Forschungsbericht 2022-04

Solar Salt – Thermal Property Analysis – Extended Version

Report on thermo-physical properties of binary $NaNO_3$-KNO_3 mixtures in a range of 55-65 wt% $NaNO_3$

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Solarkraftwerke (CSP), Thermische Energiespeicher (TES), Carnot Batterie, Flüssigsalz, Thermophysikalische Eigenschaften (Published in English)

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Solarsalz – Studie der Thermischen Eigenschaften – Erweiterte Version: Bericht über die thermo-physikalischen Eigenschaften von binären Mischungen auf Basis von $NaNO_3$-KNO_3 in einem Bereich von 55-65 gew% $NaNO_3$

Thermische Energiespeicherung spielt eine immer größer werdende Rolle bei der Implementierung von flexibel abrufbarer Stromerzeugung auf Basis fluktuierender Erneuerbarer Energien. Speicher auf Basis von Flüssigsalzen haben sich als vorteilhaft erwiesen zur Zwischenspeicherung von solar erzeugter Wärme in Solarkraftwerken. Solarsalz, eine Mischung von 60 gew% $NaNO_3$ und 40 gew% KNO_3 ist der Stand der Technik als Speicher- und Wärmetransfermedium in Zwei-Tank Speichersystemen mit einer Einsatztemperatur zwischen 290 °C und 565 °C in Kalt-, respektive Heißtank. Bei der Inbetriebnahme der Speicher werden die Einzelsalze $NaNO_3$ und KNO_3 geliefert und erst beim Vorschmelzen vermischt. In diesem Bericht wird ein neuer Ansatz verfolgt, in dem eine vorgemischte Solarsalz-Mischung im Big Bag (z.B. ~1000 kg) von der Firma SQM geliefert wird, die bereits Solarsalz-Zusammensetzung aufweist. Diese Vormischung würde den organisatorischen Aufwand während der Startphase eines Solarkraftwerks erheblich reduzieren. Die Genauigkeit, mit der die Solarsalzmischung vorgemischt wird, bestimmt hierbei die thermischen Eigenschaften des Salzes. In diesem Bericht werden Abweichungen von der idealen Solarsalz-Zusammensetzung auf wesentliche Eigenschaften der Mischungen untersucht. Hierbei liegt ein spezieller Fokus auf binären $NaNO_3$-KNO_3 Mischungen mit einem $NaNO_3$ Gehalt von 55-65 gew% $NaNO_3$, also geringen Abweichungen vom idealen 60 gew% Mischungsverhältnis. Es werden Abweichungen untersucht hinsichtlich des Schmelzverhaltens, der Wärmekapazität, Viskosität, Thermischen Leitfähigkeit sowie der Dichte der Mischungen in diesem Mischungsbereich.

Concentrating Solar Power (CSP), Thermal Energy Storage (TES), Carnot Battery, Molten Salt, Thermo-physical Properties

Alexander Bonk, Thomas Bauer
DLR, Institute for Engineering Thermodynamics, Stuttgart

Solar Salt – Thermal Property Analysis – Extended Version: Report on thermo-physical properties of binary $NaNO_3$-KNO_3 mixtures in a range of 55-65 wt% $NaNO_3$

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. 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. 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 report investigates the impact of these defined compositional changes for binary mixtures containing 55-65 wt% $NaNO_3$. The thermo-physical properties analysed are the heat capacity, viscosity, thermal conductivity and density, as well as the melting properties.

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Solar Salt – Thermal Property Analysis – Extended Version

Report on thermo-physical properties of binary $NaNO_3$-KNO_3 mixtures in a range of 55-65 wt% $NaNO_3$

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I. Introduction

This report is an extension of the report labelled DLR-FB-2021-19 and addresses a similar topic, but extends the study to a larger range of $NaNO_3$-KNO_3 compositions.

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 ±5 wt%. Consequently, the final salt composition can vary between 55 wt% $NaNO_3$ and 65 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 seven possible batches: one being the *standard* mixture (60-40 wt%), and the other mixtures containing ±1 wt%-, ±3 wt%, or ±5 wt%- $NaNO_3$. In our study, those mixtures were labelled according to their $NaNO_3$-weight fraction, e.g. SS60. It can be assumed that SS65 and SS55 represent the borderline cases, and there is a probability that they represent the content of the storage interior. In order to assess all possible compositions, we study the impact up to ±5 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. The left side represents pure KNO_3 and the right side pure $NaNO_3$. The mixture with 65 wt% $NaNO_3$ and 35 wt% KNO_3 has the highest liquidus temperature.

