

Semi-empirical density estimations for binary, ternary and multicomponent alkali nitrate-nitrite molten salt mixtures

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Abstract:

For sensible thermal energy storage in Concentrating Solar Power (CSP) plants, a molten salt mixture of 60 wt% sodium nitrate (NaNO_3) and 40 wt% potassium nitrate (KNO_3), known as Solar Salt, is commonly utilized. The paper presents semi-empirical estimation results of the density of Solar Salt and alternative molten salt mixtures with low melting temperatures in a range from 70 °C to 140 °C. These mixtures are Hitec, HitecXL, LiNO_3 - KNO_3 - NaNO_3 and a multi-component mixture. The paper shows that density values of mixtures can be closely predicted from single salt densities. The paper examines different estimation rules for mixtures. The quasilinear volumetric additivity rule (QVAR) is known for ternary reciprocal systems. For the first time, the presented work extends the QVAR to multicomponent mixtures. Temperature dependent densities of selected salt mixtures of the system $\text{Ca, Li, K, Na}/\text{NO}_2, \text{NO}_3$ were estimated. Estimations are motivated by a fast and reliable method compared to time-consuming and error-prone measurements of several mixtures.

Keywords: Concentrating Solar Power (CSP), Hitec, HitecXL, multi-component salts, quasilinear volumetric additivity rule

Highlights:

- Densities of alternative salt mixtures for line-focusing CSP systems are validated
- For the first time the quasilinear volumetric additivity rule is extended and applied to multicomponent nitrate/nitrite mixtures
- Consistent liquid density values of eight salts with Ca, K, Li, Na cations and NO_2 and NO_3 anions are given
- Obtained density values are correlated to the molar mass and temperature
- The paper confirms close prediction of liquid densities of mixtures by estimations from single salt densities

43 **Nomenclature**

44	a	Density coefficient	g/cm^3
45	b	Temperature dependent density coefficient	$\text{g}/(\text{cm}^3\text{K})$
46	V	Molar volume	cm^3/mol
47	V_i	Molar volume of i	cm^3/mol
48	M	Molecular weight	g/mol
49	M_i	Molecular weight of i	g/mol
50	ρ	Density	g/cm^3
51	X_i	Mol fraction of i	1
52	T	Temperature	$^{\circ}\text{C}$
53	E	Deviation of estimated density value	%
54			

Introduction

At present, the two-tank molten salt storage system is the established commercially available concept for solar thermal power plants, also known as Concentrating Solar Power (CSP). The thermal energy storage (TES) based on molten salt makes it possible to meet the intermediate load profile with dispatchable power generation. Different types of TES systems are distinguished: sensible heat, latent heat and chemical heat. In sensible heat storage systems the heat capacity of a solid (e.g. ceramic) or liquid (e.g. molten salt) material is utilized to store thermal energy. Due to their low vapour pressure and ease of operation, as well as comparatively high thermal stability and low costs, molten salts are suitable heat storage media [1]. Almost exclusively a non-eutectic salt mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate is utilized. This mixture is commonly called Solar Salt. This non-eutectic mixture has a melting range rather than a melting point. The typical operation range is from 290 °C to 560 °C (limited by the thermal stability). The lower limits of molten salt utilization are defined by the melting temperature (or liquidus). The upper limit is defined by factors such as a thermal decomposition process, a high vapour pressure or a high corrosion rate of the construction material.

In recent years molten salts have been used not only as heat storage medium, but also as heat transfer fluid. CSP power tower systems utilize Solar Salt as TES medium and heat transfer fluid for the absorption of solar heat in the central receiver. At the time of writing, there is also some research and development for line-focusing CSP systems to replace the current heat transfer fluid synthetic thermal oil by a molten salt mixture. The major line-focusing CSP systems are currently parabolic troughs, but there are also some demonstrations on linear Fresnel collectors. For molten salt heat transfer applications, freezing of salt should not occur and is a major concern of such systems. Unlike power tower systems, which can be drained gravitationally, line-focusing fields are large area installations with horizontal pipes with a higher risk of freezing compared to towers. Hence, for line focusing technology, alternative molten salt mixtures with a lower melting temperature are developed. These are mainly ternary molten salt mixtures based on the cations Ca, K, Li and Na and the anions NO₂ and NO₃ which are discussed within the presented paper. Furthermore, alternative molten salt mixtures can have the advantage of a larger operation window with lower melting temperatures and similar thermal stabilities as Solar Salt. Assuming the same amount of salt m and a constant heat capacity c_p , a larger temperature window ΔT directly leads to a higher TES capacity Q ($Q = m \cdot c_p \cdot \Delta T$). Hence, TES investment costs can be reduced by an enlarged operation window.

Thermal properties of molten salts, such as the density, are important for modelling and thermal design of the whole system. Density values are used to calculate the mass flow from the volume flow measurement of molten salt through pipes, but also to calculate the volumetric storage capacity. The density of molten salt is typically measured by Archimedean type methods, but other methods are also feasible. These are dilatometric, flotation, maximum bubble and pycnometric methods [2,3,4].

Temperature dependent density data of single salts are partly available from Janz [5]. Some single salt density values are not available mainly due to the instability of these salts (e.g., LiNO₂, Ca(NO₂)₂, Ca(NO₃)₂). Salt mixtures can have significantly lower melting temperatures compared to single salts. In order to estimate the density of these

low temperature mixtures, it is important to predict the unknown single salt properties to extrapolated values and determine densities of mixtures at lower temperatures [3,6]. For other substances than salts, such as organic-water mixtures and molten metals, some models exist to predict the density of mixtures from the composition, single substance densities and other parameters (e.g., excess volume) [7,8]. However, published work on the mixing behaviour of molten salts is limited. Work at Oak Ridge National Laboratory (ORNL) and Sandia National Laboratories found that the density of a molten salt mixture could be predicted by weighing the molar volumes of each of the salt constituents of the mixture by their molar fraction and summing [3,9,10,11]. This simple linear addition is also known as ideal mixture behaviour, Vegard's law and Temkin model [7,12,13]. However, some deviations from the simple rule for the addition of molar volume rule can occur [11]. Bloom, Blander, Ambrosek and others distinguished between ideal and non-ideal molten salt systems. Bloom and Blander provide examples of ideal and non-ideal binary systems [4,10]. For a non-ideal mixture typically the "excess volume" describes the deviation from linear additivity [7,12]. Powers et al. measured small positive excess volume values for the systems KNO_3 - NaNO_3 and LiNO_3 - NaNO_3 with maximum values of $0.07 \text{ cm}^3/\text{mol}$ at equimolar compositions [14]. Work at ORNL and Sandia on $\text{Ca}(\text{NO}_3)_2$, KNO_3 , LiNO_3 and NaNO_3 binary mixtures also showed that the deviation from ideal mixing is small. Hence, the density of these mixtures is accurately approximated by the linear addition of the molar volumes [11]. Bradshaw measured the density of the ternary eutectic KNO_3 - LiNO_3 - NaNO_3 and several quaternary Ca,K,Li,Na/NO_3 mixtures. He found that the molten salt mixtures showed an ideal mixing behaviour. The molar volume of multi-component mixtures could be estimated using the linear volumetric additivity rule [3]. Grin'ko and Protsenko studied the density of the ternary reciprocal system $\text{K,Ca/NO}_2,\text{NO}_3$. They found that melts of the system $\text{K,Ca/NO}_2,\text{NO}_3$ have random ion distributions, and their molar volumes can be estimated on the basis of ideal mixing behaviour [12].

It can be seen that nitrate mixtures based on the cations Ca, K, Li and Na have been previously assessed. However, there is limited work on the temperature dependent density of mixtures containing mixed NO_2 and NO_3 anions. Overall, the development and assessment of thermal estimation methods to predict densities of salt mixtures play a crucial role for the advancement of molten salt technology using alternative and optimised salt mixtures.

1. Properties of single salts and definition of salt mixtures

Table 1 gives temperature dependent density data of single salts from Janz in 1988 [5]. Molar weight data are from the CRC Handbook of Chemistry and Physics [14]. Janz does not provide all density values of single salts. For example (water-free) $\text{Ca}(\text{NO}_3)_2$ is thermally unstable above the melting temperature of about 560 °C and data of $\text{Ca}(\text{NO}_2)_2$ and LiNO_2 density data are also not provided by Janz [5].

Table 1. Temperature dependent densities of single salts [5,15].

Salt	Melting Temp. $T_m/\text{°C}$	Mol. Weight $M/(\text{g mol}^{-1})$	Equation $\rho/(\text{g cm}^{-3})$	Accuracy	Temp. range $T/\text{°C}$
$\text{Ca}(\text{NO}_2)_2$	392	132.089	N/A	N/A	N/A
$\text{Ca}(\text{NO}_3)_2$	561	164.087	N/A	N/A	N/A
KCl	771	74.551	$\rho(T) = 1.9766 - 5.831 \times 10^{-4} \cdot (T/\text{°C})$	$\pm 0.5 \%$	780-939
KNO_2	438	85.104	$\rho(T) = 1.985 - 6.67 \times 10^{-4} \cdot (T/\text{°C})$	$\pm 1.5 \%$	440 -500
KNO_3	334	101.103	$\rho(T) = 2.1087 - 7.235 \times 10^{-4} \cdot (T/\text{°C})$	$\pm 0.5 \%$	347 -457
LiCl	610	42.394	$\rho(T) = 1.7660 - 4.328 \times 10^{-4} \cdot (T/\text{°C})$	$\pm 0.5 \%$	621-781
LiNO_2	222	52.947	N/A	N/A	N/A
LiNO_3	253	68.946	$\rho(T) = 1.919 - 5.46 \times 10^{-4} \cdot (T/\text{°C})$	$\pm 1.5 \%$	272-441
NaNO_2	284	68.996	$\rho(T) = 2.022 - 7.46 \times 10^{-4} \cdot (T/\text{°C})$	$\pm 3 \%$	284-450
NaNO_3	306	84.995	$\rho(T) = 2.1247 - 7.15 \times 10^{-4} \cdot (T/\text{°C})$	$\pm 0.5 \%$	310-370

Table 2 classifies salt mixtures in terms of the number of ions. For example sodium nitrate NaNO_3 consists of the cation Na and anion NO_3^- . The table lists some important salt mixtures, but many more systems can be found in literature [16]. Selected mixtures of the presented work are underlined in column four of Table 2. Reciprocal systems do not have a common ion. They are characterized by at least two cations and at least two anions (e.g. $\text{K,Na//NO}_2,\text{NO}_3$). Salt mixtures of reciprocal salt systems can be prepared by different combination of single salts. Hence, they can be clearly defined by a list of cations and a list of anions, which are separated by the symbol “//” (see column three in Table 2).

