



Optical properties of high temperature molten salt mixtures for volumetrically absorbing solar thermal receiver applications



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ABSTRACT

Molten salts are promising candidates for liquid volumetric absorbers in concentrated solar power systems. To characterize absorption and heat transfer performance in high temperature applications, their optical properties are required. Thus a method for experimentally determining the absorption coefficient of non-scattering high temperature semi-transparent liquids for large (~1 m-deep) direct absorption solar receiver applications was developed. It was used to measure the absorption coefficient in liquids over a broad spectral range and temperatures up to 800 °C in a 40 wt.% KNO₃:60 wt.% NaNO₃ binary nitrate molten salt mixture (solar salt) and a 50 wt.% KCl:50 wt.% NaCl binary chloride molten salt mixture. The binary nitrate and binary chloride both demonstrated well distributed solar absorption (>95% absorption through 1 m and 2 m, respectively). At 400 °C, the binary nitrate is optically thick in its re-emission spectrum and behaves as a blackbody radiator. The effects of thermal decomposition were also shown to have significant consequences on the overall performance of the binary nitrate mixture, transforming it into an opaque surface absorber following thermal degradation (>95% in <0.25 m). The implications of these results for solar receiver design are discussed in terms of volumetric absorption, total effective emissivity, and capture efficiency. The measurement technique developed and results are relevant in a variety of high temperature applications including heat transfer systems, materials processing, pharmaceuticals, and food processing facilities.

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1. Introduction

Typical solar collectors absorb incident solar radiation through surface absorbers before transferring this radiation as thermal energy to a working fluid or storage material. Volumetric receivers using direct volumetrically absorbing fluids promise significant performance enhancement over current surface absorber designs and lead to increased efficiency (Khullar et al., 2014; Lenert and Wang, 2012; Ni et al., 2016). In particular, the Concentrated Solar Power on Demand (CSPonD) concept (Slocum et al., 2011) is a system which consists of a collocated volumetrically absorbing molten salt solar receiver with inherent thermal energy storage. The simultaneous use of a volumetrically absorbing high temperature fluid as storage medium and working fluid is an alternative solar absorption approach which allows incident solar radiation to be directly absorbed and stored by the working fluid and eliminates the need for intermediate surface absorbers. The candidate molten salts generally behave as semi-transparent, radiatively participating liquids which do not necessarily require nanoengineered parti-

cle suspensions to tailor their optical properties (Lenert and Wang, 2012). Radiative heat transfer is therefore expected to be a dominating mechanism for heat absorption and transport within the salts and their optical properties are required to characterize their thermal behavior.

The CSPonD Demo prototype (Gil et al., 2016) uses a 40 wt.% KNO₃:60 wt.% NaNO₃ binary nitrate molten salt mixture (solar salt) for which measured absorption properties are only available for wavelengths from 400 nm to 800 nm (Passerini, 2010) in high purity salts that do not accurately capture the behavior of commercial salts used under real operating conditions. In contrast with the typically smaller volumetrically absorbing solar receiver designs and the associated optical property data available (Drotning, 1978; Viskanta and Anderson, 1975; Webb and Viskanta, 1985), Slocum et al. have proposed a large scale commercial CSPonD design 5 m deep × 25 m diameter and consider the use of chloride salts which commonly operate at 900 °C. Ideal solar penetration depths for such volumetrically absorbing systems should closely match the depth of the absorber liquid, requiring the ability to measure nearly-transparent high-temperature materials. However, typical methods for measuring the optical properties of liquids use reflectance techniques (Makino et al., 1991; Myers et al., 2015)

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Nomenclature

List of symbols

A_m	solar-weighted absorption factor	q_s	surface radiative heat flux
C	solar concentration	R	surface reflectance
$C_1 = 3.7418 \times 10^{20} \text{ W} - \text{nm}^4/\text{m}^2$	first radiation constant	T	temperature
$C_2 = 14388.69 \times 10^3 \text{ nm} - \text{K}$	second radiation constant	\bar{T}_{op}	mean fluid operating temperature
E_{λ_o}	spectral solar irradiance	Δx_i	fluid path length
$\bar{E}_{solar} = E_{\lambda_o}/E_{\lambda_o,max}$	normalized solar spectral irradiance	$\beta(T, \lambda_o)$	attenuation coefficient
$I_i(T, \lambda_o)$	spectral intensity	$\epsilon(L_{e,E}, \bar{T}_{op})$	total emissivity of isothermal fluid layer
$I_o(\lambda_o)$	incoming light source intensity	$\eta_{capture}$	capture efficiency
$I_{b_i}(\bar{T}_{op})$	spectral emissive blackbody intensity inside the fluid	κ	absorption coefficient
$\hat{I}_{b_i, \bar{T}_{op}} = I_{b_i}(\bar{T}_{op})/I_{b,max}(\bar{T}_{op})$	normalized blackbody intensity spectra	κ_{MS}	solar-weighted absorption coefficient
L	actual thickness of fluid layer	κ_{ME}	re-emission-weighted absorption coefficient
L_m	average mean beam length	λ_o	vacuum wavelength
$L_{e,S}$	mean beam length through fluid thickness in solar spectrum	$\lambda = \frac{\lambda_o}{n}$	wavelength inside medium
$L_{e,E}$	mean beam length through fluid thickness in re-emission spectrum	σ	boltzmann constant
n	index of refraction	$\sigma_s(T, \lambda_o)$	scattering coefficient
		τ	optical thickness
		τ_{MS}	solar-weighted optical thickness
		τ_{ME}	re-emission-weighted optical thickness

