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Solar Salt – Thermal Property Analysis

Report on thermo-physical properties of binary $NaNO_3$-KNO_3 mixtures in a range of 59-61 wt% $NaNO_3$

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I. Introduction

Thermal Energy Storage (TES) plays a crucial role for the implementation of dispatchable, renewable energy systems world-wide. Molten salt storage has proven advantageous for storage units in modern CSP plants with large power and capacity levels.[1] Solar Salt, a mixture of 60 wt% $NaNO_3$ and 40 wt% KNO_3, is the state-of-the-art storage material and heat transfer fluid and is utilized in temperature regimes between 290 °C and 565 °C in a cold- and a hot tank configuration, respectively [2]. Typically, these salts are provided by salt suppliers using big bags (e.g., ~1000 kg) of the single salts. This study considers that SQM offers big bags with pre-mixed Solar Salt, which simplifies the organizational efforts during the TES start-up. The mixing accuracy is however important to ensure that the final mixture exhibits uniform physicochemical properties. This applies to both blending options, on site or blending at the supplier. SQM offers, a mixing tolerance of the desired salt composition, in our case Solar Salt, of ±1 wt%. Consequently, the final salt composition can vary between 59 wt% $NaNO_3$ and 61 wt% $NaNO_3$ (balance is KNO_3 in all cases).

This report investigates the impact of these defined compositional changes on the thermo-physical properties and melting properties of three possible batches: the first one being the *standard* mixture (60-40 wt%), the second with a 1 wt% excess of $NaNO_3$, and one with a 1 wt% excess of KNO_3. In our study, those mixtures were referred to as SS60, SS61 and SS59, respectively. The number in the name corresponds to the $NaNO_3$ wt% fraction. It was assumed that SS61 and SS59 represent the borderline cases, and that there is a probability that they represent the entity of the storage interior. In order to assess the two border-line cases (which are the least likely to occur statistically), we study the impact of ±1 wt% variations of the Solar Salt compositions on the main thermo-physical properties, which are critical for the design of a CSP plant: the heat capacity, viscosity, thermal conductivity and density, as well as the melting properties.

II. Results of the report

1. Melting Properties

The melting properties of mixture of $NaNO_3$ and KNO_3 have been assessed in the past both experimentally and by modelling approaches (See ref. [2] and literature cited therein). The phase diagram of $NaNO_3$ and KNO_3 is well established and shown in Figure 1.

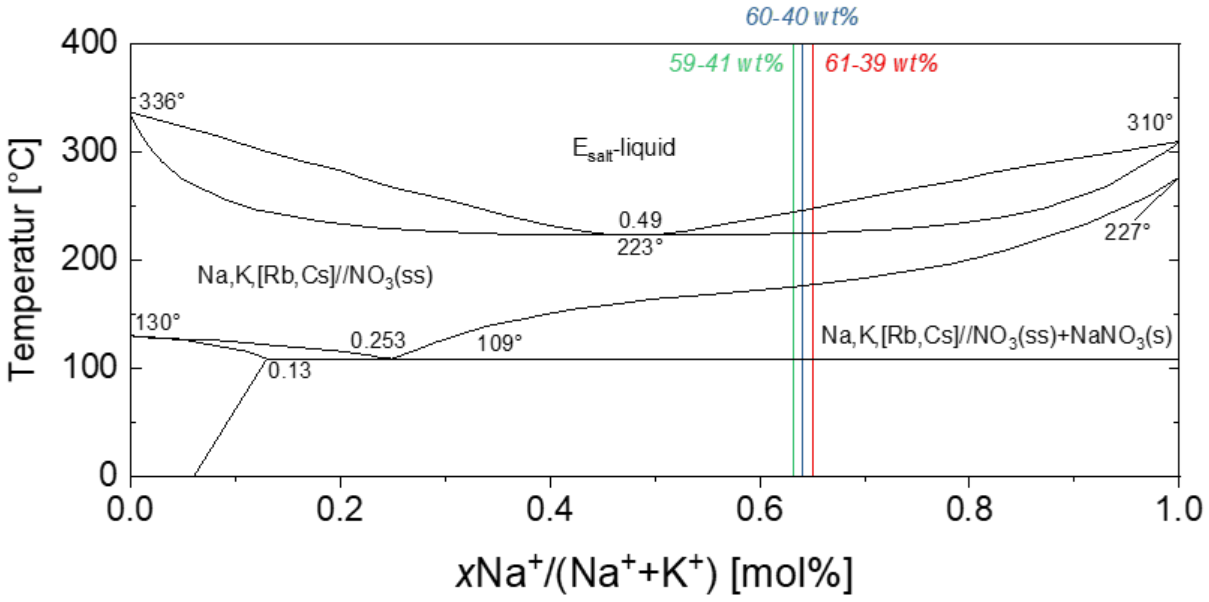

Figure 1 Phase diagram of $NaNO_3$ and KNO_3 reprinted from FactSage [3] data. The compositions of Solar Salt addressed in this work are marked and labelled in the plot.

The melting properties of the mixtures have been assessed using the FactSage software and the results are presented in Table 1. Solar Salt has no single melting temperature but a melting range. The melting range is characterized by the solidus temperature and liquidus temperature. Below the solidus temperature of about 223 °C Solar Salt is solid, between the solidus and liquidus Solar Salt is both solid and liquid (mushy zone). The relevant melting point is expressed as the liquidus temperature (at and above this temperature the salt is completely liquid).

At operating temperatures above 350 °C nitrite-ions (NO_2^-) form in Solar Salt which lower the liquidus temperature. The quantity of nitrite ions formed depends on the operation temperature (e.g. Trough CSP plant at 385 °C, tower CSP plant at 565 °C). Higher operation temperatures lead to higher nitrite levels and hence, lower liquidus temperatures. The relevant phase diagram is a ternary-reciprocal phase diagram of the type K, Na//NO_2,NO_3, which has been reprinted in ref. [2]. Due to different nitrite levels depending on operation temperature and salt being supplied as nitrate, this report focuses on Solar Salt without nitrite. It is considered reasonable and sufficient to estimate deviations using standard Solar Salt without nitrite. This is especially due to the fact, that nitrate- and nitrite levels will equilibrate at typical operating temperatures, e.g. at levels of ~5 mol% nitrite at 565 °C in a Solar Salt melt.

The KNO_3-$NaNO_3$ system has been studied in more than 40 papers since 1857. Overview papers have been written by Rogers and Janz [21], Berg and Kerridge [22] and Zhang et al. [23]. References of phase diagram measurements can be found in the references of three cited overview papers. Details of the phase diagram are not yet fully agreed upon. A discussion whether this system is a continuous solid solution or eutectic type can be found elsewhere [22,23]. The liquidus temperature of the standard Solar Salt mixture (SS60) is 246.3 °C according to FactSage simulations.[3] As pointed out in the previous discussion, this absolute value should be considered with care. The focus of this study is on relative changes and FactSage data were selected as a reliable literature source. The results show that the liquidus temperature increases by 1.7 °C and lowers by 1.7 °C when the Na content is 1 wt% higher or lower, respectively.

From DLR experiences, such a change in melting temperature is similar to the accuracy of differential scanning calorimetry (DSC) measurements. Typically, the minimum operation temperature is set 30 °C (or more) higher than the liquidus temperature. Hence, there is a large safety margin of ≥ 30 °C to reach the liquidus temperature in operation and a value of 1.7 °C is comparatively small.