Table 2. Classification of salt systems [17]. Considered mixtures in this work are underlined in column four.

Ion No.	System Classification	Example System [#]	Selected Mixture [#]
2	Single salt	NaNO_3 $T_m = 306\text{ }^\circ\text{C}$ KNO_3 $T_m = 334\text{ }^\circ\text{C}$	Not selected
3	Binary system, common anion	$\text{KNO}_3\text{-NaNO}_3$ (or K,Na//NO_3)	<u>Solar Salt:</u> $T_{\text{liquidus}} = 260\text{ }^\circ\text{C}$ $\text{KNO}_3\text{-NaNO}_3$ (40-60 wt%),
3	Binary system, common cation	$\text{NaNO}_2\text{-NaNO}_3$ (or $\text{Na//NO}_2,\text{NO}_3$) $T_{\text{min}} = 230\text{ }^\circ\text{C}$	Not selected
4	Ternary additive, common anion	$\text{Ca(NO}_3)_2\text{-KNO}_3\text{-NaNO}_3$ (or Ca,K,Na//NO_3)	<u>HitecXL:</u> $T_{\text{eu}} = 135\text{ }^\circ\text{C}$ $\text{Ca(NO}_3)_2\text{-KNO}_3\text{-NaNO}_3$ (42-43-15 wt%)
4	Ternary additive, common anion	$\text{KNO}_3\text{-LiNO}_3\text{-NaNO}_3$ (or K,Li,Na//NO_3)	<u>LiNaK-Nitrate:</u> $T_{\text{eu}} = 120\text{ }^\circ\text{C}$ $\text{LiNO}_3\text{-KNO}_3\text{-NaNO}_3$ (30-52-18 wt%)
4	Ternary reciprocal	$\text{K,Na//NO}_2,\text{NO}_3$	<u>Hitec:</u> $T_{\text{eu}} = 142\text{ }^\circ\text{C}$ $\text{KNO}_3\text{-NaNO}_2\text{-NaNO}_3$ (53-40-7 wt%)
5	Quaternary addit., common anion	Ca,K,Li,Na//NO_3 ; $T_{\text{min}} = 90\text{-}110\text{ }^\circ\text{C}$	Not selected
5	Quaternary reciprocal	$\text{Li,Na,K//NO}_2,\text{NO}_3$; $T_{\text{min}} = \sim 80\text{ }^\circ\text{C}$	Not selected
6	Quinary reciprocal	$\text{Ca,Li,Na,K//NO}_2,\text{NO}_3$	<u>CaLiNaK-NO23:</u> $T_{\text{min}} = \sim 70\text{ }^\circ\text{C}$; $\text{LiNO}_3\text{-Ca(NO}_3)_2\text{-NaNO}_2\text{-KNO}_2$ (24.6-13.6-16.8-45.0wt%)

[#] Melting temperature T_m ; Liquidus temperature T_{liquidus} ;

Eutectic melting temperature T_{eu} ; Minimum melting temperature T_{min}

2. Theory and methodology

By far the largest number of salt systems follows a linear density correlation related to the temperature (Equation 1) [5].

$$\rho(T) = a - b \cdot T \quad (1)$$

The molar volume, typically in cm³/mol, is given by the molecular weight M divided by the density (Equation 2).

$$V(T) = \frac{M}{\rho(T)} \quad (2)$$

Inserting Equation 1 in Equation 2 gives Equation 3.

$$V(T) = \frac{M}{a - b \cdot T} \quad (3)$$

Molar volume values of Eq. 3 may be approximated by a second order polynomial (Equation 4) with very small deviations (e.g., for the Hitec mixture 145 – 550 °C with a deviation of ± 0.02 %). A simpler linear fit is less accurate (e.g., for the Hitec mixture with a deviation of ± 0.4 %).

$$V(T) \approx A + B \cdot T + C \cdot T^2 \quad (4)$$

Different authors found that the density of many salt mixtures could be closely predicted by the sum of the molar volumes of each of the salt constituents V_i , weighted by the mole fraction X_i (Equation 5)[3,11]. In this text Eq. 5 is called the “**volumetric additivity rule (VAR)**”. The volumetric additivity implies that the volume of a mixtures equals the sum of the volumes of the pure components of which the mixture is compromised [3,18]. Compared to some other work [19], mixtures in the present work are considered ideal and an additional excess volume term in Eq. 5 is not included. In order words, for $V^E = 0$, the equation reduces to a simple linear combination of the molar volumes. As mentioned earlier, this assumption is referred to as ideal solution or Vegard’s law or Temkin model [3,7,11,12].

$$V(T) = \sum_{i=1}^N X_i \cdot V_i(T) + V^E(T, X_i) \quad (5)$$

The density of the mixture is obtained by Eq. 2 using the volume of the mixture (Eq. 5) and the molar weight of the mixture M from Equation 6, where M_i are the molecular weights and X_i are the molar fractions of the single salts or ions.

$$M = \sum_{i=1}^N X_i \cdot M_i \quad (6)$$

In the following the simplest reciprocal system is selected which is a ternary reciprocal system. It will be shown that the introduced VAR method cannot be simply applied to reciprocal systems. We discuss as an example the system K,Li//Cl,NO₃. Figure 1 shows the phase diagram of this system [20]. At 367 °C there are several literature density values available and this phase diagram has a large liquid area at 367 °C to select different compositions. Hence, this temperature was selected as one example to show the ambiguity of the VAR method for ternary reciprocal systems.

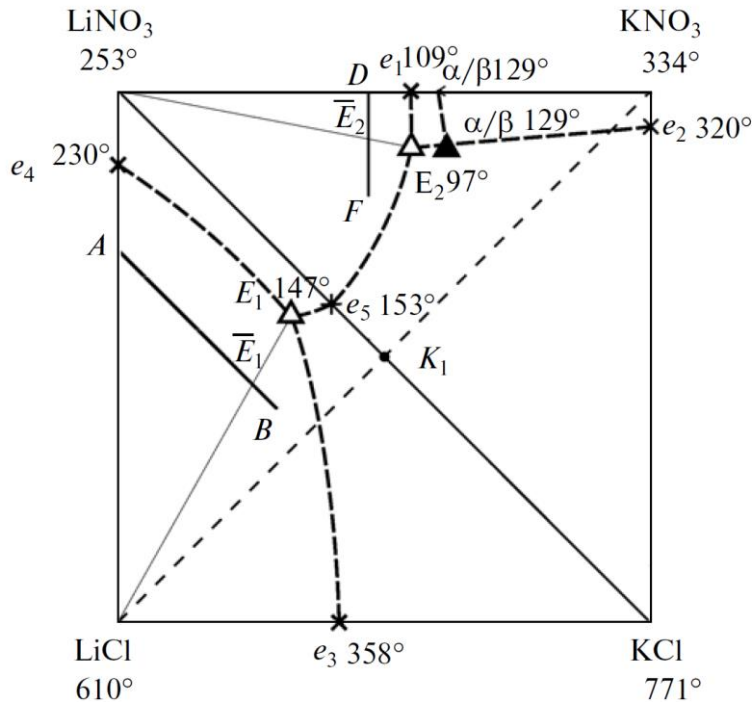


Fig 1. Phase diagram of the system K,Li//Cl,NO₃ [20].

The phase diagram of K,Li//Cl,NO₃ exhibits a minimum melting composition E2 with a defined anion (X_a) and cation (X_c) content shown in Table 3. The authors of ref. [20] suggest that composition 1a in Table 3 exhibits the minimum melting point. However, just from the molar ion fractions a different contribution of individual salts can result in the same ion ratios; this alternative composition is referred to as 1b. Applying Eq. 5 (with $V^E = 0$) to mixture 1a and 1b results in two different density values although they have the same anion and cation fractions (Table 3).

Table 3. Two salt mixtures for the minimum melting composition E2 of the system K,Li//Cl,NO₃ in mol%.

Mix.	KCl	KNO ₃	LiCl	LiNO ₃	X_{cK}	X_{cLi}	X_{aCl}	X_{aNO_3}
1a	10.5%	44.5%	0	45%	0.55	0.45	0.105	0.895
1b	0	55%	10.5%	34.5%	0.55	0.45	0.105	0.895

As this example shows and Smith and Petersen also stated: “for ternary mixtures of reciprocal salt systems [...] there is an ambiguity in the choice of components that leads to special difficulties when one attempts a straightforward extension of the additive volume principle” [18]. In order to overcome this difficulties, Smith and Petersen

proposed an adapted volumetric additivity for ternary reciprocal systems, where X_{c1} is the fraction of the first cation, X_{c2} is the fraction of the second cation, X_{a1} is the fraction of the first anion, X_{a2} is the fraction of the second anion and V_{11} , V_{12} , V_{21} and V_{22} are the four molar volumes of the single salts (Eq. 7) [18]. In the following, we use the term **“quasilinear volumetric additivity rule (QVAR)”** for this adapted version of the volumetric additivity rule (VAR). As previously discussed, the sum of all cation and anion fractions is one (Eq. 8 and 9).

$$V(T) = X_{c1}X_{a1}V_{11}(T) + X_{c1}X_{a2}V_{12}(T) + X_{c2}X_{a1}V_{21}(T) + X_{c2}X_{a2}V_{22}(T) \quad (7)$$

$$X_{c1} + X_{c2} = 1 \quad (8)$$

$$X_{a1} + X_{a2} = 1 \quad (9)$$

Smith and Petersen compared own experimental density results with different estimated densities for the ternary reciprocal system K,Li//Cl,NO₃. Table 4 shows the recalculated results, where ρ_{EXP} refers to experimental values, ρ_{VAR} to estimated values using the volumetric additivity rule (VAR) defined in Eq. 5 and ρ_{QVAR} to estimated values using the quasilinear volumetric additivity rule (QVAR) defined in Eq. 7. There are no differences between VAR and QVAR values for binary systems (or edges) of the ternary reciprocal system. Hence, binary systems are not shown and Table 4 lists values within the square of the ternary reciprocal system. Table 4 shows two alternative choices (a and b) with two or three salts giving the same molar ion fractions. From Table 4, it can be seen that ρ_{QVAR} values are not affected by these two choices of components. However, ρ_{VAR} values are inconsistent and differ depending on the choices of components. The effect also exists for mixtures with all four salts, but is not listed in Table 4 since it does not show the effect as strong as mixtures with two or three salts.