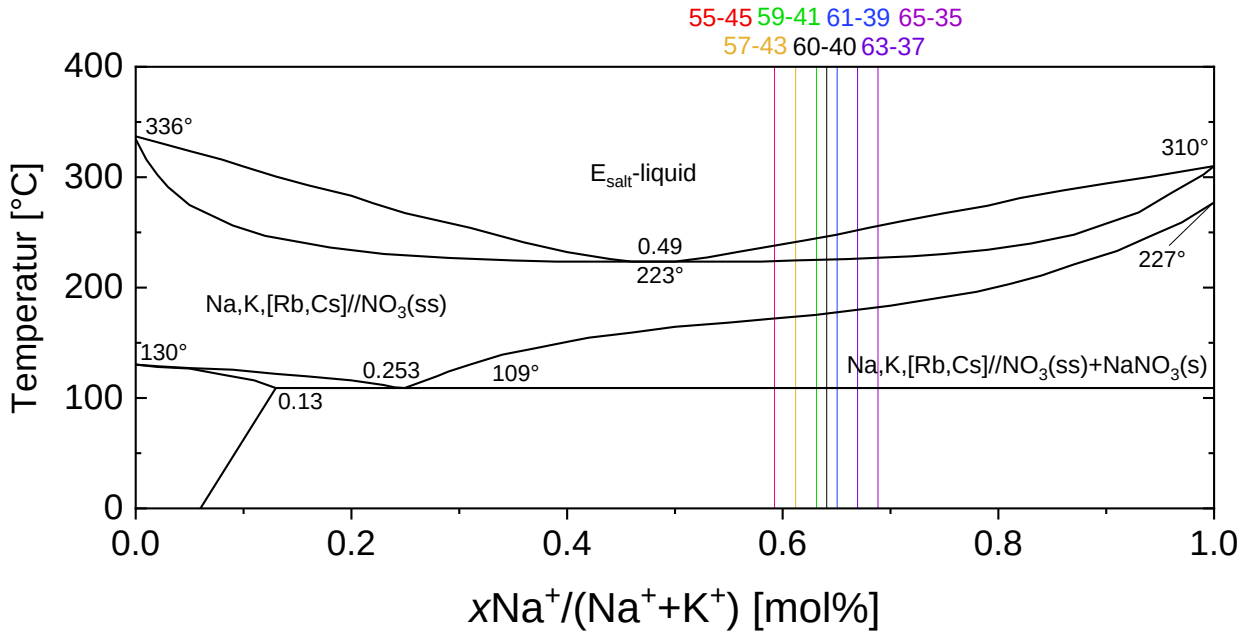

Figure 1 Phase diagram of $NaNO_3$ and KNO_3 reprinted from FactSage [3] data. The compositions of Solar Salt addressed in this work are marked and labelled in the plot.

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 in this work (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 presented in e.g. ref. [2]. Due to different nitrite levels depending on operation temperature and salt originally being supplied as nitrate, this report focuses on Solar Salt without nitrite. With regard to the fact, that nitrate- and nitrite levels will equilibrate at typical operating temperatures (e.g. at levels of

~5 mol% (~2.6 wt%) nitrite in Solar Salt at 565 °C), it is reasonable and sufficient to estimate deviations using standard Solar Salt without nitrite in this report.

The KNO_3-$NaNO_3$ system has been studied in more than 40 papers since 1857. Overview papers have been written by Carveth [4] (within a ternary $NaNO_3$-KNO_3-$LiNO_3$ system), Rogers and Janz [5], Kofler [6] and Bergman and Berul [7]. Details of the phase diagram are not yet fully agreed upon, e.g. a discussion whether this system is a continuous solid solution or eutectic type can be found e.g. in Kofler's work [6]. 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, 5.7 °C and 9.6 °C when the weight fraction of $NaNO_3$ increases to 61, 63 and 65 wt%, respectively. The melting point in turn decreases by -1.7 °C, -5 °C, and -8.2 °C when the $NaNO_3$ weight fraction is 59, 57 and 55 wt%, respectively.

From DLR experiences, a change of a few degree in melting temperature is similar to the accuracy of differential scanning calorimetry (DSC) measurements (see e.g. the discussion in ref. [2]). 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. If the actual Solar Salt mixture has been mixed with ±5 wt% accuracy, the maximum offset of the melting temperature will be in the range of ±3.9 %. For the mixture SS65, it has to be considered that the liquidus increases by 10 °C. Either a smaller safety margin can be accepted or the minimum cold tank temperature can be raised to account for this change in melting temperature.

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

Composition	Abbreviation	Weight content [wt%]		Melting Point	Deviation
		$NaNO_3$	KNO_3	[°C]	[%]
1	**SS55**	55	45	238.1	-3.33
2	**SS57**	57	43	241.3	-2.03
3	**SS59**	59	41	244.6	-0.69
4	**SS60**	60	40	246.3	0.00
5	**SS61**	61	39	248	0.69
6	**SS63**	63	37	252	2.31
7	**SS65**	65	35	255.9	3.90

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 [8]. Values of Carling [9] are slightly decreasing over temperature which, thermodynamically, is not viable, as e.g. described by d'Aguanno [10]. 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, often referred to as "salt creeping". It refers to a phenomenon where a thin film of molten salt 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 reasonable 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 dependences. D'Aguanno and co-workers [10] 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.