Table 1 Melting Points of Solar Salt with slight variations in composition

Melting Point	**SS59**	**SS60**	**SS61**
$NaNO_3$-KNO_3 content [wt%]	59-41	60-40	61-39
T_m [°C]	244.6	246.3 °C	248
Deviation in °C	-1.7°C		+1.7°C
Deviation	-0.7%		+0.7%

2. Heat capacity

Literature values for the heat capacity of KNO_3 and $NaNO_3$ have been reported in the past and a small number of them are shown in Figure 2 and in Figure 3, respectively. In the liquid range, above the melting point of single salts (306 °C $NaNO_3$; 334 °C KNO_3) and mixtures (liquidus from 223 °C to 234 °C), the heat capacity is typically constant [4]. Values of Carling [5] are slightly decreasing over temperature which, thermodynamically, is not viable. It is reasonable to assume that decreasing heat capacity values over temperature (or time in the measurement) result from side reactions, such as endothermic evaporation, salt-gas phase interactions (e.g. oxygen release, NO_x release) or interaction with the crucible materials. Especially for molten nitrate salts a variety of phenomena leads to the fact that the uncertainty of measurement is relatively large (±3-10 %), especially due to the possibility of salt evaporation, decomposition (e.g. from the nitrate ion to form nitrites), but even more so due to salt creeping (assumptions of DSC measurement principles are not valid anymore). The latter phenomenon is based on the fact that molten nitrate salts exhibit low surface tensions, or in other words, have the tendency to wet surfaces. The so called "salt creeping" refers to a phenomenon where a molten salt film will form on any available surface as long as its temperature exceeds the melting point of the salt itself.

Data for the heat capacity of KNO_3 and $NaNO_3$ are shown in Figure 2 and Figure 3, respectively. Given the wide-spread of heat capacity values and the relatively large error, it is still reliable to assume, that the heat capacity is constant over a wide temperature range, while on an industrial scale it is often expressed by a linear function of the type $c_p = a + b * T(°C)$. Yet, available datasets show negative or positive, temperature dependence. D'Aguanno and co-workers [6] have performed molecular dynamics simulations paired with laboratory experiments and stated very clearly, that the heat capacity c_p is principally independent of temperature, but that experimental control is challenging which leads to the measured temperature dependencies. In agreement with the considerations by d'Aguanno, constant values are chosen for the heat capacity of $NaNO_3$ and KNO_3, as well as the mixed salts in this work.

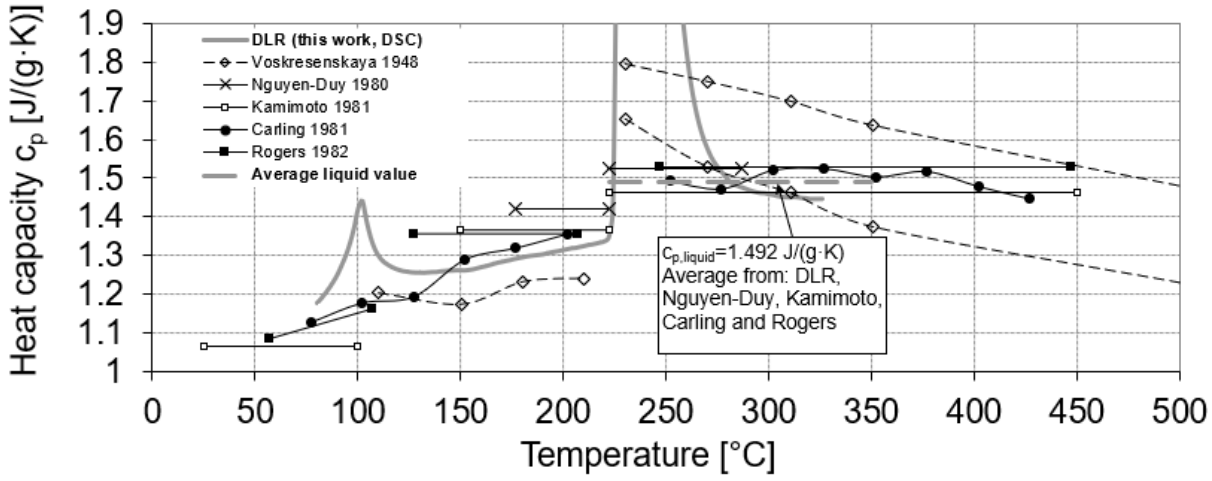

Figure 2 Literature data of the heat capacity of KNO_3 in the solid and liquid phase from different literature sources ([7-11]). The peaks in the grey curve labelled "DLR (this work, DSC)" at ~100 °C and 240 °C display a solid-solid conversion and the endothermic melting peaks and not the heat capacity.

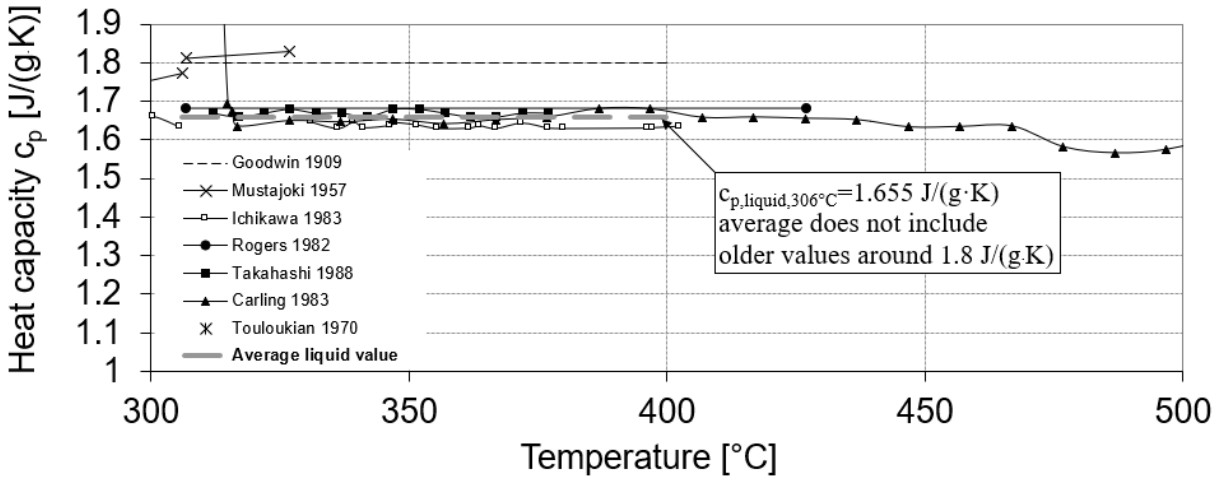

Figure 3 Heat capacity of $NaNO_3$ between 300°C and 500°C from different literature sources.[5, 11-16]