Table 4. Experimental and estimated densities of the system K,Li//NO₃,Cl at $T=367\text{ }^{\circ}\text{C}$.

Mix.	KCl	KNO ₃	LiCl	LiNO ₃	X_{cK}	X_{cLi}	X_{aNO_3}	X_{aCl}	$\rho_{\text{EXP}}(T)/(\text{g cm}^{-3})$	$\rho_{\text{VAR}}(T)/(\text{g cm}^{-3})$	$\rho_{\text{QVAR}}(T)/(\text{g cm}^{-3})$
1a	0	25%	50%	25%	0.25	0.75	0.5	0.5	1.715	1.725	1.718
1b	25%	0	25%	50%	0.25	0.75	0.5	0.5	1.715	1.711	1.718
2a	25%	0	0	75%	0.25	0.75	0.75	0.25	1.738	1.730	1.739
2b	0	25%	25%	50%	0.25	0.75	0.75	0.25	1.738	1.743	1.739
3a	16%	25%	59%	0	0.41	0.59	0.25	0.75	1.709	1.726	1.718
3b	41%	0	34%	25%	0.41	0.59	0.25	0.75	1.709	1.712	1.718
4a	0	41%	50%	9%	0.41	0.59	0.5	0.5	1.739	1.752	1.742
4b	41%	0	9%	50%	0.41	0.59	0.5	0.5	1.739	1.731	1.742
5a	25%	16%	0	59%	0.41	0.59	0.75	0.25	1.760	1.755	1.762
5b	0	41%	25%	34%	0.41	0.59	0.75	0.25	1.760	1.767	1.762
6a	0	75%	25%	0	0.75	0.25	0.75	0.25	1.799	1.811	1.802
6b	25%	50%	0	25%	0.75	0.25	0.75	0.25	1.799	1.799	1.802

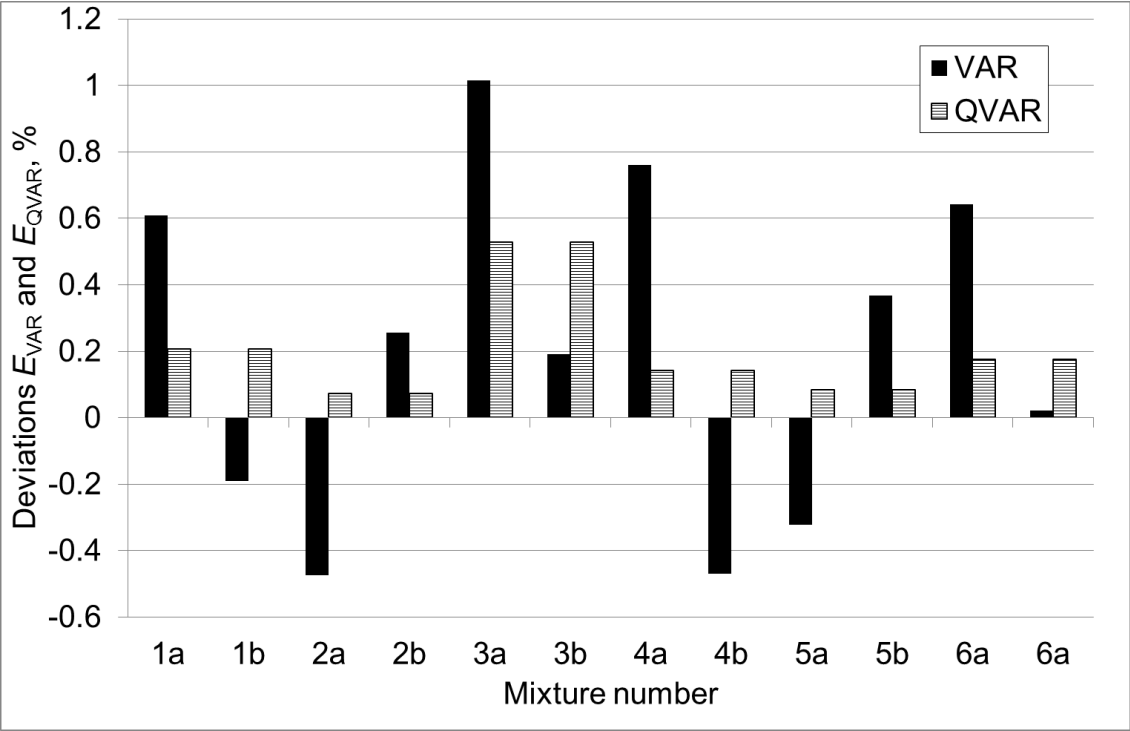
Eq. 10 and 11 define deviations between measured density values ρ_{EXP} and the two estimated values ρ_{VAR} and ρ_{QVAR} .

$E_{\text{VAR}}(T) = \frac{\rho_{\text{VAR}}(T) - \rho_{\text{EXP}}(T)}{\rho_{\text{EXP}}(T)} 100\%$	(10)
$E_{\text{QVAR}}(T) = \frac{\rho_{\text{QVAR}}(T) - \rho_{\text{EXP}}(T)}{\rho_{\text{EXP}}(T)} 100\%$	(11)

Figure 2 plots deviations of all mixtures in Table 4 as compared to the experimental values. It can be seen that a and b compositions result in the same $E_{\text{QVAR}}(T)$ value as previously discussed. Figure 2 shows that positive deviation values of the VAR method are up to about +0.5 % whereas deviations of the QVAR method show only negative deviation values. Maximum negative deviation values are about -1 % for the VAR method and -0.6 % for the QVAR method. Hence, the deviation window is only about one third, if the VAR method (-1 % to +0.5 %) and QVAR method (-0.5 % to +0 %) are compared.

The accuracy limit of single salts of the system K,Li//Cl,NO₃ is $\pm 0.5\%$ except LiNO₃ with a higher uncertainty value of $\pm 1.5\%$. These uncertainties have the same order of magnitude as the obtained deviations in Figure 2. Also, only some experimental points of the system K,Li//Cl,NO₃ are available. Hence, an absolute judgement about the improvement of the QVAR compared to the VAR method for the entire K,Li//Cl,NO₃ system is not possible. Nevertheless, the analysis showed that the QVAR method compared to the VAR method leads to lower deviations and consistent averaged density values for the examined ternary reciprocal system.

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Fig 2. Analysis of the deviation of the VAR and QVAR method for the system K,Li//NO3,Cl .

3. Results and discussion for K,Na//NO₂,NO₃ and subsystems

3.1 The ternary reciprocal system K,Na//NO₂,NO₃

Figure 3 gives the phase diagram of the system K,Na//NO₂,NO₃ from reference [21].

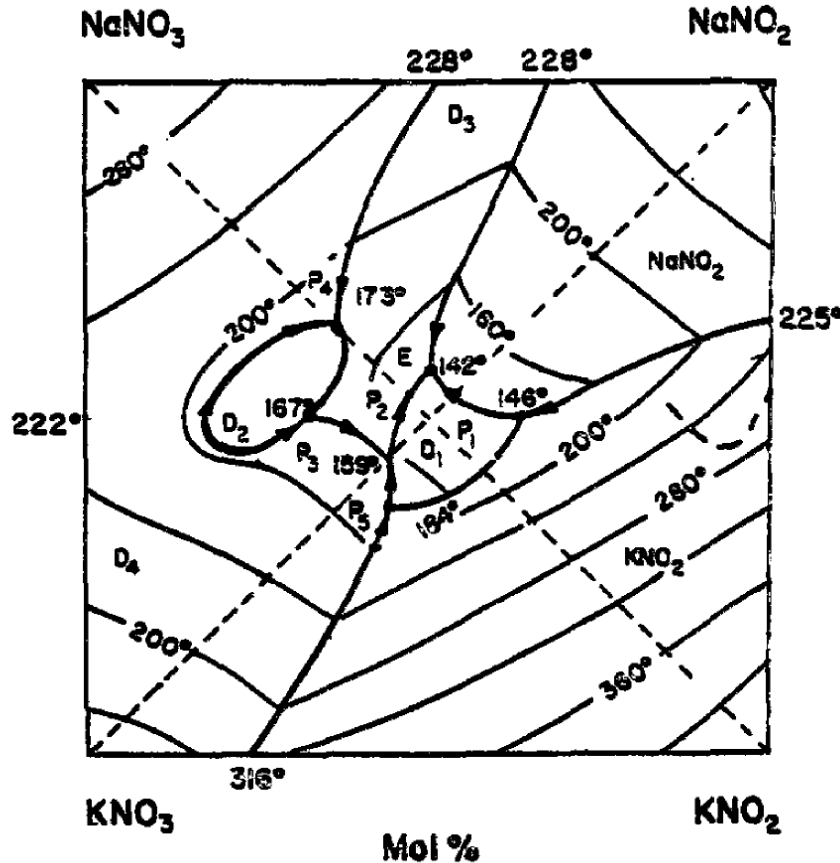


Fig 3. Phase diagram of the system K,Na//NO₂,NO₃ from Janz [21].

In reference [21], only limited further experimental density measurement data of the system K,Na//NO₂,NO₃ could be identified. Therefore, density values were estimated using experimental data from different sources. Density values of binary systems with common anions (KNO₂-NaNO₂, KNO₃-NaNO₃), cations (KNO₂-KNO₃, NaNO₂-NaNO₃) and pseudobinary KNO₂-NaNO₃ were taken from Janz [5,22]. Also values from the minimum melting mixture Hitec with the composition 53 wt% KNO₃, 40 wt% NaNO₂ and 7 wt% NaNO₃ were used [23,24]. Density values at the minimum and maximum temperature for each composition and all mixtures were selected. In total 100 experimental density values were used. We compared these experimental density values with computed values in terms of the deviation $E_{QVAR}(T)$ (Eq. 11).

Figure 4 shows minimum and maximum deviations $E_{QVAR}(T)$ for these binary systems and the Hitec mixture (for simplicity single computed values of all mixtures are not shown). For comparison, Figure 4 gives the uncertainty of single salt density as compared to experimentally gained values.

