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Predictive Model for the Phase Diagrams of Ternary Mixtures Composed of Calcium, Lithium and Sodium/Potassium Nitrates

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Abstract. The study and development of multi-component alkaline nitrates systems is of utmost interest to investigate low melting and low cost HTFs and HSMs, to be used in CSP plants. At this aim, several binary and ternary mixtures have been proposed as feasible and promising materials in the scientific literature. In order to evaluate the most feasible HTF and HSM, the simulation campaign proposed in this work was focused on economical and readily available compounds, ruling out rare and costly species.
A semi-predictive model, based on the regular solution theory, was employed to draw the ternary phase diagrams of $LiNO_3/NaNO_3/Ca(NO_3)_2$ and $LiNO_3/KNO_3/Ca(NO_3)_2$, from which it was possible to select the lower melting zones and the compositions. The binary sub-systems were the starting point for the employed approach. The results showed a good agreement with literature experimental data, and new low melting compositions were simulated and experimentally validated. It is noteworthy that it was possible to identify in great detail the zones of the two ternaries presenting the lowest freezing points and this can allow the design of interesting and cost-effective low melting mixtures.

INTRODUCTION

The development of ternary mixtures containing alkaline nitrates is a key point to obtain low melting and low cost HTFs and HSMs to be used in CSP plants. Several binary and multicomponent mixtures have been proposed as feasible and promising materials at this purpose. Considering the necessary thermal stability needed for the mixture components, and ruling out rare and costly species, only few nitrate and nitrite can be practically considered. In previous works [1]–[3] the several binary nitrate/nitrite combinations were considered and simulated following a regular solution model. Those data were meant to be propaedeutic for developing prediction tools of ternary systems. Actually, a throughout experimental determination of ternary or multi-component phase diagrams is very costly and time consuming and, for this reason, the assessment of proper simulation cost seems the only practical way to determine the compositions presenting the most favourable phase transition temperatures. In particular, considering the current state of the art, a couple of very promising ternary materials present little characterization and very few experimental data, namely the $LiNO_3/NaNO_3/Ca(NO_3)_2$, $LiNO_3/KNO_3/Ca(NO_3)_2$ mixtures.

To simulate the two diagrams, the binary fitting parameters were taken from the previous literature and, in the $Ca/Li//NO_3$ system was appositely modelled in this work. The two ternary phase diagrams were compared with literature experimental results and showed several zones presenting liquidus temperatures below 150°C. It was noteworthy that replacing sodium cation with the costlier potassium in the ternary leads to a limited decrease of the freezing points, evaluable at around 30°C.

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MATERIALS AND METHODS

To prepare the ternary mixtures, pure $NaNO_3$ (CAS 7631-99-4), KNO_3 (CAS 7757-79-1) and $Ca(NO_3)_2$ (CAS 13477-34-4) and $LiNO_3$ (CAS 7790-69-4) (all from Sigma Aldrich), analytical grade, were heated in a flask up to ~320 °C, i.e., above the melting temperatures of each component. After adequate stirring, the salts were poured out on an aluminium sheet and cooled down. Afterwards, they were powdered inside a mortar. DSC determinations were carried out by a Mettler Toledo DSC1 calorimeter. The heating/cooling rates were 10 °C/min in the temperature range from 25 to 300 °C (heating and cooling down), this ramp was repeated two times in order to remove water from salt during the first cycle. Details on the procedure used to obtain initial freezing and initial melting temperature of the mixtures by DSC measurement are reported in a previous work [2], [4].

In particular, solidus temperature is defined as the initial liquefaction temperature (from solid to liquid) that is, the peak onset during the heating ramp; liquidus temperature corresponds to the initial solidification temperature (from liquid to solid) that is, the peak onset during the cooling ramp.

According to regular solution method only the excess enthalpy is considered for non-ideality, and in this work it is used the approach of *Kramer et al* expressing this value as function of three fitting parameters [5]. The system equations are solved with the function "fsolve" of the Matlab R2018 analogously to the procedure described in a previous article[2].

RESULT AND DISCUSSION

Considering the great interest in developing nitrate compounds including calcium as cation, given its low price, two ternary mixtures were selected to be investigated and simulated: $LiNO_3/NaNO_3/Ca(NO_3)_2$ and $KNO_3/LiNO_3/Ca(NO_3)_2$. The thermophysical properties needed for the simulation are reported in Table 1 for each pure salt.