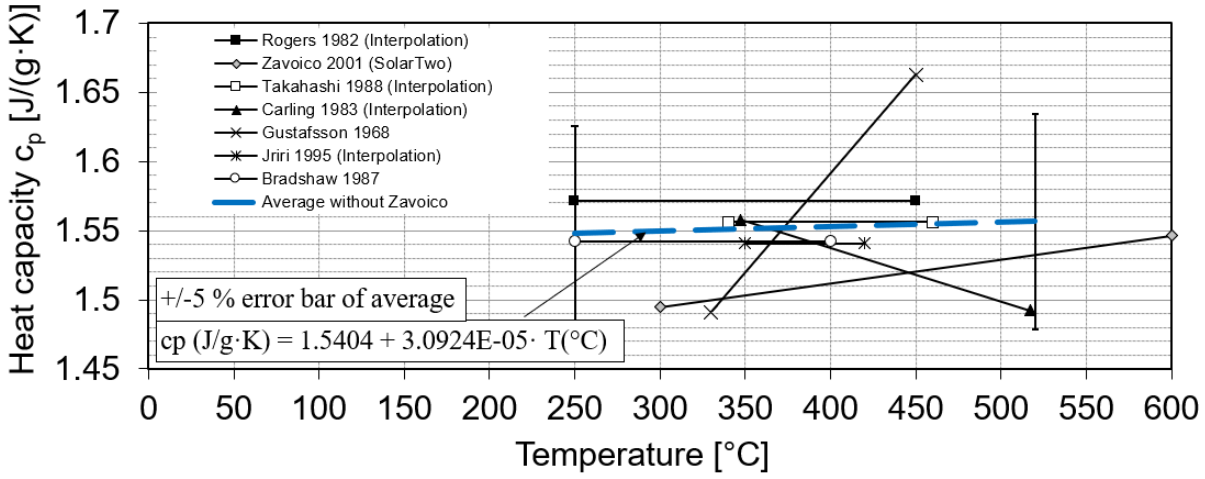

Figure 4 Heat capacity of the standard Solar Salt mixture, reprinted from ref. [4].

For the pure salts $NaNO_3$ and KNO_3 there has been consensus on the heat capacity from work by a variety of authors, e.g. Ichikawa [14], Carling [5], Takahashi [15], and Rogers [11], most of them are represented in Figures 2 and 3. From the gained literature data we extracted an average value for the heat capacity of the single salts (also marked in Figures 2 and 3) KNO_3:

$$c_{p,KNO_3}(310 - 565°C) = 1492\ [J/(g \cdot K)] \quad (1)$$

and for $NaNO_3$ (see Figure 3):

$$c_{p,NaNO_3}(334 - 565°C) = 1655\ [J/(g \cdot K)] \quad (2)$$

The heat capacity of molten nitrate salts with univalent cations follows the basic additivity rule, where the heat capacity of a mixture is determined by the product of the quantity and heat capacity of the individual salts [6, 17]. With the assumption of a constant molar heat capacity the individual salts, it is possible to calculate the heat capacity of Solar Salt and other mixtures with the mole fraction *x* and the heat capacity c_p of the two salts $NaNO_3$ and KNO_3:

$$c_{p,total} = c_{p,NaNO_3} \cdot x_{NaNO_3} + c_{p,KNO_3} \cdot x_{KNO_3} \quad 3$$

For a perfectly mixed salt with Solar Salt composition (SS60) the linear additivity rule suggests a heat capacity of 1.596 J/(g·K) at 565 °C (see Table 1) using single salt heat capacities of 1.492 J/g·K (KNO_3) and 1.655 J/g·K ($NaNO_3$). This is slightly higher than the average literature (1.5578 J/g·K at 565 °C, calculated from the correlation presented in Figure 4), but still within the error of measurement.

Table 2 Heat capacity of Solar Salt compositions with slightly varying mixing ratio (± 1 wt%), labelled as SS60, SS61 and SS59.

Heat Capacity	**SS59**	**SS60**	**SS61**
$NaNO_3$-KNO_3 content [wt%]	59-41	60-40	61-39
Cp [J/(g·K)]	1.59498	1.59646	1.59802
Deviation in J/(kg·K)	-0.00157	-	+0.00156
Deviation	-0.098 %	-	0.097 %

The heat capacity of SS61 and SS59 only vary slightly at values of 1.598 and 1.595, respectively. The deviation of S61 and S59 is around 0.1 %. This suggests, that neither theoretical nor practical limitations would arise from the use of either of the three mixtures. It has to be noted here, that the measured heat capacity of Solar Salt appears somewhat lower (around 1.540 J/g·K according to our recommended data in ref. [2]). The difference is around 3 % between the extrapolated and the measured value, which is slightly lower than the experimental error (3-7 %). Therefore, the change of the heat capacity is below ±0.002 J/g·K or about ±0.1 %, and is more than one order of a magnitude below the error of measurement.

3. Viscosity

Molten nitrate salts can be considered Newtonian fluids and exhibit low viscosities, similar to values of water at room temperature, or even lower [18, 19]. Due to safety concerns, effort has historically been put into understanding the viscosity near the crystallization point to foresee phenomena such as pipe degradation by abrasion with salt crystallites [20]. At higher temperatures the viscosity of the liquids is changing only marginally and does not vary with composition to a large extent, as we have already highlighted in one of our recent publications.: "The very low viscosity requires sensitive techniques and within the literature large errors can be found.", cited from ref. [2].

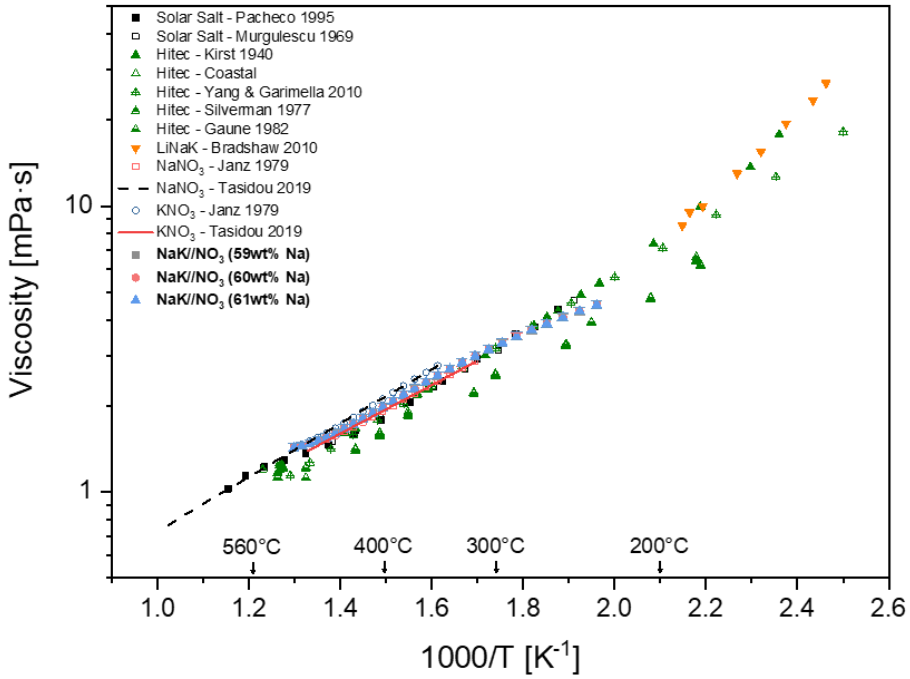

Figure 5 Viscosity data of reference molten salts (Solar Salt, Hitec (Na,K//NO_2,NO_3) and a LiNaK//NO_3 mixture; reprinted from ref. [2]) from literature data, as well as single salts $NaNO_3$ and KNO_3 from ref. [21]. Viscosity values calculated for SS59, SS60 and SS61 according to Eq. 6 and literature data are plotted. Viscosities of SS59, SS60 and SS61 are almost identical, thus symbols are on top of each other.

