 with temperature.[12−13] At some temperatures the differences can

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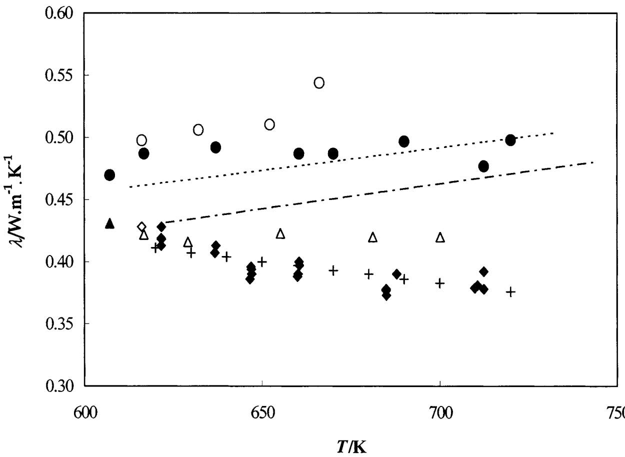

Figure 1. Thermal conductivity of molten potassium nitrate: ◆, Kitade et al.;[3] ○, Bloom et al.;[4] ▲, White and Davies;[5] △, Tufeu et al.;[6] +, Nagasaka et al.;[7] ●, Gustafsson et al.;[8] ◇, Turnbull;[9] · · ·, McDonald and Davies;[10] - - -, Santini et al.[11]

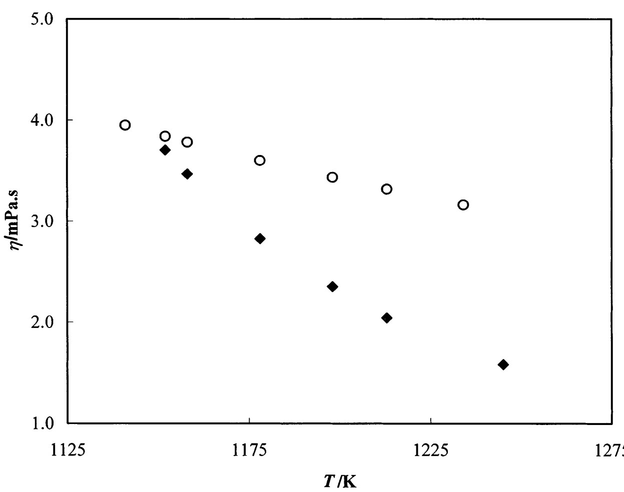

Figure 2. Viscosity of molten sodium carbonate: ◆, Janz;[12] ○, Sato et al.[13]

amount to 50%. Also the activation energy of viscous flow, E_η, is very different, a fact that is very significant in terms of the theoretical interpretation of the melt behavior.[14]

It is evident from the previous explanation that the accuracy of the data is still a subject of controversy, and this fact must have implications in the implementation of molten salts as heat-transfer or solvent media.

Thermal Storage and High Temperature Heating Medium

Molten salts are used as heating media, for example, the binary mixture of $NaNO_3$ and KNO_3 (60−40% w/w). To dimension relevant equipment, we need to calculate heat-transfer coefficients that depend on the thermal conductivity, viscosity, and heat capacity of the fluid.

Modern solar power equipment uses a molten salt receiver, as a thermal energy storage system that captures the sun's energy and stores it in hot molten sodium nitrate or molten nitrates mixtures, so that power can be generated when needed, not just when the sun is shining. One of these systems involves the heat transfer from a collector field from some kind of oil and a thermal storage medium such as a molten salt through an oil to salt heat exchanger,[15] of the shell and tube type; see Figure 3.

The aim of our calculations is to demonstrate the implications of the uncertainty of the molten salt thermal

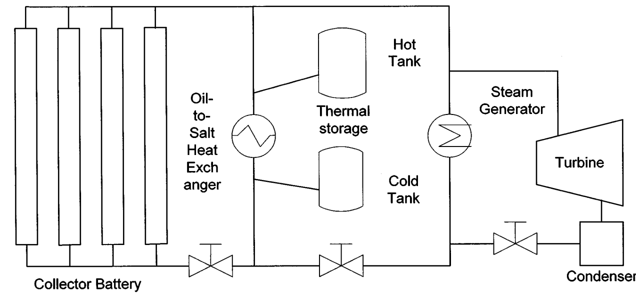

Figure 3. Schematic of a two-tank molten salt thermal storage system.

conductivity and viscosity on the design of the heat exchangers. To do that, we will consider that the properties of the oil are well-known in order to calculate changes in design due to alteration of molten salt transport coefficients.