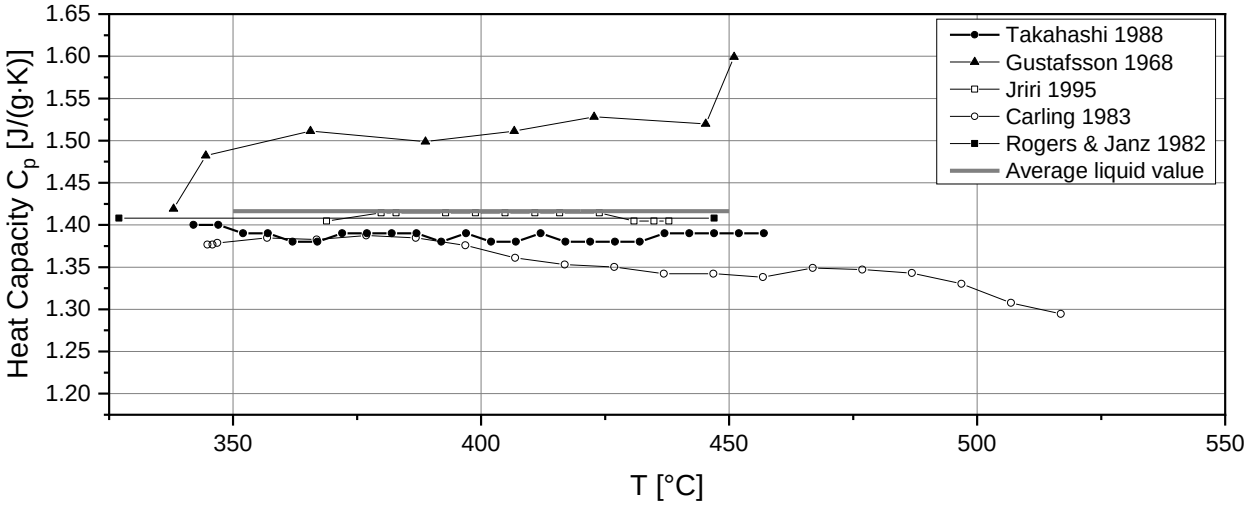

Figure 2 Heat capacity of KNO_3 in the liquid state from different literature sources ([5, 9, 11-13]) as well as mathematical average value obtained by the OriginPro software [14].

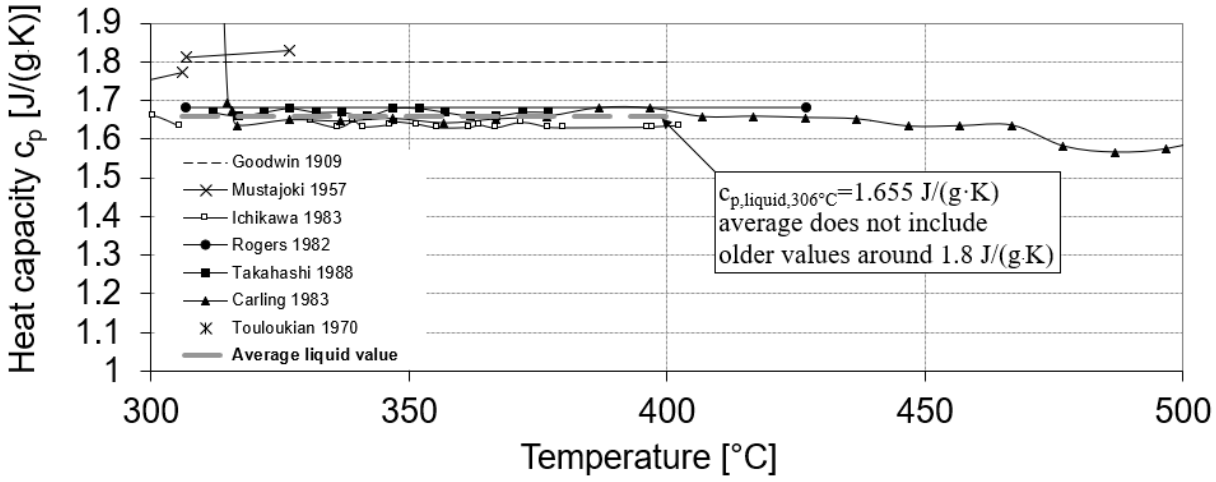

Figure 3 Heat capacity of $NaNO_3$ between 300 °C and 500 °C from different literature sources.[5, 9, 11, 15-18]