Since minimum operation temperatures are typically 30 K from the crystallization temperature of the molten salt, technical drawbacks from increasing viscosities very close to the freezing point will not play a significant role. Despite, measuring the viscosity is technically challenging, since e.g. creeping of the molten salt can lead to misinterpretation of results. Overall, an error of ±1 % (or ±0.25 % when measured with great care) can be expected for a capillary-type viscometer.[22]" (all cited from [2]).

For the single salts, recommendations for datasets have been published by Tasidou [23] and co-workers. For KNO_3, the authors stated that "Following an examination of all viscosity measurements in the period 1907–1978, the measurements of Zuca and Costin (cited in Janz' work [22]) were selected as the recommended reference dataset, consequently forming the recommendations in the 1988 publication of Janz.[24] These measurements were included in the

primary dataset. We also included the measurements of Lanca et al., [25] Tolbaru et al., [26] Schardey et al. [27] and Abe et al. [28], which were obtained in oscillating body viscometers […]."

For $NaNO_3$ the recommended data sets date back to Janz' work in 1988 [24], which was reprinted from his 1968-report [29] and dates back to work by Dantuma [30] in 1928. This dataset was complemented with measurements from Smotrakov *et al.* [31], Protsenko [32] as well as Zuca [33], Karpachev [34] and Nunes [35] and is the foundation of the recommended data provided by NIST. The temperature correlations for $NaNO_3$ and KNO_3 can be found hereafter. The recommended temperature correlations for both $NaNO_3$ and KNO_3 from Tasidou [23] (expressed by an exponential function of the type $\eta = A \cdot e^{B/RT(K)}$) and Janz [21] (expressed by a polynomial function) yield almost identical data and are both shown in Eq. 4-7.

Tasidou 2019	$\eta_{NaNO_3} = 0.1037 \cdot e^{\frac{16250.7}{RT(K)}}$	4
	$\eta_{KNO_3} = 0.0840 \cdot e^{\frac{17994.1}{RT(K)}}$	5
Janz 1979	$\eta_{NaNO_3} = 25.0987 - 6.0544 \cdot 10^{-2} \cdot T(K) + 3.8709 \cdot 10^{-5} \cdot T^2(K)$	6
	$\eta_{KNO_3} = 28.404 - 6.752062 \cdot 10^{-2} \cdot T(K) + 4.220783 \cdot 10^{-5} \cdot T^2(K)$	7

The viscosity data of a number of mixtures based on nitrate and nitrite salts is shown in Figure 5. It features the viscosity of Solar Salt, Hitec ($NaNO_3$-$NaNO_2$-KNO_3) and LiNaK ($LiNO_3$-$NaNO_3$- KNO_3) between their melting point and their high temperature limit. It is obvious, that the viscosity of all of these mixtures, despite their huge compositional differences, is very similar over a wide temperature range. Williams [17] suggested that the viscosity if ideal molten salt mixtures can be approximated from the molar quantities and viscosities of the single salts according to:

$$\eta_{ideal} = \left\{\sum \left(x_i \cdot \eta_i^{1/3}\right)\right\}^3 \quad 8$$

where x_i is the mole fraction of component *i* and η_i is the dynamic viscosity (mPa·s) of component *i*. This equation was used to estimate the difference between Solar Salt and mixture of 59 wt% and 61 wt% $NaNO_3$ at the critical lower temperature limit of 290 °C. It can be seen that deviation is small with a value of about 0.1 %.

Table 3 Dynamic viscosity of SS59, SS60, and SS61 from calculations according to Eq. 8 and the temperature correlations from Janz [21].

Viscosity	**SS59**	**SS60**	**SS61**
$NaNO_3$-KNO_3 content [wt%]	59-41	60-40	59-41
η @ 290°C [mPa·s]	3.456	3.452	3.447
Deviation in [mPa·s]	+0.004	-	-0.005
Deviation	+0.12 %	-	-0.14 %

4. Thermal Conductivity

Nunes summarized thermal conductivity values of KNO_3 as a function of temperature. The differences among different sets of data can be as high as 25%. Also dk/dT is either positive or negative [36]. Bauer [37] summarized thermal conductivity values of $NaNO_3$ and this data is represented in Figure 6. White and Davis [38] proposed a temperature correlation for the thermal conductivity of $NaNO_3$ according to:

$$k_{NaNO_3} = 0.419 + 4.77 \cdot 10^{-4} T \qquad \text{for } 340 \leq T \leq 420\ °C \qquad (9)$$

Some authors propose that the thermal conductivity of $NaNO_3$ is constant over temperature (see ref. [39]) with a value of 0.512 W/(m·K) (between 320 and 399.7 °C).

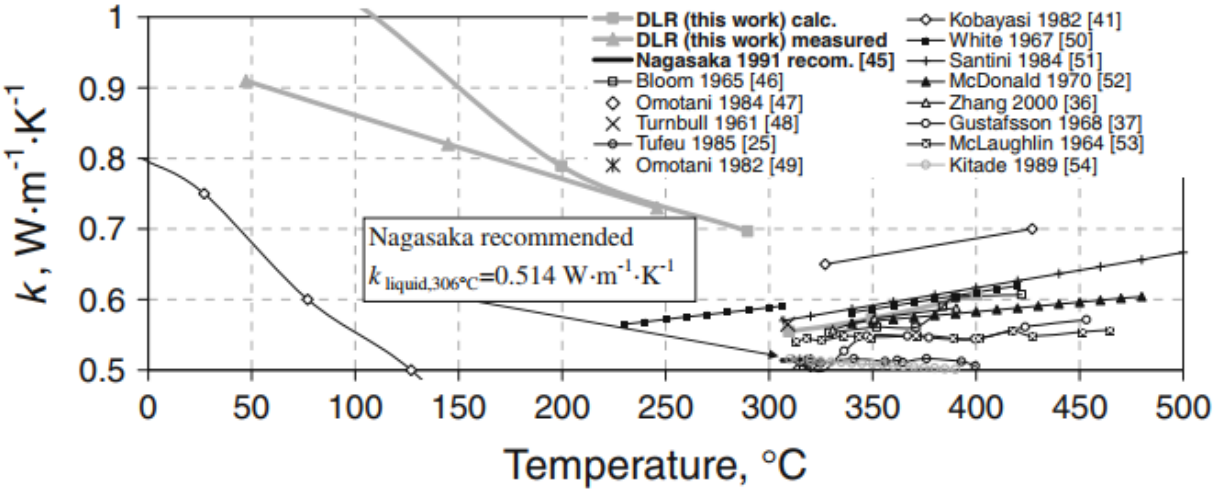

Figure 6 Thermal conductivity of $NaNO_3$, summarized from Bauer et al., *from different literature sources ([38-51]) reprinted from ref. [37].*

For KNO_3, White and Davis propose a temperature correlation of:

$$k_{KNO_3} = 0.2627 + 4.98 \cdot 10^{-4} T \qquad \text{for } 340 \leq T \leq 430\ °C \qquad (10)$$