For the heat balance, Newton's law of cooling reads[16]

$$Q = U_0 A_0 (\Delta T)_{\text{lm}} \tag{1}$$

where Q is the rate of heat transfer, U_0 is the overall heat transfer coefficient, A_0 is the area across which the heat is being transferred, and $(\Delta T)_{\text{lm}}$ is the logarithmic mean temperature difference between the inlet and outlet stream temperatures of the two fluids. For a particular duty, the only design parameter allowed to depend on transport properties is the area for heat transfer. For our purpose we will calculate the variation of the area of the exchanger.

The overall heat transfer coefficient measures the "barrier resistance" to the heat transfer and includes all the resistances to heat transfer, namely the contribution due to convection at the tubes inner and outer surfaces and across the tube walls. Convection transfer is determined by the boundary layers developed at the surfaces, thus depending on several properties, like thermal conductivity, viscosity, density, and heat capacity. For circular tubes the overall heat-transfer coefficient may be calculated by

$$\frac{1}{U_0} = \frac{1}{h_\text{o}} + \frac{1}{h_\text{i}}\frac{D_\text{o}}{D_\text{i}} + R \tag{2}$$

where D_o is the outside tube diameter, D_i is the inside tube diameter, and R represents the combined resistance of the tube wall and other factors considered constant (the resistance of the tube wall and the fouling resistances). The heat-transfer coefficients for the inside and outside film of fluids are represented by h_i and h_o.

To obtain optimal heat transfer, the flow must be turbulent. There are many equations relating heat-transfer coefficients to fluid properties, and the most utilized in practice was adopted, the Sieder and Tate correlation:[17]

$$\frac{h_\text{i} D_\text{i}}{\lambda} = 0.027 Re^{0.8} Pr^{1/3} \left(\frac{\eta}{\eta_\text{s}}\right)^{0.14} \tag{3}$$

where $Re = \rho u D/\eta$ is the Reynolds number, $Pr = C_\text{p}\eta/\lambda$ is the Prandtl number, λ is the thermal conductivity of the fluid, η is the viscosity, C_p is the heat capacity, ρ is the fluid density, and u is the mean fluid velocity over the tube cross section. All the properties are evaluated at the mean bulk temperature of the fluid, except for η_s, which is the fluid viscosity at the wall temperature. Since viscosity, thermal conductivity, heat capacity, and density are functions of the fluid, only the fluid velocity must be fixed,

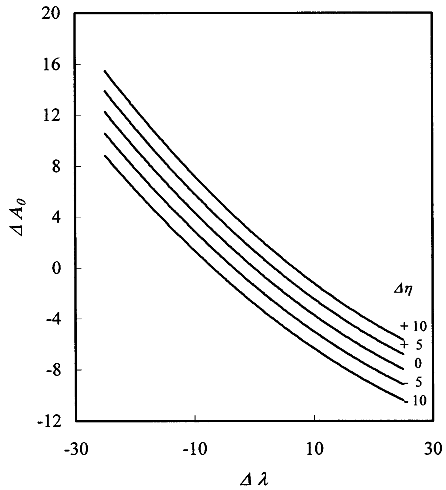

Figure 4. Effect of uncertainty of thermal conductivity (in %) and viscosity (in %) on the area of a shell and tubes heat exchanger.

which for the calculations of the total area of tubes will be considered constant.

For the calculation of a reference area, we use thermal conductivity data for a molten nitrate mixture (60/40% mol/mol) at 590 K from Omotani et al.,[18] that is, $\lambda \approx 0.46$ $W \cdot m^{-1} \cdot K^{-1}$. From Figure 1 it can be seen that for this property the difference between different author measurements deviates up to about 25%. For viscosity it was not possible to find data for the same mixture. For this exercise the data of Nissen et al. for an equimolar mixture of $NaNO_3$ and KNO_3 at the same temperature[19] were used, this value being $\eta = 2.360$ mPa·s. This choice has no significant effect on the results obtained in the present calculations, because it affects the reference area and the calculated area in the same way. If the available literature on viscosity of molten nitrates[20] is analyzed, it can be seen that the percent deviation between different authors can go up to ±5%. Not enough data are available for mixtures, and an uncertainty of ±10% will be assumed. Finally, a reference density for the mixture at 590 K was taken from Zhu et al.[21] to be $\rho = 1903$ $kg \cdot m^{-3}$, the heat capacity being taken from Rogers et al.,[22] $C_p = 1.55$ $kJ \cdot kg^{-1} \cdot K^{-1}$. Using this reference data, a total reference area of the tubes of the heat exchanger $A_{0,r} \approx 60.3$ m^2 was obtained. If this uncertainty in viscosity and thermal conductivity is introduced in the calculations, maintaining all other parameters constant, the area can be recalculated. The results were expressed in terms of percent deviation relative to the above-mentioned reference area:

$$\Delta A_0 = \left(\frac{A_0 - A_{0,r}}{A_{0,r}}\right) \times 100 \quad (4)$$

Figure 4 shows the results obtained for the error in the reference area of the heat exchanger (in %) as a function of the uncertainty in thermal conductivity, using the uncertainty in viscosity as a parameter for the curves. As an example, if we use a value of the thermal conductivity of the molten nitrate mixture 25% lower than the reference value and a viscosity 10% higher than the corresponding reference value, the calculated total area of the heat exchanger would increase about 16%, with the corresponding effect on the capital and operational costs of the equipment.

In some solar plants, the molten nitrate transfers directly the heat through a steam generator (kettle-boiler) to produce superheated steam for a conventional Rankine

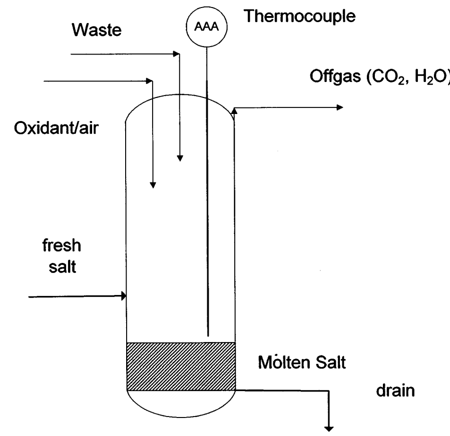

Figure 5. Schematic of the molten salt oxidation of wastes process.

cycle turbine generator system. The heat is stored in a direct absorption receiver containing the molten nitrate mixture.[23] The basic assumptions and calculus are similar, and the same conclusions can be obtained.

Molten Salt Oxidation of Wastes

The industrial society is nowadays responsible for the generation of millions of tons of waste. At least in part, some of this waste may be considered as hazardous due to its effect on human or animal health or impact on the environment. The most commonly used technique for destroying this waste is incineration. This process has disadvantages such as the high temperatures needed, high consumption of combustibles, and the generation of toxic byproducts. More and more, in some places the public opinion is reluctant in accepting this method. One of the promising alternatives is waste processing in a molten salt bath.[24] This process is called molten salt oxidation (MSO). The MSO process is relatively simple. The waste is injected in a molten salt bed at temperatures around 1173 K, hundreds of degrees lower than those in an incineration. The process is highly exothermic, so after an initial heating, the combustion of the waste keeps the salt molten. Acid gases are retained in the reactor in the form of benign salts, so the process does not need a scrubbing system. Besides, the molten salt provides a stable heat-transfer medium that ensures temperature uniformity. Figure 5 shows a schematic diagram of the process.

For the implementation of this process, several properties are needed. Sodium carbonate, Na_2CO_3, is used, due to its stability, no toxicity at high temperatures, ability to retain acidic gaseous products, and high thermal conductivity. The viscosity of the medium is another important property, as it limits the extent of the reaction. After some time of operation, the reactor has to be filled with fresh salt. This salt must be pumped from a reservoir through a cold pipe, so it is very important to calculate how far the molten salt can flow through a cold pipe before freezing. This length is sometimes called the penetration distance, z. Again, there are several correlations relating the axial distance a fluid can flow in a cold pipe. For our purpose we will use the following:[25]

$$\frac{z}{D} = 0.23 Pr^{1/2} Re^{3/4} (\alpha_m/\alpha_s)^{1/9} [\Delta_{fus}H/(C_{ps}(T_f - T_w))]^{1/3} [1 + \gamma C_{pm}(T_0 - T_f)/\Delta_{fus}H] \quad (5)$$

where z is the distance to freeze closed, D is the diameter of the pipe, Pr is the Prandtl number, Re is the Reynolds