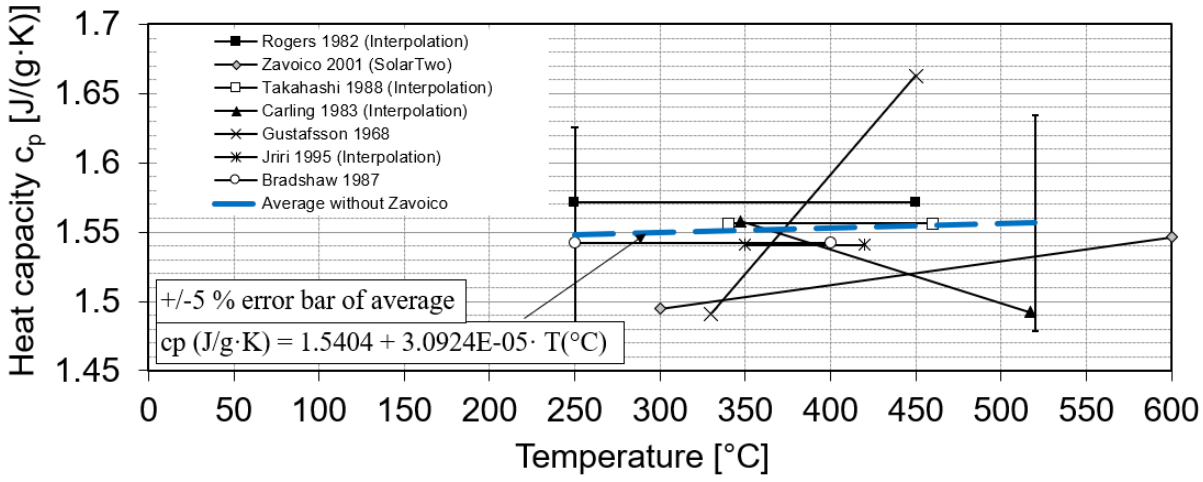

Figure 4 Heat capacity of the standard Solar Salt mixture, reprinted from ref. [8].

For the pure salts $NaNO_3$ and KNO_3 there has been consensus on the heat capacity from work by a variety of authors. Data on KNO_3 (Figure 2) has been published by e.g. Takahashi [11], Carling [9], Gustafsson [12], Jriri [13] and is shown in Figures 2. Data on $NaNO_3$ (Figure 3) was published by Rogers [5], Carling [9], Takahashi [11], Goodwin [15], Mustajoki [16], Ichikawa [17], and Touloukian[18]. From the gained literature data, we extracted an average value for the heat capacity of the single salts and gained the heat capacities in their liquid state. The heat capacity of KNO_3 is expressed by:

$$\boldsymbol{c_{p,KNO_3}(334-565°C) = 1416\ [J/(g \cdot K)]} \quad 1$$

and for $NaNO_3$ (see Figure 3):

$$\boldsymbol{c_{p,NaNO_3}(310-565°C) = 1655\ [J/(g \cdot K)]} \quad 2$$

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 weight fraction and heat capacity of the individual salts [10, 19]. With the assumption of a constant heat capacity of the individual salts, it is possible to calculate the heat capacity of Solar Salt and other mixtures with the weight fraction x and the heat capacity c_p of the two salts $NaNO_3$ and KNO_3:

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

For a perfectly mixed salt with Solar Salt composition (SS60) the linear additivity rule suggests a heat capacity of 1.559 J/(g·K) at 565 °C using single salt heat capacities of 1.416 J/g·K (KNO_3) and 1.655 J/g·K ($NaNO_3$). This is in line with the average literature values (1.558 J/g·K at 565 °C, calculated from the correlation presented in Figure 4).

Table 2 Heat capacity of Solar Salt compositions with varying mixing ratio (±5 wt%).

Abbreviation	Weight content [wt%]		Cp	Deviation
	$NaNO_3$	KNO_3	[J/(g·K)]	[%]
SS55	55	45	1.547	-0.761
SS57	57	43	1.552	-0.457
SS59	59	41	1.557	-0.152
SS60	60	40	1.559	0.000
SS61	61	39	1.562	0.152
SS63	63	37	1.567	0.457
SS65	65	35	1.571	0.761

The heat capacity of a mixture with ±5 wt% $NaNO_3$-fraction only varies slightly between 1.571 and 1.547 J/(g·K), respectively. The maximum deviation of the heat capacity as opposed to the ideal Solar mixture is ± 0.736 %. This suggests, that neither theoretical nor practical limitations

would arise from the use of either of the 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 2 % 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 ±0.761 %, and is about 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 [20, 21]. 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 [22]. 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].