TABLE 1. List of enthalpies of fusion, melting temperatures and molar masses of the pure salts

	ΔH (KJ/mol)	**ΔCp (J/mol)**	**Tmelt (K)**	**MW**	**[ref]**
$NaNO_3$	15	–9.46	580	84.99	[1]
KNO_3	10	–3.01	607	101.10	[1]
$LiNO_3$	25	17.2	526	68.95	[1]
$Ca(NO_3)_2$	24	–2.09	834	164.08	[6]

Regarding the model parameters, Coscia [1] reported them for the case of the $NaNO_3/LiNO_3$ and $KNO_3/LiNO_3$ binaries, while for the systems $NaNO_3/Ca(NO_3)_2$ and $KNO_3/Ca(NO_3)_2$ the fitting values were calculated in a previous work [7].

No data were present for the $LiNO_3/Ca(NO_3)_2$ system and it was therefore simulated in this work, using the available phase diagram [7]. The results are shown in Figure 1 and the comparison between experimental [7] and modeled points shows a very good match for the liquidus temperatures, with an average deviation of 2 K, while no literature data were not found for the solidus transition. Considering the expected limited solubility between the two nitrates, as discussed for similar systems in a previous work [2], the experimental values are only reported up to a calcium nitrate molar percentage of about 40%. Table 2 reports the comparison between experimental and simulated points regarding the lithium-calcium nitrate system. Table 3 summarizes all the binary fitting parameters used as input for the ternary simulation campaign.

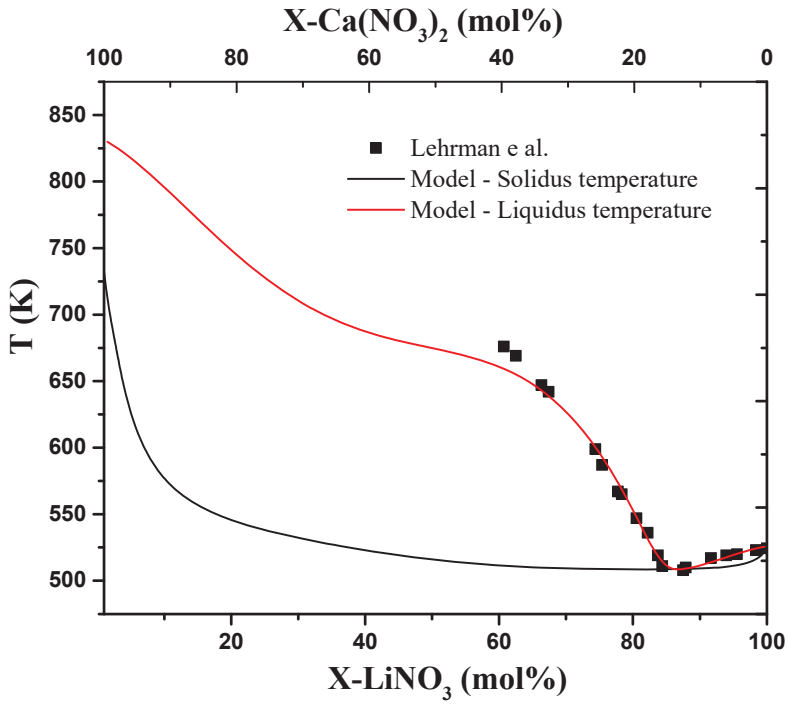

FIGURE 1. $LiNO_3/Ca(NO_3)_2$ system: comparison between experimental data [7] (dots) and modelled results (line)

TABLE 2. Comparison between experimental [7] and modelled liquidus temperature results for the $LiNO_3/Ca(NO_3)_2$ system:

$LiNO_3$ (mol%)	Exp	Model
100	524	
98.4	523	522
95.5	520	519
93.9	519	518
91.7	517	514
87.9	510	508
87.5	508	508
84.4	511	512
83.7	519	516
82.2	536	531
80.5	547	546
78.3	565	565
77.7	567	570
75.4	587	591
74.4	599	598
67.4	642	640
66.3	647	643
62.5	669	656
60.7	676	659

TABLE 3. Fitting parameters for binary mixing enthalpies

Binary	Liquidus (kJ/mol)			Solidus (kJ/mol)			Ref
	a	b	c	a	b	c	
$LiNO_3/KNO_3$	–9.2	–0.4	0	10.5	1.9	0	[1]
$LiNO_3/NaNO_3$	–1.9	–2.9	0	9.2	3.3	0	[1]
$NaNO_3/Ca(NO_3)_2$	–7.5	–6.27	0	7.9	1.3	0	[2]
$KNO_3/Ca(NO_3)_2$	–6.3	–16.7	–29.3	0	0	0	[2]
$LiNO_3/Ca(NO_3)_2$	–13.4	0.4	41.8	8.8	0.83	–8.4	This work

Regarding the modelling of these mixtures, it is in general more useful to determine the liquid surface, as for practical applications the most valuable information is the initial solidification point. Moreover, the liquidus temperatures are generally measurable with more accuracy and the correspondent fitting parameters are consequently more precise.