, while Tufeu [39] proposes a constant value of 0.4202 between 343.6 °C and 427 °C. The error from experimental methods for the determination of the thermal diffusivity (which is later converted to the thermal conductivity via the density and heat capacity) varies drastically and can be as high as 15-25 % [52]. The high error may be attributed to different aspects: the molten salt's characteristic "wetting"-ability due to low surface tension, compatibility with container materials and uncertainties in the measurement principles (e.g. heat losses, parasitic heat transfer such as convection and radiation, thermal expansion and distances). For example, for the laser flash measurement the thermal diffusivity a is obtained. For the measurement there is a square dependency of the sample thickness (errors have also a square dependency). Additional errors may arise for laser flash measurements due other heat transfer modes (radiation, convection, parasitic crucible conduction) and due to the conversion of the measured thermal diffusivity *a* in thermal conductivity *k*. The thermal conductivity is obtained as follows:

$$k = a \cdot \rho \cdot c_p \qquad 11$$

The thermal conductivity of molten salt mixtures typically changes over composition, e.g. McDonald [47] measured a linear relation in a varying $NaNO_3$-KNO_3 system, while Otomani [48] found a local minimum in thermal conductivity (Figure 7). It has been well established that lattice vibrations are responsible for the conduction of thermal energy amongst neighbouring molecules. In close proximity to the melting point, the thermal conductivity typically increases, probably due to the disorder of the short-range quasicrystal line lattice of the molten salt. This effect increases the salt resistance to the lattice vibration modes, which are transferring heat energy (see ref. [53]).

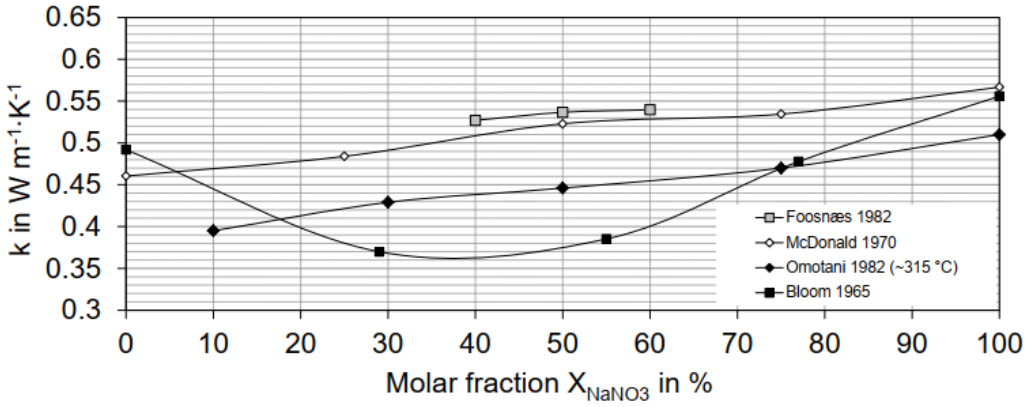

Figure 7 Literature values of the thermal conductivity of the system KNO_3-$NaNO_3$ at 340 °C except data at 315 °C from Omotani [47, 48, 51, 54] (figure and caption reprinted from ref. [4])

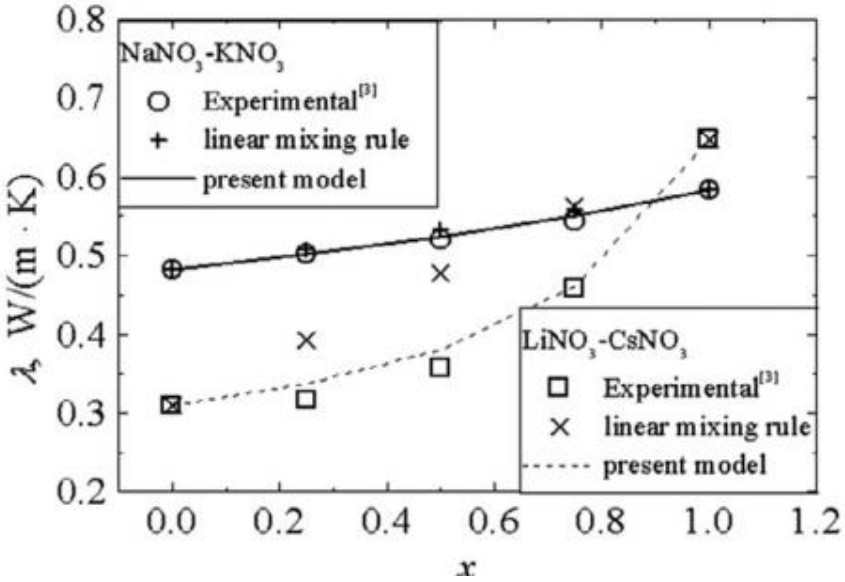

Figure 8 Figure of of thermal conductivity of $NaNO_3$-KNO_3 from Zhao (cross symbols and solid line) [55], as well as McDonald (reprinted from ref [47])

Modelling the thermal conductivity of molten salts appears to be complex for a number of reasons. Firstly, the model needs to be based on the chemical nature of the anions, e.g.

monoatomic salts (e.g. halide salts) can be modelled using simple hard sphere models while complex nitrate salts require for other techniques. Zhao *et al.* [55] have used a two-dimensional macro-scale continuum model for prediction of the thermal conductivity of binary nitrate-based salts. They were able to predict the thermal conductivity of binary molten salts with an accuracy of lower than ~6 % (compared to experimental literature data), which is more accurate than the results of classical experiments. For mixtures of $NaNO_3$-KNO_3 correlations of *k* over composition are scarce. Zhao *et al*. used the data from McDonald and Davis for comparison with his modelling results and the data are plotted in Figure 8. The correlation of *k* vs. composition can be expressed by:

$$k_{Na_xK_{1-x}NO_3}(565\,°C) = 0.483 + 0.1047 \cdot x \qquad 12$$

, whereas *x* is the molar fraction of Na in a mixture of $Na_xK_{1-x}NO_3$ [55]. For the three defined compositions, the molar quantities (*x*) are 65.042 mol% (SS61), 64.085 mol% (SS60) and 63.142 mol% (SS59). This yields thermal conductivity values that are almost identical for all three compositions (see values in Table 4).

Table 4 Values of the thermal conductivity calculated from Eq. 12 as described in the text.

	SS59	**SS60**	**SS61**
$NaNO_3$-KNO_3 content [wt%]	59-41	60-40	61-39
x_{Na} [mol%]	63.124	64.085	65.042
k [W/(m·K)] @565°C	0.5491	0.5501	0.5511
Deviation in W/(m·K)	-0.001	-	+0.001
Deviation	-0.2%	-	+0.2%

As can be seen, measurements deviate in a range from 0.35 W/(m·K) to 0.55 W/(m·K) for KNO_3 and $NaNO_3$ and mixtures (see plots above). Assuming for example a measurement deviation of ±0.1 W/(m·K) related to 0.55 W/(m·K) results in an uncertainty of ±18%. Hence, the measurement uncertainty is two orders of magnitude above the deviation due to a change in composition of ±1%.