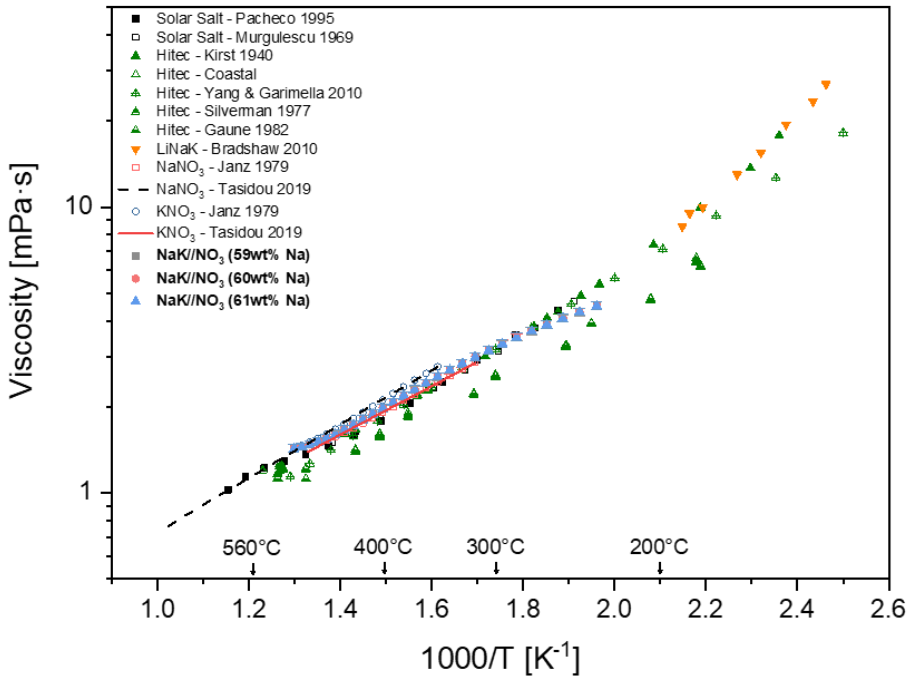

Figure 5 Viscosity data of reference molten salts (Solar Salt, Hitec (Na,K//NO_2,NO_3) and a LiNaK//NO_3 mixture; reprinted from ref. [2]) from literature data, as well as single salts $NaNO_3$ and KNO_3 from ref. [23]. Viscosity values calculated for SS59, SS60 and SS61 according to Eq. 6 and literature 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 above the liquidus 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.[24]" (all cited from [2]).

For the single salts, recommendations for datasets have been published by Tasidou [25] 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 [24]) were selected as the recommended reference dataset, consequently forming the recommendations in the 1988 publication of Janz.[26] These measurements were included in the primary dataset. We also included the measurements of Lanca et al., [27] Tolbaru et al., [28] Schardey et al. [29] and Abe et al. [30], which were obtained in oscillating body viscometers […]."

For $NaNO_3$ the recommended data sets date back to Janz' work in 1988 [26], which was reprinted from his 1968-report [31] and dates back to work by Dantuma [32] in 1928. This dataset was complemented with measurements from Smotrakov *et al.* [33], Protsenko [34] as well as Zuca [35], Karpachev [36] and Nunes [37] 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 [25] (expressed by an exponential function of the type $\eta = A \cdot e^{B/RT(K)}$) and Janz [23] (expressed by a polynomial function) yield almost identical data and are both shown in Eq. 4-7.

Tasidou 2019	$\boldsymbol{\eta_{NaNO_3} = 0.1037 \cdot e^{\frac{16250.7}{RT(K)}}}$	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 [19] suggested that the viscosity if ideal molten salt mixtures can be approximated from the molar quantities and viscosities of the single salts according to:

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

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 the mixtures with up to ±5 wt% $NaNO_3$ content at the critical lower temperature limit of 290 °C. It can be seen that deviation is small, with a maximum deviation of about ±0.661 %.

Table 3 Dynamic viscosity of SS55, SS57, SS59, SS60, SS61, SS63, and SS65 from calculations according to Eq. 8 and the temperature correlations from Janz [23].

Abbreviation	Weight content [wt%]		η @ 290°C	Deviation
	$NaNO_3$	KNO_3	[mPa·s]	[%]
SS55	55	45	3.475	0.661
SS57	57	43	3.465	0.390
SS59	59	41	3.456	0.121
SS60	60	40	3.452	0.000
SS61	61	39	3.447	-0.146
SS63	63	37	3.438	-0.410
SS65	65	35	3.429	-0.673

4. Thermal Conductivity

The limited number of literature sources featuring the thermal conductivity of molten nitrate salts, displays how challenging and erroneous experimental measurements are. The differences among different sets of data can be as high as 25% for a number of reasons, which will be presented throughout this chapter. Presented values for the single salts $NaNO_3$ and KNO_3 have either positive or negative trends for $d\lambda/dT$ [38]. Bauer [39] summarized thermal conductivity values of $NaNO_3$ and some of the data is reprinted inFigure 6. White and Davis [40] proposed a temperature correlation for the thermal conductivity of $NaNO_3$ according to Eq. 9, while others propose that the thermal conductivity of $NaNO_3$ is constant over temperature (see ref. [41]) with a value of 0.512 W/(m·K) (between 320 and 399.7 °C).

$$\boldsymbol{\lambda_{NaNO_3} = 0.419 + 4.77 \cdot 10^{-4} T} \quad \text{for } 340 \leq T \leq 420\ ^\circ C \qquad 9$$

Overall, the data by McLaughlin and Omotani showed the highest reproducibility, but the deviation of all measurements is in the range of 10 %.