For all estimations the deviation between computed and experimental values was below $\pm 1.15\%$. For all other systems, it can be seen that deviations between estimated and experimental values are within the uncertainty of the density values of the single salts.

Although there is an incomplete set of experimental density data inside the system $\text{K,Na/NO}_2,\text{NO}_3$ it can be assumed that the QVAR method can be applied for the entire $\text{K,Na/NO}_2,\text{NO}_3$ system with a high accuracy, since deviations of the four edge systems, a crossing line and the Hitec system are within the uncertainty of the density values of the single salts.

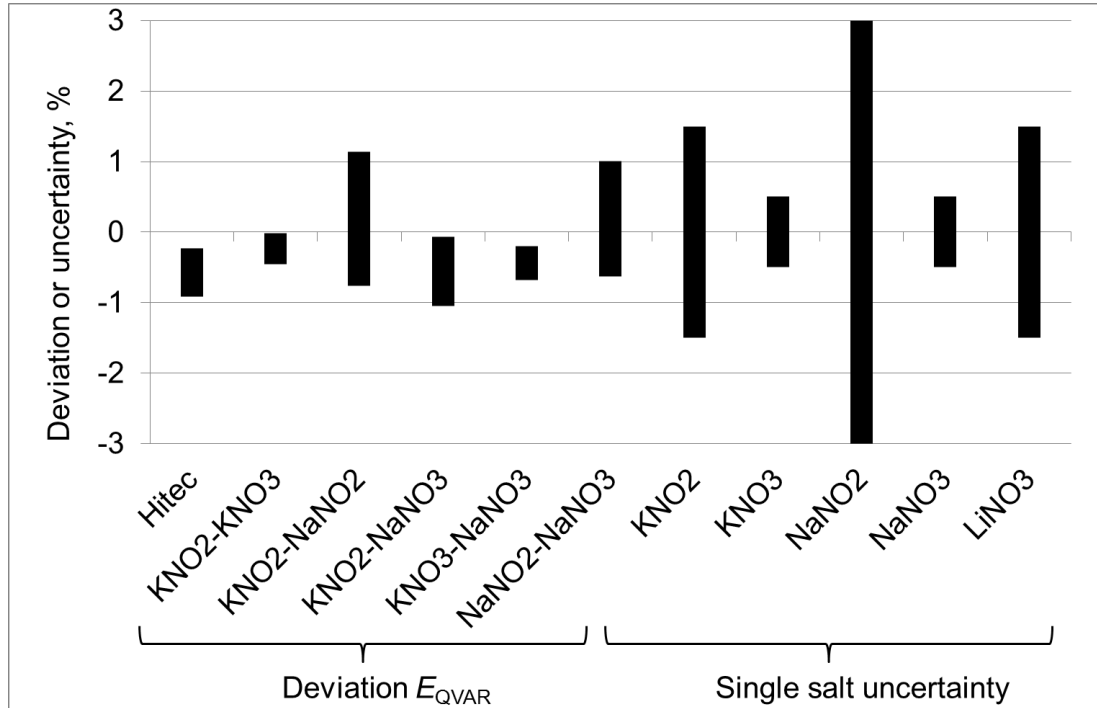


Fig 4. Analysis of the deviations of the QVAR method for the system $\text{K,Na/NO}_2,\text{NO}_3$ compared to single salt density uncertainties [5].

3.2 “Solar Salt” mixture

For sensible thermal energy storage and as heat transfer fluid in CSP plants, a molten salt mixture of 60 wt% sodium nitrate (NaNO_3) and 40 wt% potassium nitrate (KNO_3), or 64.1 mol% NaNO_3 and 35.9 mol% KNO_3 is almost exclusively utilised [25]. Compared to the eutectic composition with 46 wt% NaNO_3 and 54 wt% KNO_3 (or 50-50 mol%), Solar Salt contains a larger fraction of NaNO_3 , which has a higher heat capacity and typically also lower costs compared to KNO_3 . Hence, it is advantageous to increase the fraction of NaNO_3 compared to the eutectic mixture. Figure 5 plots density values versus the composition of the system $\text{KNO}_3\text{-NaNO}_3$ for the three temperatures 450, 500 and 550 °C. **Janz** reviewed density measurements of the entire system $\text{KNO}_3\text{-NaNO}_3$ from 12 groups and recommended density values in 1972, which are also presented in Figure 5 [22]. Table 5 gives the interpolated density equations of Solar Salt from the mixtures 70 mol% NaNO_3 - 30 mol% KNO_3 and 60 mol% NaNO_3 - 40 mol% KNO_3 reported by Janz from 1972 [22]. It should be noted that the upper temperature limit of this data is 450 °C and Figure 5 shows extrapolated values to 550 °C for comparison. **Nissen** measured the density of the 50-50 mol% $\text{NaNO}_3\text{-KNO}_3$ mixture from 300 °C to 600 °C [26]. Although, these measurements were performed for the equimolar mixture and not for Solar Salt, correlations based on these measurements are widely accepted for Solar Salt (e.g. Bradshaw [27], Pacheco [28], System Advisor Model (SAM)). Figure 5 shows this approximation with grey arrows. It is pointed out that utilization of equimolar mixture as Solar Salt data leads to an overestimation of density of about 0.4 % at 550 °C.

For estimated Solar Salt densities from single salts, the uncertainty of single salt values can be another significant error source. For example Janz revised widely accepted density correlations from 1972 for KNO_3 and NaNO_3 in 1988 with changes up to 1.2 %. In 1988, **Janz** reported revised KNO_3 and NaNO_3 density correlation with lower density values (Table 1, Figure 5)[5]. Figure 5 shows estimated density values for the system KNO_3 - NaNO_3 using single salt data from Janz [5] and the VAR method. Single salt values are valid until 460 °C (KNO_3) and 370 °C (NaNO_3) [5] and Figure 5 shows extrapolated values until 550 °C. It can be seen that values at 550 °C deviate slightly more than 1 % between data from Nissen and the VAR method. It can be concluded that differences occur mainly due to corrected density values from Janz from 1972 [22] to 1988 [5]. Newer values are lower, e.g. for extrapolated values at 550 °C for NaNO_3 about 1.2 % and for KNO_3 about 0.2 %.

Another aspect is the non-ideal mixing behaviour of Solar Salt. **Powers** measured a small positive excess volume of the system KNO_3 - NaNO_3 [14]. For Solar Salt a value of 0.06 cm^3/mol can be estimated ($V^E = 0.26 \text{ cm}^3/\text{mol} \cdot 0.64(1-0.64)$). This value corresponds to a density increase of about 0.1 %. It can be concluded that the density increase of 0.1% is rather small and can be neglected compared to other effects discussed previously.

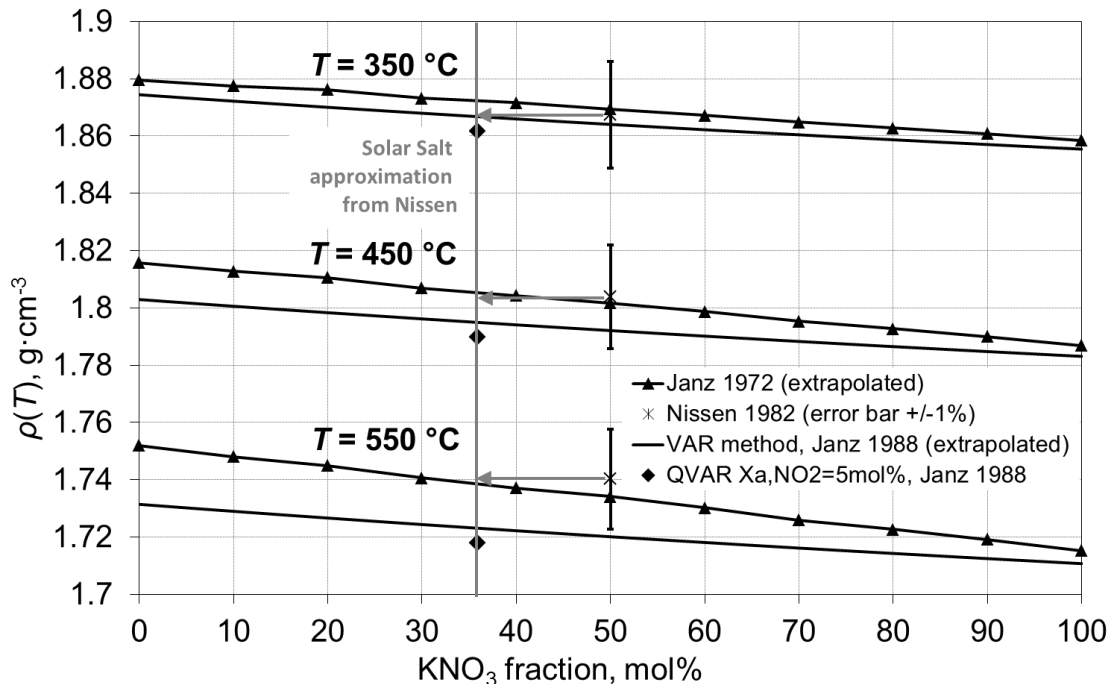


Fig 5. Liquid density values of the system KNO_3 - NaNO_3 for three temperatures from different sources [22,26] and own estimations based on data from Janz 1988 [5].

Another source of uncertainty is the formation of nitrite ions in Solar Salt at high operation temperatures. The equilibrium of nitrate and nitrite depends on the temperature and oxygen partial pressure (Eq. 12)[29]. In fact nitrite formation occurs also in other alkali nitrate mixtures. Nitrite formation is pronounced for low partial pressure of oxygen (e.g. lower oxygen partial pressure than in atmospheric air) and at higher temperatures (e.g. above 400 °C). Hence, due to this nitrate decomposition with release of oxygen as gas some errors of density values can occur for all alkali nitrate mixtures.



Table 5 and Figure 5 show results about the impact of nitrite formation on the density of Solar Salt. For high-temperature operation an approximate value of $X_{\text{aNO}_2} = 5 \text{ mol\%}$ can be assumed [17]. The formation of nitrite ions reduces the density of Solar Salt. In order to assess the impact of nitrite formation on the Solar Salt density, density values of mixtures with the VAR-method (without nitrite) and QVAR-method (with 5 mol% nitrite) were computed (using salt properties from Janz [5]). It was found that the impact of nitrite formation on density variation is rather small. For the formation of 5 mol% nitrite in Solar Salt, the density values are reduced by about 0.005 g/cm^3 or 0.3 %. Hence, this conversion leads to an overestimation of Solar Salt density values of about 0.3 %, if nitrite formation is neglected.