with small sample thicknesses (≤ 10 mm). The measurement resolution for these techniques is typically $>100 \text{ m}^{-1}$ which does not accurately capture the properties of nearly transparent liquids. In addition, these techniques are often used in conjunction with spectrometers (Otanicar et al., 2009; Passerini, 2010; Passerini and McKrell, 2012) which do not provide accurate measurements for high temperature materials at infrared wavelengths. The high operating temperatures also suggest participating media effects within the salts are non-negligible, further emphasizing the necessity of measuring optical properties over a wide spectral range extending into the mid-infrared spectrum. It is therefore of great value to characterize the solar absorption, the internal re-emission, and the radiative losses for these systems at elevated temperatures.

In this work, we present a simple and accurate apparatus that allows for the precise measurement of light attenuation in high temperature, nearly transparent liquids, over a broad spectrum extending from the visible region (400 nm) into mid-infrared (8 μm). The apparatus is used to measure the attenuation of light in the 40 wt.% KNO_3 :60 wt.% NaNO_3 binary nitrate and the 50 wt.% KCl :50 wt.% NaCl binary chloride molten salt mixtures. The attenuation measurements provide direct insight into the absorption properties of non-scattering liquids. The effects of salt contamination due to thermal decomposition are also evaluated. Sources of contamination in the CSPonD include thermal decomposition due to unexpected heating conditions and local hot spots, and sand/dust contamination due to the open receiver design. The implications of the results are discussed in the context of the CSPonD Demo and for general volumetrically absorbing solar receiver applications.

2. Experimental procedure

2.1. Apparatus description

The attenuation coefficient is a function of temperature and wavelength and is expressed in terms of absorption and scattering as:

$$\beta(T, \lambda_o) = \kappa(T, \lambda_o) + \sigma_s(T, \lambda_o) \quad (1)$$

where $\beta(T, \lambda_o)$ is the attenuation coefficient, $\kappa(T, \lambda_o)$ is the absorption coefficient, and $\sigma_s(T, \lambda_o)$ is the scattering coefficient, each eval-

uated at temperature T and (vacuum) wavelength λ_o . There are several ways of measuring the attenuation coefficient (Modest, 2013; Myers et al., 2015; Otanicar et al., 2009; Passerini and McKrell, 2012). The method selected in this work evaluates the attenuation coefficient by measuring and comparing the transmission of light through different material thicknesses and relating them via the Beer-Lambert's Law:

$$\beta(T, \lambda_o) = \frac{-1}{\Delta x_j - \Delta x_i} \ln \left(\frac{I_j(T, \lambda_o)}{I_i(T, \lambda_o)} \right) \quad (2)$$

where $I_i(T, \lambda_o)$ and $I_j(T, \lambda_o)$ are the transmitted outgoing intensities measured by the FTIR detector for corresponding path lengths Δx_i and Δx_j through the fluid at temperature T , for a constant collimated incoming light source $I_o(T, \lambda_o)$ perpendicularly incident to the cuvette windows. The attenuation can therefore be calculated from any combination of measured outgoing intensities.

To carry out the optical measurements, the furnace based apparatus developed by Passerini (Passerini, 2010; Passerini and McKrell, 2012) was modified and adapted to be used in conjunction with a Bruker VERTEX 70 Fourier Transform Infrared (FTIR) spectrometer with a 150 W tungsten lamp externally adapted light source, which replaces the integrating sphere and spectrometer in the original experimental setup. FTIRs operate over a much wider spectral range than dispersive infrared spectrometers used in previous studies. One of the main disadvantages of dispersive methods is that the radiation emitted by the apparatus at high temperatures inevitably contributes to the overall IR radiation signal for temperatures above 700 °C. To circumvent this challenge, the FTIR uses a Michelson Interferometer to modulate the source and differentiate it from the unmodulated high temperature emissions.

The apparatus consists of a vertically oriented and electrically heated split tube furnace, as shown in Fig. 1a. Two coaxial quartz cuvettes are positioned inside the furnace. Both cuvettes are closed at the bottom with fire polished quartz windows. The sample fluid is added to the outer cuvette only and the inner cuvette is partially immersed in the fluid and has an adjustable vertical position. Attenuation measurements can therefore easily be made for different fluid thicknesses by adjusting the inner cuvette's height. Relevant applications call for semi-transparent fluids 1 m in depth and optical thickness $\tau \approx 1$. The FTIR can readily resolve attenuations

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