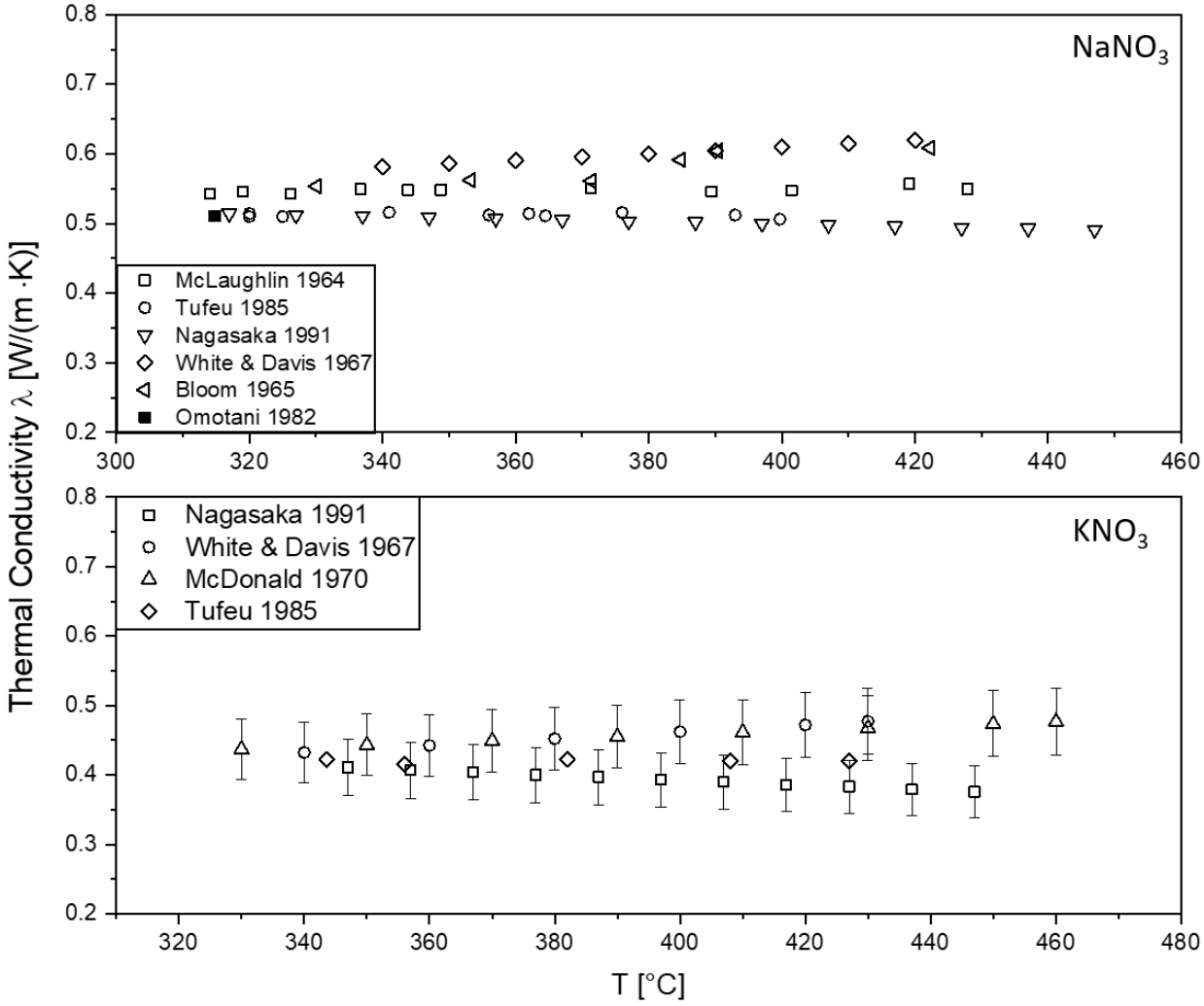

Figure 6 Thermal Conductivity of $NaNO_3$ (top) and KNO_3 (bottom) from different literature sources. [40-45] Error bars in the bottom graph equal 10% measurement error for clarity.

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

$$\boldsymbol{\lambda_{KNO_3} = 0.2627 + 4.98 \cdot 10^{-4} T} \quad \text{for } 340 \leq T \leq 430\ °C \qquad 10$$

, while Tufeu [41] proposes a constant value of 0.4202 W/(m·K) between 343.6 °C and 427 °C. Nagasaka [43] [43] states that thermal conductivity values of KNO_3 rather decrease as a function of temperature.

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 % [46]. 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 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 λ. The thermal conductivity is obtained as follows:

$$\boldsymbol{\lambda = a \cdot \rho \cdot c_p} \qquad 11$$

, where a is the thermal diffusivity, ρ is the density and c_p is the heat capacity. The thermal conductivity of molten salt mixtures typically changes over composition, e.g. McDonald [45] measured a linear relation in a varying $NaNO_3$-KNO_3 system, while Omotani [47] found a local minimum in thermal conductivity (Figure 7). It has been well established that 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 quasi-crystalline lattice of the molten salt. This effect increases the salt resistance to the lattice vibration modes, which are transferring heat energy (see ref. [48]).

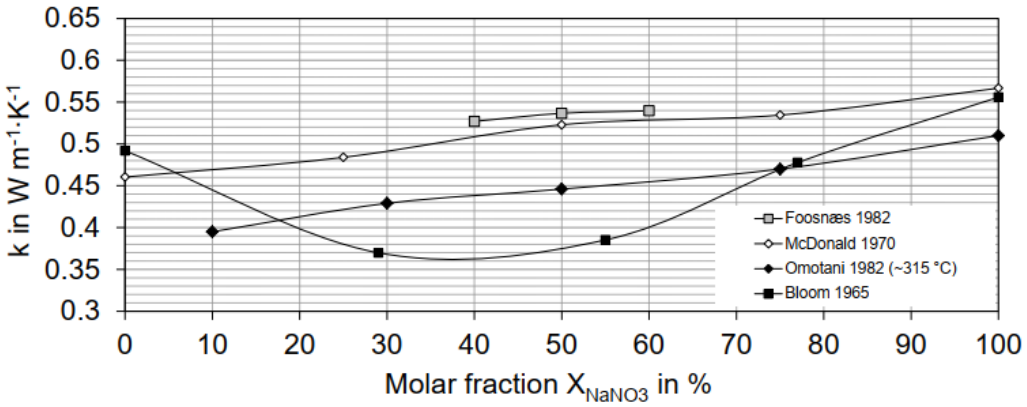

Figure 7 Literature values of the thermal conductivity of the system KNO_3-$NaNO_3$ at 340 °C except data at 315 °C from Omotani [44, 45, 47, 49] (figure and caption reprinted from ref. [8])