Table 5. Density of Solar Salt from different authors (* interpolated values).

Author, year	Equation $\rho(T)$ / (g cm^{-3})	Temp. range	Reference
Janz 1972	$\rho(T) = 2.106 - 6.684 \times 10^{-4} \cdot (T/^{\circ}\text{C})$	350-450 $^{\circ}\text{C}$	21
Nissen 1982*	$\rho(T) = 2.090 - 6.36 \times 10^{-4} \cdot (T/^{\circ}\text{C})$	300-600 $^{\circ}\text{C}$	25
VAR, Janz 1988	$\rho(T) = 2.118 - 7.185 \times 10^{-4} \cdot (T/^{\circ}\text{C})$	See Table 1	5
QVAR, $X_{\text{aNO}_2}=5 \text{ mol\%}$, Janz 1988	$\rho(T) = 2.113 - 7.184 \times 10^{-4} \cdot (T/^{\circ}\text{C})$	See Table 1	5

* Equimolar mixture measurements utilized as Solar Salt data

Overall, it can be stated that different effects lead to lower density values of Solar Salt compared to published values by Nissen. Newer revised lower single salt values from Janz in 1988, the assumption of 5 mol% NO_2^- formation and the application of the QVAR method lead to a 1.2 % lower density value at 550 $^{\circ}\text{C}$ of Solar Salt compared to the commonly applied value from Nissen (Figure 5)[25].

3.3 “Hitec” mixture

Since about 1940 a ternary molten salt mixture is commercially used as heat transfer fluid [23,30]. Figure 3 gives the literature phase diagram with the minimum melting composition E with a melting temperature of 142 $^{\circ}\text{C}$. This minimum melting mixture is typically called Hitec. Table 6 gives this minimum melting composition 1a in mol%. Table 6 also shows the fraction of the anions and cations and an alternative mixture 1b which has the same molar ion fractions as mixture 1a.

There are several literature sources which give the density of Hitec as a function of temperature [23,31,32] and these values agree closely (deviations smaller $\pm 1 \%$). Janz gives a linear fit for density values in g/cm^3 using original values from Kirst [23] for the temperature range from 197 $^{\circ}\text{C}$ to 597 $^{\circ}\text{C}$ with an uncertainty of $\pm 2 \%$ [21]. The original linear equation from Janz was converted from Kelvin to $^{\circ}\text{C}$ (Eq. 13).

$\rho_{\text{EXP,Hitec}}(T) = 2.0889 - 7.497 \times 10^{-4} \cdot (T/^{\circ}\text{C})$	(13)
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Table 6 shows the density values at 150 °C for experimental values (Eq. 13), the VAR method (Eq. 5) and the QVAR method (Eq. 7). As discussed before, the VAR method gives ambiguous values. Hence it is inconsistent and is purely shown for completeness. Figure 6 shows an error analysis of the minimum melting Hitec mixture depending on the temperature. It can be seen that the deviations between measured and estimated densities is larger at lower temperatures. Estimated densities are lower in all cases compared to the measured densities for this particular mixture. This may be due to an excess volume of this ternary mixture or inaccurate experimental values of single salts or the ternary mixture. The uncertainty of the single salts KNO_3 and NaNO_3 is low ($\pm 0.5\%$). The nitrite salts show a larger uncertainty ($\text{KNO}_2 \pm 1.5\%$ and $\text{NaNO}_2 \pm 3\%$). Janz gives an uncertainty of $\pm 2\%$ Hitec measurement values. The deviation between QVAR method and measured results is smaller than 1%. Hence, deviations of estimated densities by the QVAR method are within the uncertainty of measured values.

Table 6. Two salt mixtures for the minimum melting Hitec composition of the system $\text{K}_2\text{Na}/\text{NO}_2, \text{NO}_3$ in mol%. The temperature T for the density values is 150 °C.

Mix.	KNO_2	KNO_3	NaNO_2	NaNO_3	X_{cK}	X_{cNa}	X_{aNO_2}	X_{aNO_3}	$\rho_{\text{EXP}}(T)/$ (g cm ⁻³)	$\rho_{\text{VAR}}(T)/$ (g cm ⁻³)	$\rho_{\text{QVAR}}(T)/$ (g cm ⁻³)
1a	0	44.2%	48.9%	6.9%	0.442	0.558	0.489	0.511	1.976	1.964	1.958
1b	44.2%	0	4.7%	51.1%	0.442	0.558	0.489	0.511	1.976	1.952	1.958

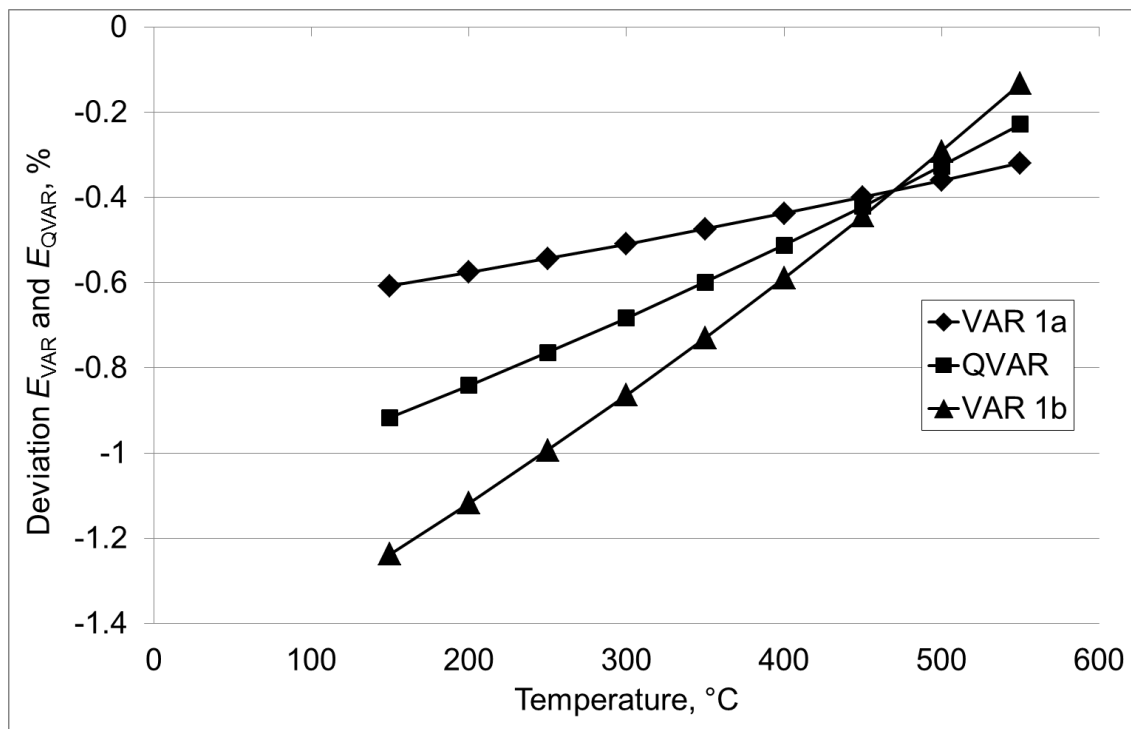


Fig 6. Analysis of the deviations of VAR and QVAR method compared to measured values for the minimum melting Hitec mixture of the system $\text{K}_2\text{Na}/\text{NO}_2, \text{NO}_3$.

4. Results and discussion for the ternary additive “LiNaK-Nitrate” mixture

Applications of the nitrite-free binary mixture K,Li//NO₃ include vulcanization of rubber in salt baths and the heat transfer fluid area [33]. Compared to K,Li//NO₃, the ternary system Li,K,Na//NO₃ (named LiNaK-Nitrate here) shows improved properties in terms of reduced LiNO₃ contents (as an expensive compound) and a lower melting temperature. In addition to vulcanization and heat transfer applications, thermal energy storage systems in concentrating solar power plants is another potential application field for this ternary mixture [34-37]. Figure 7 shows the phase diagram of the system LiNaK-Nitrate from Bergman [38]. In addition, Carveth and Mantha also studied the phase diagram of this system (not shown) [39,40]. Bergman gives the ternary eutectic point with a melting temperature of 120 °C with a composition of 30.0 wt% LiNO₃, 52 wt% KNO₃ and 18 wt% NaNO₃. For further density estimation, this composition is selected.

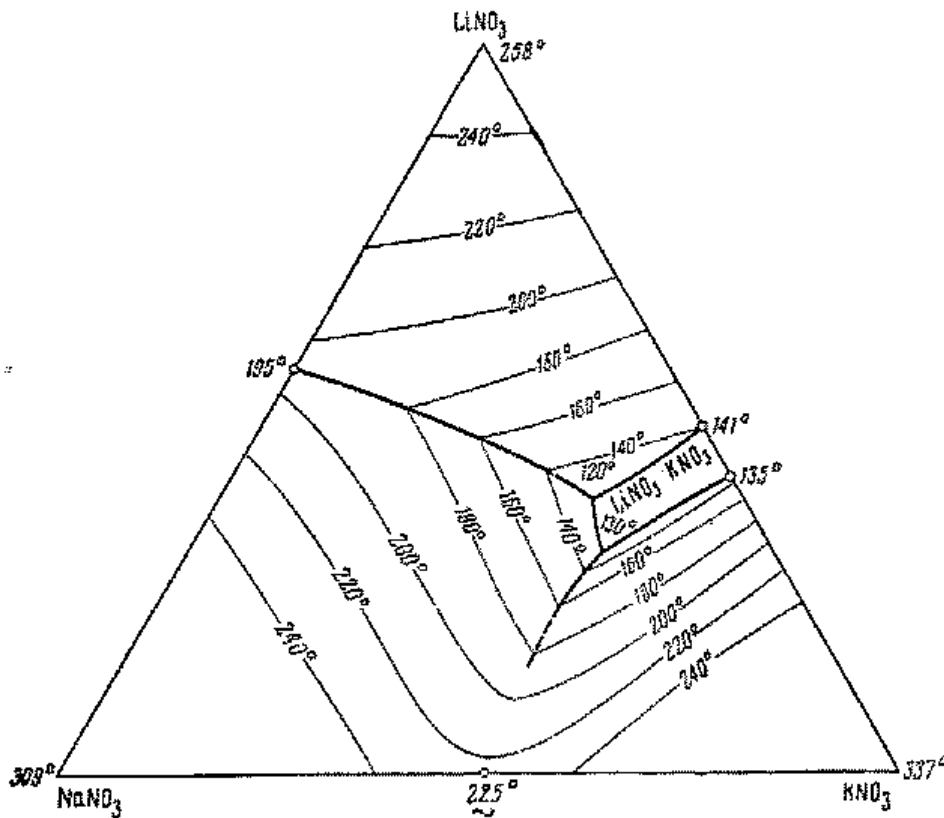


Fig 7. Phase diagram of the LiNaK-Nitrate system from Bergman [39].