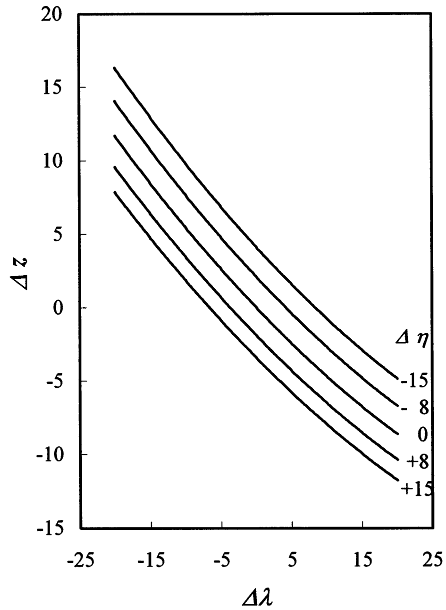

Figure 6. Effect of uncertainty of thermal conductivity (in %) and viscosity (in %) on the penetration distance (in %) in a cold pipe.

number, α_m and α_s are the thermal diffusivity of the liquid and of the solid, respectively, and $\Delta_{fus}H$ is the enthalpy of fusion of the solid; C_{pm} and C_{ps} are the corresponding specific heat capacity of liquid and solid, T_f is the freezing point, T_w is the wall temperature, T_0 is the inlet liquid temperature, and γ is a constant, normally 0.7.

The aim of our calculation is to demonstrate how the uncertainty in the thermophysical properties of molten sodium carbonate will be reflected in the calculation of the distance to freeze in a cold pipe, keeping all other parameters constant. For this calculation we assumed an inlet temperature of 1173 K, well above the freezing temperature (1131 K), and a wall temperature of 298.15 K. The other parameters that can be controlled are the fluid velocity and pipe diameter, herein considered constant. For viscosity the reference value of Sato et al.[13] was used, $\eta = 3.646$ mPa·s. Comparing with other authors,[12] we can see that at about 1173 K the differences between different sets of data can go up to ±15%. For thermal conductivity the data are very scarce. We used the data of Otsubo et al.,[26] for thermal diffusivity of the melt to obtain the thermal conductivity by the simple expression

$$\lambda = \alpha C_p \rho \tag{6}$$

Density was taken from Spedding,[27] $\rho = 1953$ kg·m^{-3}, and the heat capacity was taken from Janz et al.,[28] $C_p = 1.837$ kJ·kg^{-1}·K^{-1} at 1173 K. The thermal conductivity of molten carbonate can then be estimated to be $\lambda = 0.822$ W·m^{-1}·K^{-1}. If we look to recent data on thermal diffusivity and thermal conductivity of molten carbonate mixtures, we can see that differences between different authors can be as large as 50%.[29]

The enthalpy of fusion is $\Delta_{fus}H = 264.5$ kJ·kg^{-1}, and the heat capacity of the solid near the freezing temperature is[28] 1.892 kJ·kg^{-1}·K^{-1}. The term $(\alpha_m/\alpha_s)^{1/9}$ is considered to be almost unity. Using reference data, we obtain a penetration distance of about 27 m for a pipe with a 5 cm diameter. Figure 6 shows the percent differences between this reference value and the values obtained allowing the viscosity to change ±15% and the thermal conductivity to change ±20%. The difference in z can go up to 16%. This again shows how important is the knowledge of those properties to design properly the equipment dimensions.

Conclusions

We have shown some of the recent applications of ionic liquids at high temperatures and how the knowledge of thermophysical properties is important for proper and optimal technological design. To illustrate this, two examples have been chosen among many possible. The results obtained support that those applications need a careful selection of experimental data; otherwise, equipment will be either under- or overdimensioned, with the consequent ill operation and increased capital and operational costs. It is evident that if other uncertainties were taken into account, the total uncertainty in the global design used will have been larger. The calculations herein reported showed the importance in selecting the best thermophysical data available for a good engineering practice (GEP). In the absence of standard reference data, this can be done by correlation, prediction, or estimation, for instance, by empirical or theoretical methods.[30]

Molten salt technology faces a wide range of possibilities, and future tasks will certainly imply the optimization of technology through the use of more accurate molten salt properties.

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