5. Density

Recommended density values of single salts and the $NaNO_3$-KNO_3 system are given by Janz [56]. Data show that the density of $NaNO_3$ is higher compared to KNO_3. It is generally accepted that the density decreases linearly with temperature. Especially at high temperatures larger deviations among measurements can be expected due to experimental difficulties (e.g., chemical reactions salt-gas phase, salt-measurement equipment, temperature measurement and uniformity). Figure 9 shows the density of $NaNO_3$ vs. temperature as an example [57].

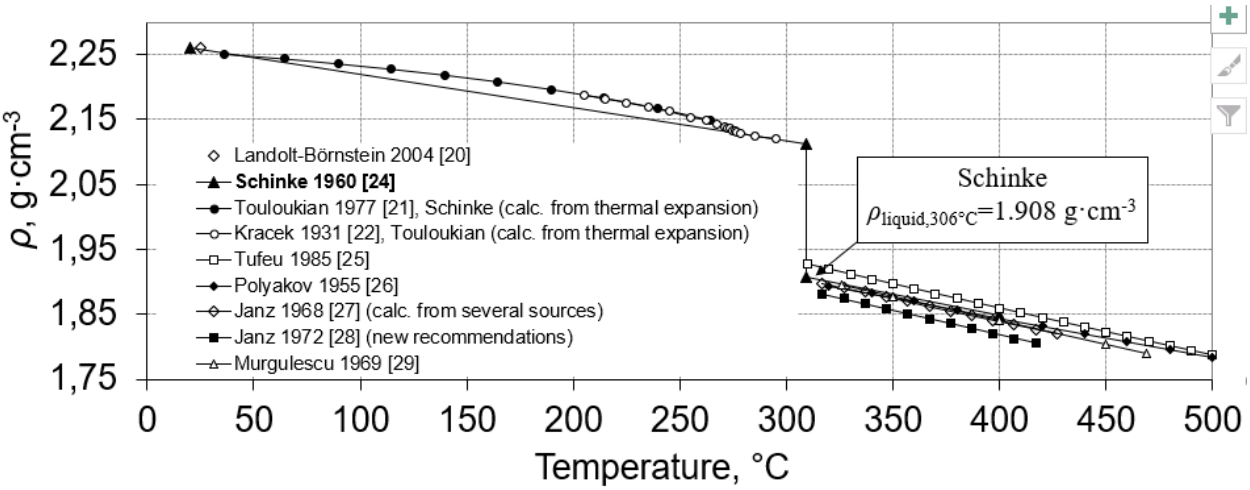

Figure 9 Literature data of the density of $NaNO_3$ in the solid (left below 306 °C) and liquid (right above 306 °C) phase, reprinted from ref. [4].

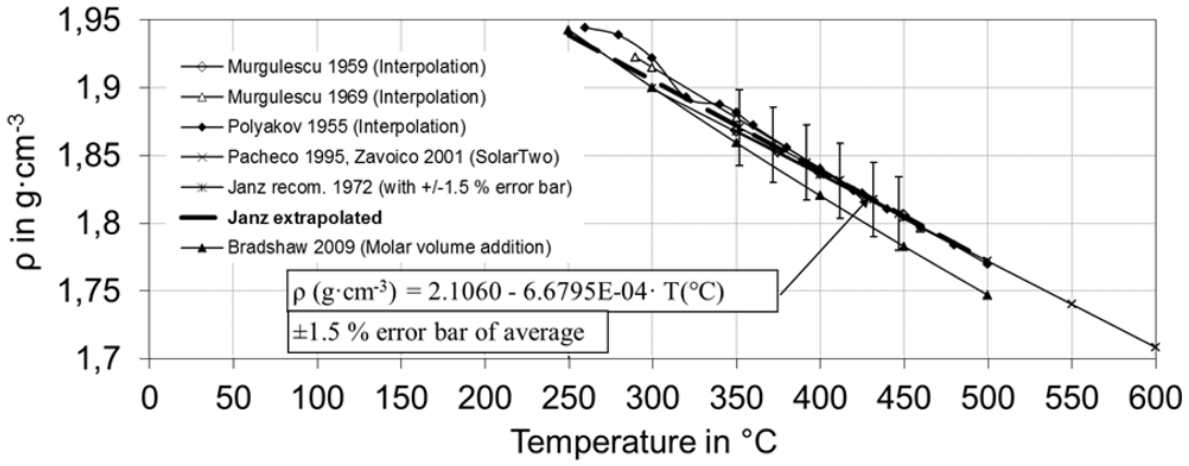

Figure 10 Literature data of the density of Solar Salt reprinted from ref. [4].

The correlation of density vs. composition and temperature has been assessed by the authors of this work recently and the work was published in ref. [58]. The work demonstrates that the density of complex, even reciprocal systems, can be calculated using a quasilinear volumetric additivity rule (QVAR). This approach uses the molar fractions of all anions and cations, as well as the molar volumes of their combined components according to Eq. 13:

$$V_{QVAR}(T) = x_{Na^+}x_{NO_3^-} \cdot V_{NaNO_3} + x_{K^+}x_{NO_3^-} \cdot V_{KNO_3} \quad 13$$

where *x* is the molar fraction of the respective cation or anion (in our case $x_{NO_3^-} = 1$), and *V* is the molar volume at a defined temperature. At 565 °C the molar volumes are 49.395 cm³/mol for $NaNO_3$, and 59.476 cm³/mol for KNO_3 (both from ref. [59]). The correlation yields the density values shown in Table 5. The obtained density values are very similar to those extrapolated from different literature reports, which are summarized in Figure 10. The deviation between the S59 and S61 values vs. S60 is lower than 0.1% (Table 5).

Table 5 Density correlations for Solar Salt and compositions of ±1 wt%.

	SS59	**SS60**	**SS61**
$NaNO_3$-KNO_3 content [wt%]	59-41	60-40	61-39
x_{Na} [mol%]	63.124	64.085	65.042
ρ [kg/m³] @ 565°C	1712.12	1712.33	1712.54
Deviation in kg/m³	-0.21	-	+0.21
Deviation	-1.22E-4 %	-	+1.22E-4 %

III.Summary and Conclusions

This report has evaluated the possible impact of slight variations of Solar Salt composition within ±1 wt% of the classical 60-40 wt% ($NaNO_3$-KNO_3) ratio. The focus of this study was on relative changes and not on absolute values for the physicochemical properties of Solar Salt. This work reviews and discusses the thermophysical- and melting properties of those compositions and draws a conclusion based on a theoretical analysis of available literature data. An experimental approach has been neglected due to the fact that expected experimental errors are too significant to allow for a representative evaluation. As a general summary it can be said, that on the five physicochemical properties, that are most critical for the design of the molten salt systems, namely the melting properties, heat capacity, viscosity, density and thermal conductivity, a small deviation of the Solar Salt composition results in only minor changes of these properties (see Table 6). For all properties, the difference stays below ±1%, in comparison to that of the standard Solar Salt mixture. All of the results indicate that operation with Solar Salt with a deviation of +/-1% in composition would not be affected molten salt system operation. It should be considered that this result is based on a **systematic error** of the composition. Hence, it can be considered as worst-case scenario.

Table 6 Summary of thermal properties of Solar Salt with varying composition of ±1%, extrapolated from different literature sources, and the deviation amongst them.