Bradshaw gives experimental density data in g/cm³ of the ternary eutectic LiNaK-Nitrate in a range from 150 °C to 500 °C. The deviation of single measurement points from the linear equation (Equation 14) was less than 0.2 % [3].

$\rho_{\text{EXP, LiNaK-Nitrate}}(T) = 2.0777 - 7.352 \times 10^{-4} \cdot (T/^{\circ}\text{C})$	(14)
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Figure 8 shows minimum and maximum deviations $E_{\text{VAR}(T)}$ for ternary eutectic LiNaK-Nitrate of experimental data from Bradshaw (Equation 14) and estimated values by the VAR method (since this system has only one anion the QVAR method is not employed). Experimental data were extrapolated from 500 °C to 550 °C. Above about 380 °C estimated data are larger than experimental density data, whereas below 380 °C

estimated data are smaller than experimental data. It can be seen that the maximum deviation is 0.9 %. For comparison, Figure 4 gives the uncertainty of single salt density values ($\text{KNO}_3 \pm 0.5 \%$, $\text{LiNO}_3 \pm 1.5 \%$, $\text{NaNO}_3 \pm 0.5 \%$) [5]. Hence, deviations between estimated and measured values are within the uncertainty of LiNO_3 density value.

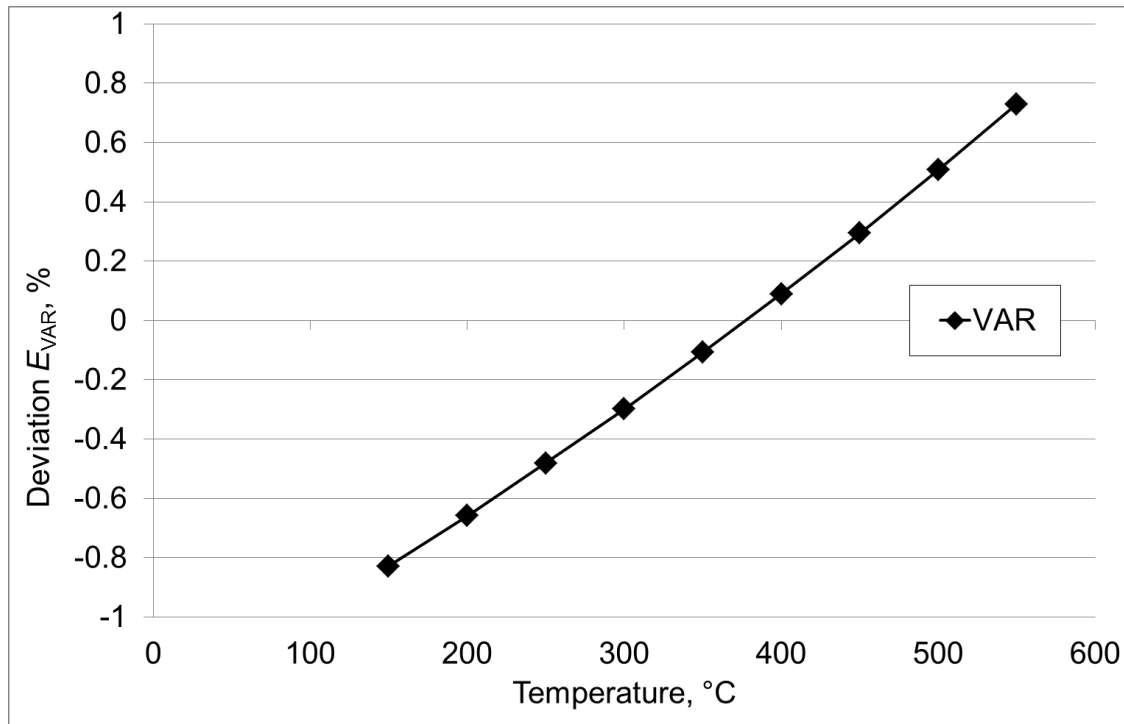


Fig 8. Analysis of deviations of the VAR method compared to measured values for the LiNaK-Nitrate mixture .

5. Results and discussion for the “HitecXL” mixture

Figure 9 shows the phase diagram of the ternary additive system Ca,K,Na//NO₃ from Bergman [41]. There is some discussion about the eutectic composition as discussed by Gomez and Bauer [42,43]. For further discussion we assume the following minimum melting composition: Ca(NO₃)₂-KNO₃-NaNO₃ (42-43-15 wt%) and use HitecXL as an abbreviation.

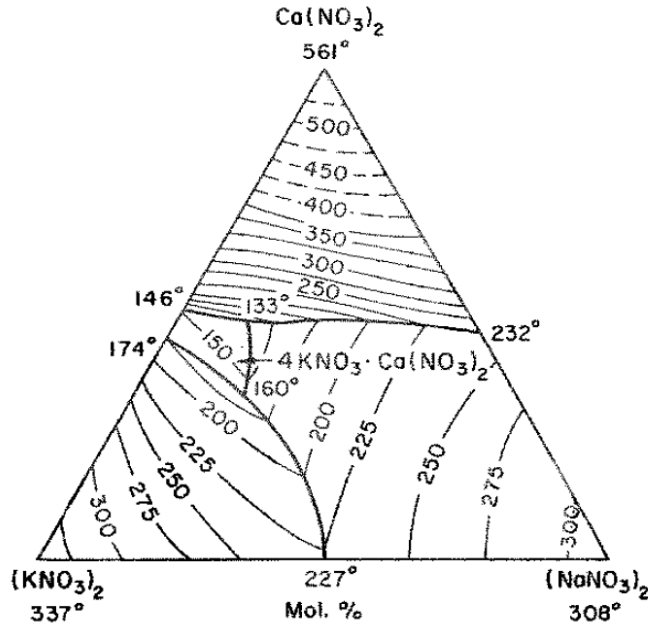


FIG. 1074.—System (KNO₃)₂-(NaNO₃)₂-Ca(NO₃)₂.

A. G. Bergman, I. S. Rassonskaya, and N. E. Shmidt,
*Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg.
 Khim., Akad. Nauk S.S.S.R., 26, 156 (1955).*

Fig 9. Phase diagram of the system Ca,K,Na//NO₃ from Bergman [41].

Measurement values of the density of the single salt Ca(NO₃)₂ are not available due to its instability above the melting temperature of about 560 °C. Hence, we use a backward approach to estimate an artificial density value for Ca(NO₃)₂ from the experimental density values of mixtures at lower temperatures. For this purpose Equation 5 is rearranged and gives Equation 15. Equation 2 converts molar volumes of Ca(NO₃)₂ to artificially estimate liquid densities values $\rho_{\text{Ca(NO}_3)_2^*}$. This estimated values are below the freezing temperature of Ca(NO₃)₂ with the aim to estimate densities of low-melting temperature salt mixtures containing Ca(NO₃)₂.

$$V_{\text{Ca(NO}_3)_2}(T) = \frac{V_{\text{exp,Ca,K,Na//NO}_3}(T) - X_{\text{KNO}_3} \cdot V_{\text{KNO}_3}(T) - X_{\text{NaNO}_3} \cdot V_{\text{NaNO}_3}(T)}{X_{\text{Ca(NO}_3)_2}} \quad (15)$$

Figure 10 plots estimated artificial Ca(NO₃)₂ liquid density values $\rho_{\text{Ca(NO}_3)_2^*}$ using Equation 2 and 15. A large number of molar volume values $V_{\text{exp,Ca,K,Na//NO}_3}$ in Equation 15 from the systems Ca(NO₃)₂-KNO₃, Ca(NO₃)₂-NaNO₃ and Ca(NO₃)₂-KNO₃-NaNO₃ from Janz were used [5]. In order to reduce the errors of estimated $V_{\text{Ca(NO}_3)_2}$ values, data with molar calcium nitrate fraction $X_{\text{Ca(NO}_3)_2} < 0.2$ were excluded. Petersen also gives measured temperature dependent densities of the two mixtures 20 mol% Ca(NO₃)₂-80 mol% KNO₃ and 30 mol% Ca(NO₃)₂-70 mol% KNO₃ [44]. The plotted data points in Figure 10 refer to the minimum and maximum temperature for the

given temperature range. A fit with a linear regression was applied. Single data points from Janz are all within an deviation band of $\pm 1\%$ compared the linear fit. It can be seen that the slope coefficient of the function from Janz and Petersen is virtually the same. There is an offset of the density values from Janz and Petersen. Data from Janz are about 1.5 % higher compared to data from Petersen in the temperature range 250 °C to 450 °C [5,44]. Due to the larger data basis, for further estimations the linear fit from data from Janz is selected (Equation 16).