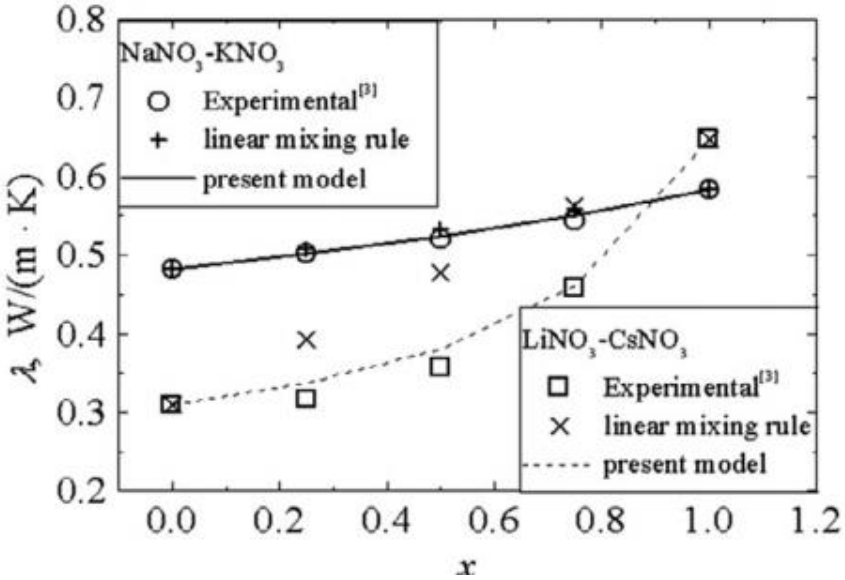

Figure 8 Figure of of thermal conductivity of $NaNO_3$-KNO_3 from Zhao (cross symbols and solid line) [50], as well as McDonald (reprinted from ref [45])

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 other techniques. Zhao *et al.* [50] 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 λ 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 λ vs. composition can be expressed by:

$$\boldsymbol{\lambda_{Na_xK_{1-x}NO_3}(565\,^{\circ}C) = 0.483 + 0.1047 \cdot x} \qquad 12$$

, where *x* is the molar fraction of Na in a mixture of $Na_xK_{1-x}NO_3$ [50]. For the varying compositions of Solar Salt and the molar quantities, the thermal conductivity values are very similar with a maximum deviation of -0.92 % at a composition of 55-45 wt%, and +0.9 % at 65-35 wt% $NaNO_3$-KNO_3 respectively (see values in Table 4).

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

Abbreviation	Weight content [wt%]		k	Deviation
	$NaNO_3$	KNO_3	[W/(m K)]	[%]
SS55	55	45	0.545	-0.92
SS57	57	43	0.547	-0.55
SS59	59	41	0.549	-0.18
SS60	60	40	0.55	0.00
SS61	61	39	0.551	0.18
SS63	63	37	0.553	0.54
SS65	65	35	0.555	0.90

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 almost two orders of magnitude above the deviation due to a change in composition of ±5 %.

5. Density

Recommended density values of single salts and the $NaNO_3$-KNO_3 system are given by Janz [51]. 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 reaction with the gas phase and containers, as well as accuracy of the salt-measurement equipment, temperature measurement and temperature uniformity). Figure 9 shows the density of $NaNO_3$ vs. temperature as an example [52].