		SS59	SS60	SS61
Melting Point	**[°C]**	244.6	246.3	248.0
	Deviation	-0.7 %	0%	+0.7 %
Heat capacity	**[J/gK]**	1.59498	1.59646	1.59802
	Deviation	-0.098 %	0%	+0.097 %
Viscosity @290°C	**[mPa·s]**	3.456	3.452	3.447
	Deviation	+0.12 %	0%	-0.14 %
Thermal Conductivity	**[W/(mK)]**	0.5491	0.5501	0.5511
	Deviation	-0.2%	0%	+0.2%
Density @565 °C	**[kg/m³]**	1712.12	1712.33	1712.54
	Deviation	-1.22E-4 %	0%	+1.22E-4 %

From a **statistical error** point of view, the final composition in a TES unit, which is made up by statistically distributed variations of big bags containing ±1 wt%-Solar Salt compositions, will eventually be close to the 60-40 wt% composition. If the chances for each big bag to contain one of the three compositions (SS59, SS60, SS61) is equal (statistically randomized), the probability distribution of the average of a few thousand bags will closely approximate a normal distribution. In that normal distribution, the probability for the full tank containing either extreme end of the

concentration range (+1% or -1% excess of $NaNO_3$) is $\left(\frac{1}{3}\right)^{Number\ of\ Bags}$. Since a CSP plant typically requires several thousand big bags of salt, it can be assumed that the probability for receiving a mixture with an average composition close to the standard 60-40 wt% mixture is the highest. Therefore, systematic errors rather than statistical errors are considered relevant.

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V. References

[1] M. Mehos, H. Price, R. Cable, D. Kearney, B. Kelly, G.J. Kolb, F. Morse, *NREL/TP-5500-75763*, Concentrating Solar Power Best Practices Study, 2020.

[2] A. Bonk, S. Sau, N. Uranga, M. Herainz, T. Bauer, Advanced heat transfer fluids for direct molten salt line-focusing CSP plants, *Progress in Energy and Combustion Science*, 67C (2018) 69-87.

[3] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, A.E. Gheribi, K. Hack, I.H. Jung, Y.B. Kang, J. Melançon, A.D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, M.A.V. Ende, FactSage thermochemical software and databases, 2010–2016, *Calphad*, 54 (2016) 35-53.

[4] T. Bauer, N. Pfleger, N. Breidenbach, M. Eck, D. Laing, S. Kaesche, Material aspects of Solar Salt for sensible heat storage, *Applied Energy*, 111 (2013) 1114-1119.

[5] R.W. Carling, Heat capacities of NaNO3 and KNO3 from 350 to 800 K, *Thermochimica Acta*, 60 (1983) 265-275.

[6] B. D'Aguanno, M. Karthik, A.N. Grace, A. Floris, Thermostatic properties of nitrate molten salts and their solar and eutectic mixtures, *Sci Rep*, 8 (2018) 10485.

[7] N.K.e.a. Voskresenskaya, Nitrite und Nitrate von Natrium und Kalium, *Zhurnal Neorganicheskoi Khimii*, 21 (1948) 18-25.

[8] P. Nguyen-Duy, E.A. Dancy, Calorimetric Determination of the Thermodynamic Properties of the Alkali Metal Salts NaNO3, KNO3, Na2Cr2O7, K2Cr2O7 and their Binary Eutectic Solutions, *Thermochimica Acta*, 39 (1980) 95-102.

[9] M. Kamimoto, Thermodynamic Properties of 50mole% NaNO3 – 50% KNO3, *Thermochimica Acta*, 49 (1981) 319-331.

[10] R.W. Carling, R.W. Mar, *SAND81-8020*, Industrial use of molten nitrate/nitrite Salts, 1981.

[11] D.J. Rogers, G.J. Janz, Melting-crystallization and premelting properties of sodium nitrate-potassium nitrate. Enthalpies and heat capacities, *Journal of Chemical & Engineering Data*, 27 (1982) 424-428.

[12] H.M. Goodwin, H.T. Kalmus, On the Latent Heat of Fusion and the Specific Heat of Salts in the Solid and Liquid State, *Phys. Rev. (Series I)*, 28 (1909) 1-24.

[13] A. Mustajoki, Kalorimetrische Untersuchungen mit Bezug auf die Umwandlung in NaNO3 und dessen Schmelzvorgang, *Ann. Acad. Sci. Fenn.*, 5 (1957) 17.

[14] K. Ichikawa, T. Matsumoto, The Heat Capacities of Lithium, Sodium, Potassium, Rubidium, and Caesium Nitrates in the Solid and Liquid States, *Bul Chem Soc Japan*, (1983) 2093-2100.

[15] Y. Takahashi, R. Sakamoto, K. M., Heat capacities and latent heats of LiNO3, NaNO3 and KNO3, *Int J Thermophys*, 9 (1988) 1081-1090.

[16] Y.S. Touloukian, Thermophysical Properties of Matter - the TPRC Data Series. Volume 5. Specific Heat - Nonmetallic Solids, *Plenum*, (1970) 1145-1147; 1649-1650.

[17] D.F. Williams, *ORNL/TM-2006/69*, Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop, 2006.

[18] R.W. Bradshaw, *SAND2009-8221*, Effect of composition on the density of multi-component molten nitrate salts, 2009.

[19] I.G. Murgulescu, S. Zuca, Viscosity of binary mixtures of molten nitrates as a function of ionic radius--II, *Electrochimica Acta*, 14 (1969) 519-526.

[20] R.W. Bradshaw, *SAND2010-1129*, Viscosity of multi-component molten nitrate salts - Liquidus to 200°C, 2010.

[21] G.J. Janz, C.B. Allen, N.P. Bansal, R.M. Murphy, R.P.T. Tomkins, NSRDS-NBS 61 Part II - Physical Properties Data Compilations Relevant to Energy Storage. II. Molten Salts: Data on Single and Multi-Component Systems, 1979.

[22] G.J. Janz, Molten Salts Data as Reference Standards for Density, Surface Tension Viscosity and Electrical Conductance: KNO3 and NaCl, *J. Phys. Chem. Ref. Data*, 9 (1980) 791-829.

[23] K.A. Tasidou, C.D. Chliatzou, M.J. Assael, K.D. Antoniadis, S.K. Mylona, M.L. Huber, W.A. Wakeham, Reference Correlations for the Viscosity of 13 Inorganic Molten Salts, *Journal of Physical and Chemical Reference Data*, 48 (2019).