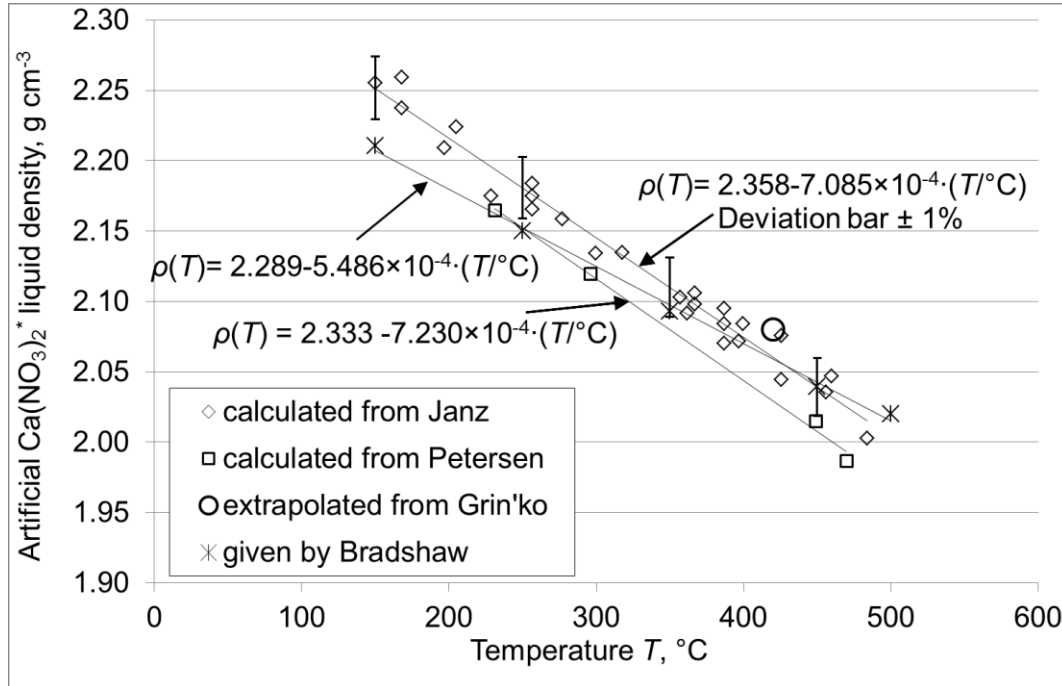


Fig 10. Estimated artificial $\text{Ca}(\text{NO}_3)_2^*$ liquid density values from densities of K,Ca,Na/ NO_3 mixtures by Bradshaw, Janz, Grin'ko and Petersen [3,5,12,44].

$\rho_{\text{Ca}(\text{NO}_3)_2}(T)^* = 2.358 - 7.085 \times 10^{-4} \cdot (T/^\circ\text{C})$	(16)
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Figure 11 shows temperature dependent density data of the mixture HitecXL. Data are from Siegel which refers to a personal communication to the company Coastal Chemical) [45] and own estimations. Own estimations are based on the VAR method with density equations of single salts from Table 1 (for NaNO_3 and KNO_3) and Equation 16 (for $\text{Ca}(\text{NO}_3)_2$). As can be seen that these estimations are in agreement to data provided by Siegel within $\pm 1.5\%$.

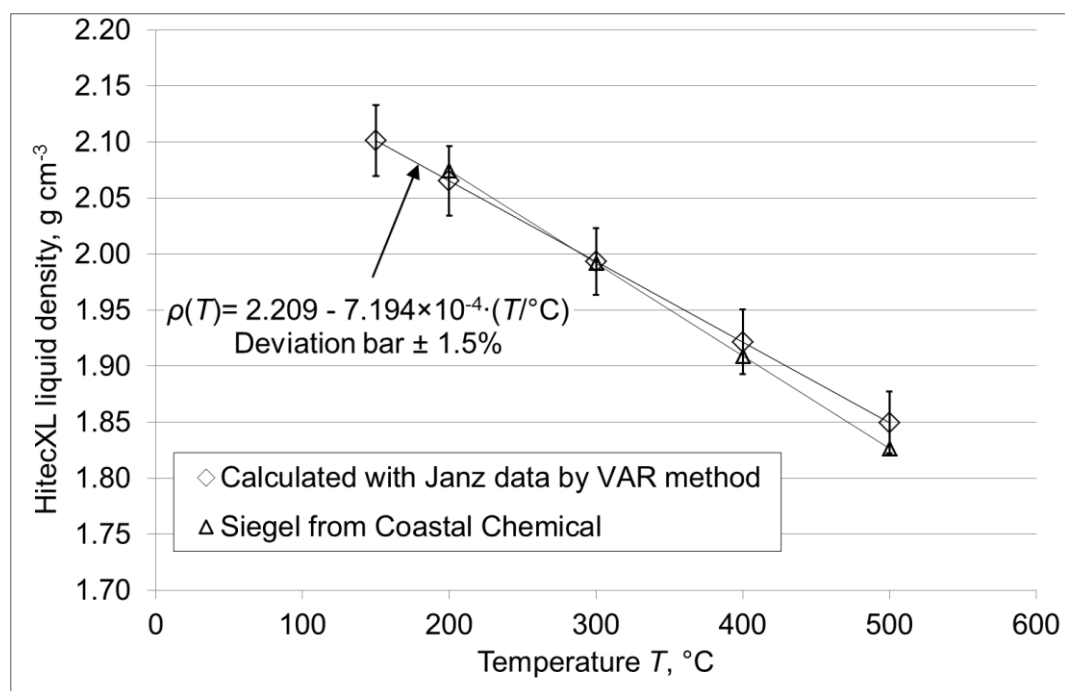


Fig 11. HitecXL liquid density values from Siegel [45] and estimated values within this work from Janz using the VAR method [5,44].

6. Results and discussion for the “CaLiNaK-NO23” mixture

For density estimation of the quinary reciprocal system Ca,K,Li,Na/NO₂,NO₃ density data of Ca(NO₂)₂ and Li(NO₂)₂ are required. As for Ca(NO₃)₂ in the previous section, density values of Ca(NO₂)₂ and Li(NO₂)₂ are commonly not available. In a previous work, the minimum melting composition LiNO₃-Ca(NO₃)₂-NaNO₂-KNO₂ (24.6 - 13.6 - 16.8 - 45.0 wt%) was identified [46]. CaLiNaK-NO23 is the abbreviation of this mixture. In order to estimate the temperature dependent density of this mixture, in the following the density functions of Ca(NO₂)₂ and Li(NO₂)₂ are identified. Grin'ko and Protsenko give the projection of the density isotherms of the system Ca,K/NO₂,NO₃ at 420 °C (Figure 12)[12]. They also give a direct temperature dependent correlation of the density of Ca(NO₂)₂ for the temperature range 398 °C to 434 °C (Equation 17).

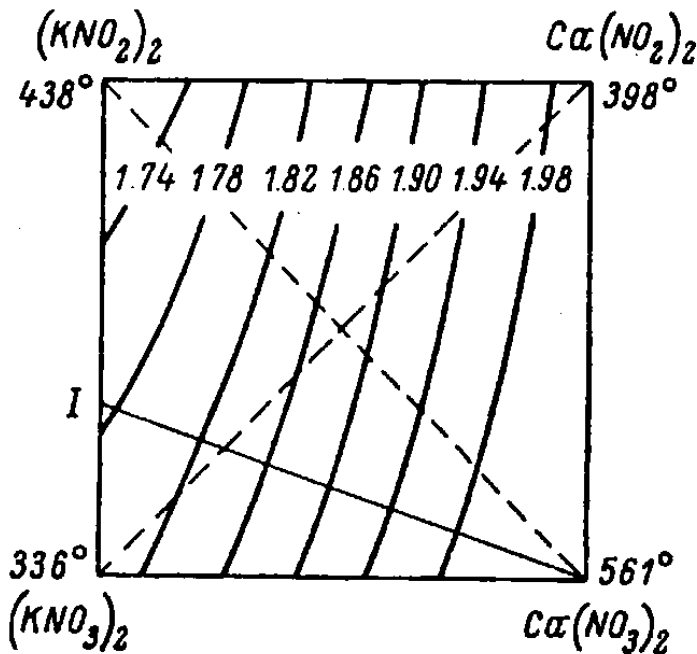


Fig 12. Projection of the density isotherms of the system Ca,K/NO₂,NO₃ at 420 °C from Grin'ko and Protsenko [12].

$$\rho_{\text{Ca(NO}_2)_2}(T)^* = 2.289 - 5.4 \times 10^{-4} \cdot (T/^{\circ}\text{C}) \quad (17)$$

Protsenko et al. also measured the temperature dependent densities of the binary system LiNO₂-LiNO₃. They found that the density and molar-volume isotherms of this system are strictly linear and these properties are additive [47]. Extrapolated measured values of LiNO₃ from Protsenko agree within a deviation of $\pm 0.8\%$ compared to values for LiNO₃ from Janz (see Table 1). Hence, it can be assumed that also LiNO₂ values have a high accuracy. Equation 16 is a linear fit for the LiNO₂ density values for the measurement range 220-280 °C.

$$\rho_{\text{LiNO}_2}(T)^* = 1.742 - 4.70 \times 10^{-4} \cdot (T/^{\circ}\text{C}) \quad (18)$$

Equation 7 gives the molar volume for ternary reciprocal systems using the QVAR method. In order to estimate the molar volume of the quinary reciprocal systems Equation 7 is extended. Equation 19 gives the molar volume for quinary reciprocal systems (e.g., Li,K,Ca,Na //NO₂,NO₃), where the sum of all cations and anions remains unity (Equation 20 and 21).

$$V(T) = X_{c1}X_{a1}V_{11}(T) + X_{c1}X_{a2}V_{12}(T) + X_{c2}X_{a1}V_{21}(T) + X_{c2}X_{a2}V_{22}(T) + X_{c3}X_{a1}V_{31}(T) + X_{c3}X_{a2}V_{32}(T) + X_{c4}X_{a1}V_{41}(T) + X_{c4}X_{a2}V_{42}(T) \quad (19)$$

$$X_{c1} + X_{c2} + X_{c3} + X_{c4} = 1 \quad (20)$$

$$X_{a1} + X_{a2} = 1 \quad (21)$$

Table 8 gives the equation of the temperature dependent density of the LiNO₃-Ca(NO₃)₂-NaNO₂-KNO₂ (24.6 - 13.6 - 16.8 - 45.0 wt%) minimum melting temperature mixture using the QVAR-method. The density value at 300 °C of this quinary reciprocal system is about 6 % lower compared to Solar Salt.

7. Summary of available and estimated density correlations of single salts

This work lists known temperature dependent density equation of single salts from literature (Table 1). Density equations for Ca(NO₂)₂, Ca(NO₃)₂, LiNO₂ were not available, since these compounds tend to be unstable above their melting temperature. Nevertheless in order to estimate the density of molten salt mixtures with lower melting temperatures, it is useful to define an artificial density function for these density estimations (Table 7). The accuracy of the Ca(NO₂)₂, Ca(NO₃)₂, LiNO₂ density equations was estimated by an empirical correlation. Figure 13 shows the liquid density versus the molecular weight of the single salts defined in Table 1 and Table 7. It can be seen that for both 100 °C and 500 °C density values follow an empirically fitted second order polynomial. The maximum deviation of ± 4 % between each single salt value and the polynomial is assumed to be the accuracy for the Ca(NO₂)₂, Ca(NO₃)₂, LiNO₂ salts. With respect to the temperature range, it should be noted that the melting temperature and the thermal stability limit of the selected mixture can restrict the temperature range 100 to 500 °C.