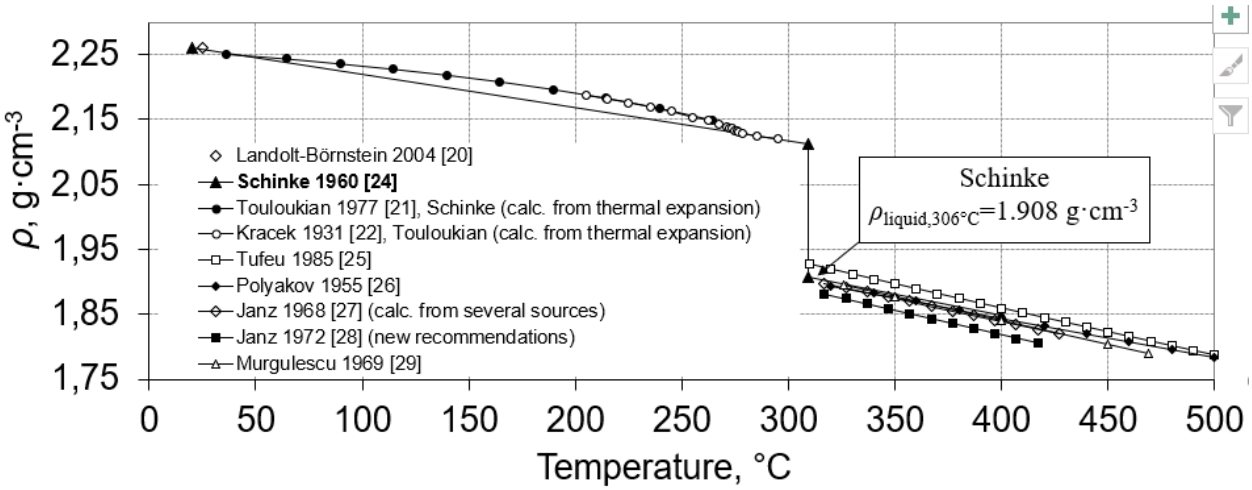

Figure 9 Literature data of the density of $NaNO_3$ in the solid (left below 306 °C) and liquid (right above 306 °C) phase, reprinted from ref. [8].

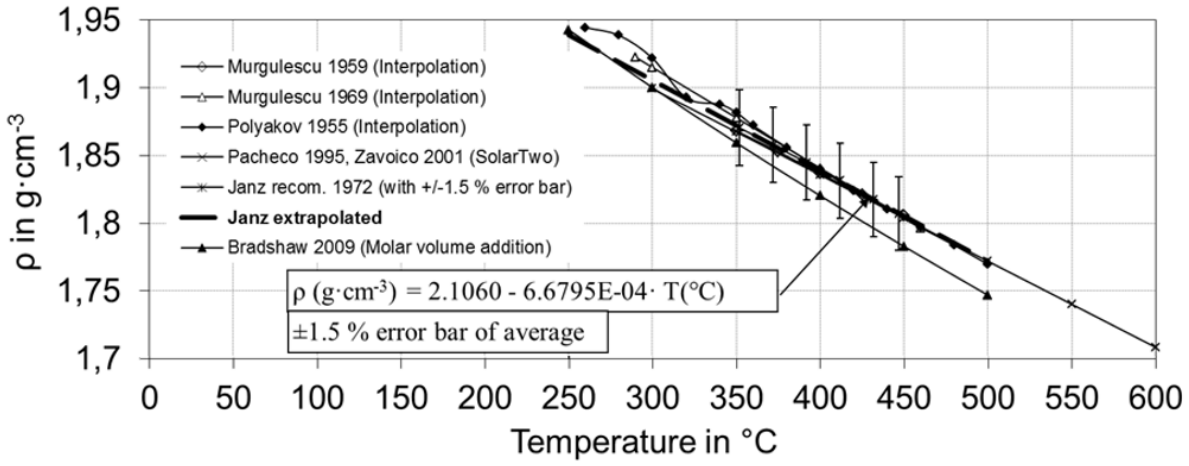

Figure 10 Literature data of the density of Solar Salt reprinted from ref. [8].

The correlation of density vs. composition and temperature of nitrate-nitrite mixtures has been assessed by the authors of this work recently and the work was published in ref. [53]. 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. [54]). 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 SS55 and SS65 values vs. SS60 is lower than ±0.1 % (Table 5).

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

Abbreviation	Weight content [wt%]		ρ	Deviation
	$NaNO_3$	KNO_3	[kg/m³]	[%]
SS55	55	45	1712.34	-0.059
SS57	57	43	1712.75	-0.035
SS59	59	41	1713.15	-0.012
SS60	60	40	1713.35	0.000
SS61	61	39	1713.55	0.012
SS63	63	37	1713.95	0.035
SS65	65	35	1714.34	0.058

III.Summary and Conclusions

This report has evaluated the possible impact of slight variations of Solar Salt composition within ±5 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. One exception is the liquidus temperatures with a deviation of ±3.9 %. All of the results indicate that operation with Solar Salt with a deviation of ±5% 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 ±5 wt%, extrapolated from different literature sources, and the deviation amongst them.

	SS55	SS57	SS59	SS60	SS61	SS63	SS65
T_m [°C]	238.1	241.3	244.6	246.3	248	252	255.9
Deviation	-3.3 %	-2.0 %	-0.7 %	-	0.7 %	2.3 %	3.9 %
c_p [J/(g K)]	1.547	1.552	1.557	1.559	1.562	1.567	1.571
Deviation	-0.76 %	-0.46 %	-0.15 %	-	0.15 %	0.46 %	0.76 %
η [mPa s] @290°C	3.475	3.465	3.456	3.452	3.447	3.438	3.429
Deviation	0.66 %	0.39 %	0.12 %	-	-0.15 %	-0.41 %	-0.67 %
λ [W/(m K)]	0.545	0.547	0.549	0.550	0.551	0.553	0.555
Deviation	-0.92 %	-0.55 %	-0.18 %	-	0.18 %	0.54 %	0.90 %
ρ [kg/m³] @565°C	1712.34	1712.75	1713.15	1713.35	1713.55	1713.95	1714.34
Deviation	-0.06 %	-0.04 %	-0.01 %	-	0.01 %	0.04 %	0.06 %

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 ±5 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 (+5 % or -5 % 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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