[24] G.J. Janz, Thermodynamic and transport properties for molten salts: correlation equations for critically evaluated density, surface tension, electrical conductance, and viscosity data, *Journal of physical and chemical reference data*, 17 (1988).
[25] M.J.C. Lanca, M.J.V. Lourenco, F.J.V. Santos, V.M.B. Nunes, C.A. Nieto de Castro, Viscosity of molten potassium nitrate, *High Temperatures - High Pressures*, 33 (2001) 427 - 434.
[26] D. Tolbaru, R. Borcan, S. Zuca, Viscosity Measurements on Molten Salts with an Oscillating Cup Viscometer: Viscosity of Molten KNO3 and NaCl, *Berichte der Bunsengesellschaft für physikalische Chemie*, 102 (1998) 1387-1392.
[27] A. Schardey, J. Richter, H.A. Øye, Viscosity of Potassium Nitrate + Silver Nitrate Melt Mixtures, *Berichte der Bunsengesellschaft für physikalische Chemie*, 92 (1988) 64-68.
[28] Y. Abe, O. Kosugiyama, H. Miyajima, A. Nagashima, Determination of the viscosity of molten KNO3 with an oscillating-cup viscometer, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 76 (1980).
[29] G.J. Janz, G.R. Dampier, G.R. Lakshminarayanan, P.K. Lorenz, R.P.T. Tomkins, Molten Salts: Volume 1, Electrical Conductance, Density, and Viscosity Data, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 15 (1968).
[30] R.S. Dantuma, IV. Über die genaue Bestimmung des Koeffizienten der inneren Reibung von geschmolzenen Salzen, *Zeitschrift für anorganische und allgemeine Chemie*, 175 (1928) 1-42.
[31] V.G. Smotrakov, N.P. Popovskaya, V.A. Tereshchenko, *Zh. Prikl. Khim.*, 45 (1972) 2627.
[32] P.I. Protsenko, O.N. Razumovskaya, *Zh. Prikl. Khim.*, 38 (1965) 2355.
[33] S. Zuca, Viscosity of some molten nitrates, *Revue Roumaine de Chimie*, 15 (1970) 1277.
[34] S. Karpachev, *Zh. Fiz. Khim.*, 6 (1935) 1079.
[35] V.M.B. Nunes, M.J.V. Lourenço, F.J.V. Santos, C.A.N. de Castro, Viscosity of Molten Sodium Nitrate, *International Journal of Thermophysics*, 27 (2006) 1638-1649.
[36] V.M.B. Nunes, M.J.V. Lourenço, F.J.V. Santos, C.A. Nieto de Castro, Importance of Accurate Data on Viscosity and Thermal Conductivity in Molten Salts Applications, *Journal of Chemical & Engineering Data*, 48 (2003) 446-450.
[37] T. Bauer, N. Pfleger, D. Laing, W.-D. Steinmann, M. Eck, S. Kaesche, 20 - High-Temperature Molten Salts for Solar Power Application, in: F. Lantelme, H. Groult (Eds.) Molten Salts Chemistry, Elsevier, Oxford, 2013, pp. 415-438.
[38] L.R. White, T.H. Davis, Thermal Conductivity of Molten Alkali Nitrates, *The Journal of Chemical Physics*, 47 (1967) 5433-5439.
[39] R. Tufeu, J.P. Petitet, L. Denielou, B. Le Neindre, Experimental determination of thermal conductivity of molten pure salts and salt mixtures, *International Journal of Thermophysics*, 4 (1985) 315-330.
[40] Y. Nagasaka, A. Nagashima, The thermal conductivity of molten NaNO3 and KNO3, *International Journal of Thermophysics*, 12 (1991) 769-781.
[41] S. Kitade, Y. Kobayashi, Y. Nagasaka, A. Nagashima, Measurement of the thermal conductivity of molten KNO3 and NaNO3 by the transient hot-wire method with ceramic-coated probes, *High Temperatures - High Pressures*, 21 (1989) 219-224.
[42] S.E. Gustafsson, N.-O. Halling, R.A.E. Kjellander, Optical Determination of Thermal Conductivity with a Plane Source Technique, *Zeitschrift für Naturforschung A*, 23 (1968) 44-47.
[43] E. McLaughlin, The Thermal Conductivity of Liquids and Dense Gases, *Chemical Reviews*, 64 (1964) 389-428.
[44] A.G. Turnbull, The thermal conductivity of molten salts II Theory and results for pure salts, *Australian J. Appl. Sci.*, 12 (1961).
[45] X. Zhang, M. Fujii, Simultaneous Measurements of the Thermal Conductivity and Thermal Diffusivity of Molten Salts with a Transient Short-Hot-Wire Method, *International Journal of Thermophysics*, 21 (2000) 71-84.
[46] K. Kobayasi, N. Araki, Y. Lida, Thermophysical properties of molten salts as thermal energy storage materials, in: International Heat Transfer Conference 7, Munich, Germany, 1982, pp. 467 - 472.
[47] J. McDonald, H.T. Davis, Thermal conductivity of binary mixtures of alkali nitrates, *The Journal of Physical Chemistry*, 74 (1970) 725-730.

[48] T. Omotani, Y. Nagasaka, A. Nagashima, Measurement of the thermal conductivity of KNO3-NaNO3 mixtures using a transient hot-wire method with a liquid metal in a capillary probe, *International Journal of Thermophysics*, 3 (1982) 17-26.
[49] T. Omotani, A. Nagashima, Thermal Conductivity of Molten Salts, Hts and the LiNO3 NaNO3 System, Using a Modified Transient Hot-Wire Method, *Journal of Chemical and Engineering Data*, 29 (1984) 1-3.
[50] R. Santini, L. Tadrist, J. Pantaloni, P. Cerisier, Measurement of thermal conductivity of molten salts in the range 100–500°C, *International Journal of Heat and Mass Transfer*, 27 (1984) 623-626.
[51] H. Bloom, A. Doroszkowski, S.B. Tricklebank, Molten salt mixtures. IX. The thermal conductivities of molten nitrate systems, *Aust. J. Chem.*, 18 (1965) 1171-1176.
[52] B. Muñoz-Sánchez, J. Nieto-Maestre, J. González-Aguilar, J.E. Julia, N. Navarrete, A. Faik, T. Bauer, A. Bonk, M.E. Navarro, Y. Ding, N. Uranga, E. Veca, S. Sau, P. Giménez, P. García, J.I. Burgaleta, Round Robin Test on the Measurement of the Specific Heat of Solar Salt, *AIP Conference Proceedings*, 1850 (2017) 080017.
[53] M.Z. Malik, F. Musharavati, F.W. Ahmed, S. Khanmohammadi, A.G. Fernandez, Mathematical modeling of melting point and viscosity of a new molten salt for concentrating solar plant, *Journal of Thermal Analysis and Calorimetry*, (2021).
[54] Foosnæs T, Hafskjold B, Neerland G, Østvold T, Ø. HA, *SAND80-8191*, Thermal conductivity of nitrate mixtures, 1982.
[55] Q.-G. Zhao, S.-J. Liu, H. Guo, X. Chen, A theoretical model for predicting the thermal conductivity of binary molten salts, *International Journal of Heat and Mass Transfer*, 92 (2016) 639-642.
[56] G.J. Janz, U. Krebs, H.F. Siegenthaler, R.P.T. Tomkins, Molten Salts: Volume 3 Nitrates, Nitrites, and Mixtures: Electrical Conductance, Density, Viscosity, and Surface Tension Data, *Journal of Physical and Chemical Reference Data*, 1 (1972) 581-746.
[57] T. Bauer, D. Laing, R. Tamme, Characterization of sodium nitrate as phase change material, *International Journal of Thermophysics*, 33 (2012) 91-104.
[58] T. Bauer, A. Bonk, Semi-empirical Density Estimations for Binary, Ternary and Multicomponent Alkali Nitrate--Nitrite Molten Salt Mixtures, *International Journal of Thermophysics*, 39 (2018).
[59] G.J. Janz, Thermodynamic and transport properties for molten salts : correlation equations for critically evaluated density, surface tension, electrical conductance, and viscosity data, American Chemical Society and the American Institute of Physics, 1988.