Table 7. Temperature dependent artificial densities of single salts obtained in this work.

Salt	Melting Temp. $T_m/^\circ\text{C}$	Mol. Weight $M/(\text{g mol}^{-1})$	Density equation $\rho(T)/(\text{g cm}^{-3})$	Accuracy	Temp. range, °C
Ca(NO ₂) ₂	392	132.089	$\rho(T)^* = 2.289 - 5.40 \times 10^{-4} \cdot (T/^\circ\text{C})$	± 4 %	100 – 500
Ca(NO ₃) ₂	561	164.087	$\rho(T)^* = 2.358 - 7.085 \times 10^{-4} \cdot (T/^\circ\text{C})$	± 4 %	100 – 500
LiNO ₂	222	52.947	$\rho(T)^* = 1.742 - 4.70 \times 10^{-4} \cdot (T/^\circ\text{C})$	± 4 %	100 – 500

* = artificial density below the melting temperature to estimate densities of mixtures

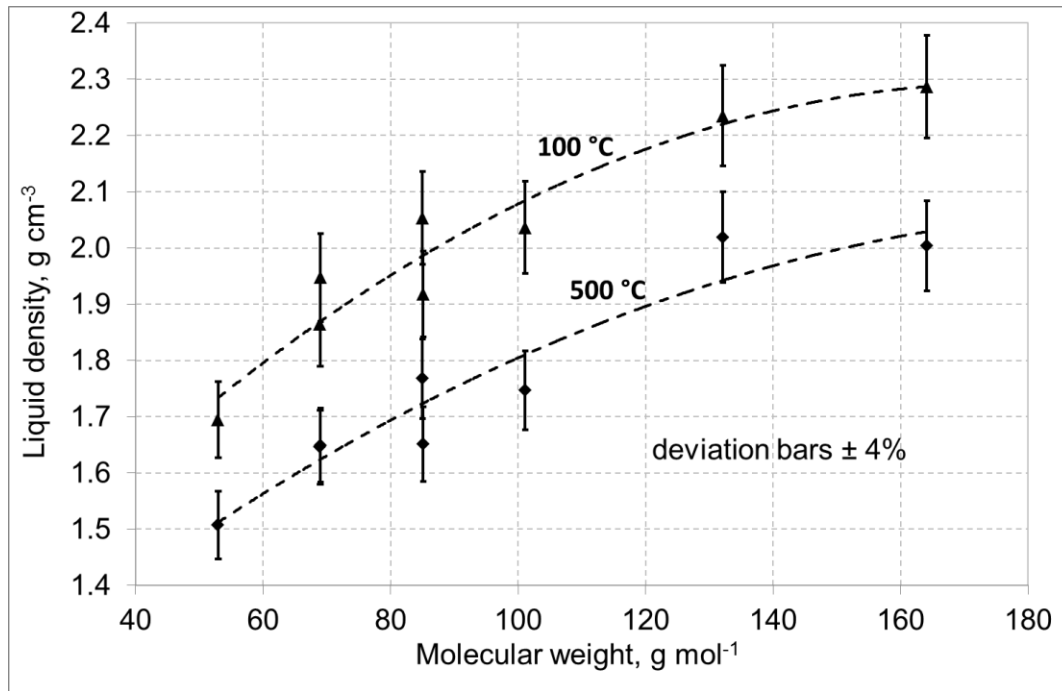


Fig 13. Liquid (artificial) density vs. molecular weight of the single salts $\text{Ca}(\text{NO}_2)_2$, $\text{Ca}(\text{NO}_3)_2$, LiNO_2 , LiNO_3 , KNO_2 , KNO_3 , NaNO_2 and NaNO_3 at 100 °C and 500 °C to estimate the uncertainty of $\text{Ca}(\text{NO}_2)_2$, $\text{Ca}(\text{NO}_3)_2$ and LiNO_2 values.

8. Summary and conclusion

Exact knowledge of molten density values of salt mixtures is essential for modelling, thermal design, as well as process measuring and control technology for Concentrating Solar Power (CSP) plants. At the time of writing, Solar Salt (60 wt% NaNO_3 and 40 wt% KNO_3) represents the heat storage medium in virtually all commercial CSP plants. For line-focusing CSP systems, there is currently some research and development interest to replace synthetic thermal oil by a molten salt mixture as heat transfer fluid. This demands salt mixtures with sufficiently low melting temperatures to avoid freezing and sufficiently high thermal stabilities. The paper presented density values of promising salt mixtures for this purpose. It is feasible to measure the density of such mixture (e.g. Archimedean method). However, such measurements are time-consuming and error-prone. Also, there is not only the salt mixture density, but there are multiple selection criteria. Hence, a fast density assessment of a plurality of salt mixture is of interest. For these reasons, we presented in this paper methods to estimate densities of molten salt mixtures based on single salt properties.

Table 8 presents density correlations of commonly considered mixtures for line-focusing CSP systems. For **Solar Salt**, most commonly a correlation from Nissen is utilized. We critically assessed uncertainties of Solar Salt density values in this paper. Aspects included the selection of the correct composition, the uncertainty of single salt values, the non-ideal mixing behaviour and the nitrite formation. Considering a correct composition and newer single salt values, it can be stated that Solar Salt has 10 % lower density values at 550 °C compared to commonly applied values from Nissen (see Table 8). This density value is about 1.2 % lower, if additionally nitrite formation is included.

The **Hitec** mixture is a well-known mixture but a theoretical prediction of the density based on single salt densities was not available. The system is a ternary reciprocal system with two cations and two anions. It was shown in this paper that simple estimation by the VAR method gives ambiguous results and should not be utilized. We present for the first time a density estimation of Hitec by the QVAR method from the single salts. The deviation between QVAR results and measurements were smaller than 1 %.

For the **LiNaK-Nitrate** mixture single salt densities were readily available. It is a ternary additive system which can be estimated by the VAR. The deviation between VAR results and measurements were smaller than ± 0.9 % and this is below the uncertainty of the LiNO_3 density values of ± 1.5 %.

HitecXL is also a ternary additive system which contains $\text{Ca}(\text{NO}_3)_2$. $\text{Ca}(\text{NO}_3)_2$ is thermally unstable above the melting temperature. Hence, liquid density data are not readily available. Hence, we used a backward approach to estimate and compare artificial density correlations for $\text{Ca}(\text{NO}_3)_2$ from different literature sources.

Experimental HitecXL data from Siegel and estimated values by the VAR method agreed within a deviation band of ± 1.5 %.

As a result it can be stated that for Solar Salt, Hitec, LiNaK-Nitrate and HitecXL differences between available measurement values and estimated density values by the VAR and QVAR deviated less than ± 1.5 %. Considering typical uncertainties of single salt densities and typical measurement uncertainties of mixtures (typically ± 0.5 -3 %), the VAR and QVAR can closely predict densities of mixtures. Several subsystems of the system $\text{Ca}, \text{K}, \text{Li}, \text{Na} / \text{NO}_2, \text{NO}_3$ were analysed. We could not identify hints of significant non-ideal mixing behaviour within these subsystems. Hence, it can be assumed that the entire system $\text{Ca}, \text{K}, \text{Li}, \text{Na} / \text{NO}_2, \text{NO}_3$ shows as a good approximation

ideal mixing properties (or additional excess volumes can be neglected). With this work consistent density correlations of all eight single salts of the system Ca,K,Li,Na/NO₂,NO₃ are available including artificial liquid density correlations for Ca(NO₃)₂, LiNO₂ and Ca(NO₂)₂, which tend to be unstable above the their melting temperature.

The known QVAR method for the ternary reciprocal system was extended to the quinary reciprocal **CaLiNaK-NO23** mixture. The extended QVAR method allowed estimation of the density of this minimum melting composition (see Table 8).

Table 8. Summary of density equations for discussed molten salt mixtures. Common equation from literature and equations using the VAR and QVAR-method with consistent single salt densities are given.

Acronym, Salt mixture (composition)	Density Equation $\rho(T)/(\text{g cm}^3)$	Temp. range
Solar Salt, KNO ₃ -NaNO ₃ (40-60 wt%)	$\rho(T) = 2.090 - 6.36 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ [26] $\rho(T) = 2.118 - 7.185 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ (VAR)	300 – 600 °C 290 – 560 °C
Hitec KNO ₃ -NaNO ₂ -NaNO ₃ (53-40-7 wt%)	$\rho(T) = 2.084 - 7.32 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ [31] $\rho(T) = 2.065 - 7.140 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ (QVAR)	200 – 500 °C 150 – 500 °C
LiNaK-Nitrate LiNO ₃ -KNO ₃ -NaNO ₃ (30-52-18 wt%)	$\rho(T) = 2.0777 - 7.352 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ [3] $\rho(T) = 2.051 - 6.639 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ (VAR)	200 – 500 °C 150 – 500 °C
HitecXL Ca(NO ₃) ₂ -KNO ₃ -NaNO ₃ (42-43-15 wt%)	$\rho(T) = 2.240 - 8.27 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ [45] $\rho(T) = 2.209 - 7.194 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ (VAR)	200 – 500 °C 200 – 500 °C
CaLiNaK-NO23 LiNO ₃ -Ca(NO ₃) ₂ -NaNO ₂ -KNO ₂ (24.6 - 13.6 - 16.8 - 45.0 wt%)	$\rho(T) = 2.035 - 6.506 \times 10^{-4} \cdot (T/^{\circ}\text{C})$ (QVAR)	100 – 400 °C

Overall, the presented work contributed to a better understanding of density estimation of salt mixtures from single salt data. The accuracy could be improved further, if a better data basis of single salt density equations with lower uncertainties would be available in the future. If ideal mixing properties of mixtures can be confirmed, estimations by the VAR and QVAR is a more efficient way of density determination compared to individual measurements of mixtures. As shown in this paper, density estimations are also applicable for reciprocal and multicomponent mixtures. This will allow for efficient optimisation of salt mixtures for line-focusing CSP systems in the future. In addition, the applied methodology can be used not only for the discussed system Ca,K,Li,Na/NO₂,NO₃ and its subsystems, but also for other salt systems with ideal mixing properties.

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