FIGURE 2 shows the modelled ternary diagram for the system $NaNO_3/LiNO_3/Ca(NO_3)_2$. The low melting zone is located at low calcium nitrate molar percentages and the lowest value is around 160°C.

The data from Wang et al [8] were used as a comparison and the deviation with the model results are reported in Table 4.

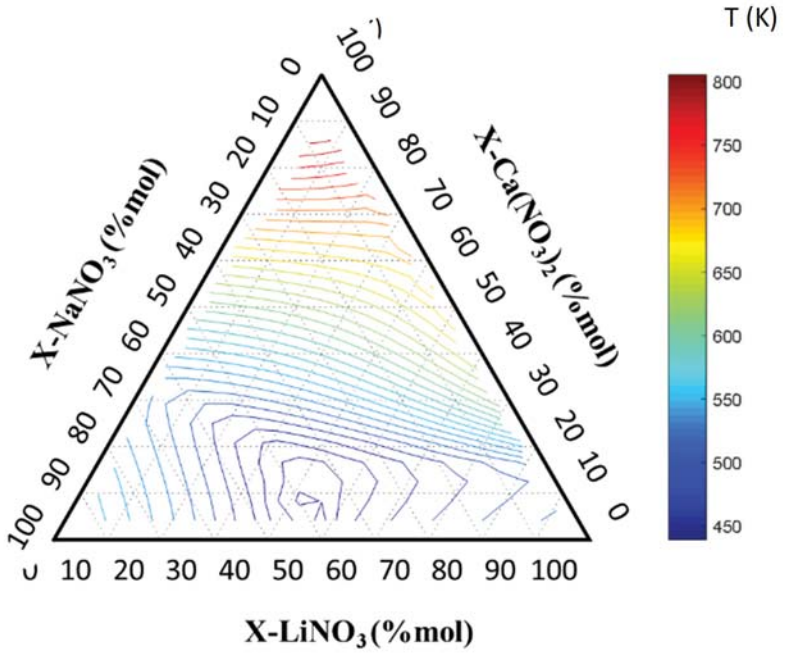

FIGURE 2. Ternary phase diagram of $LiNO_3/NaNO_3/Ca(NO_3)_2$

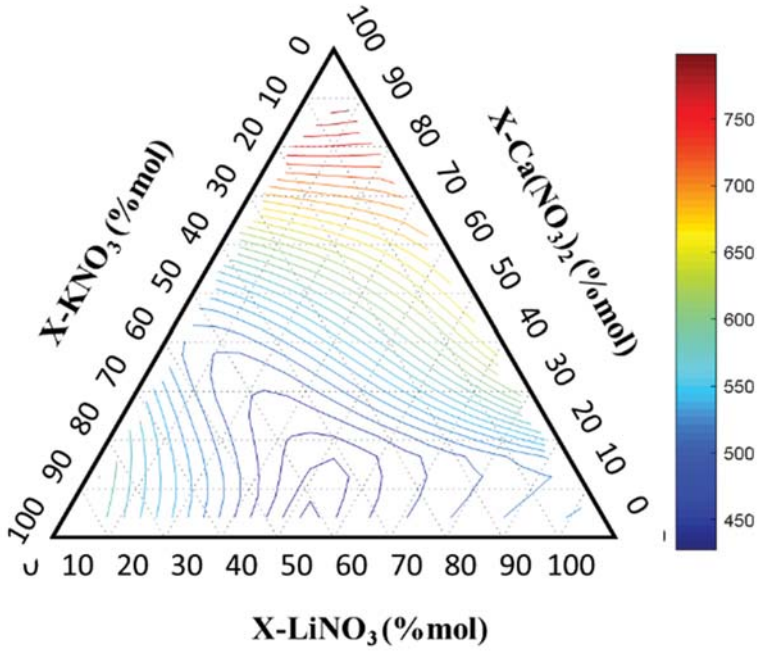

FIGURE 3. Ternary phase diagram of $LiNO_3/KNO_3/Ca(NO_3)_2$

The pattern for the potassium nitrate containing system, namely $KNO_3/LiNO_3/Ca(NO_3)_2$, is illustrated in Figure 3 and, also in this case, the work of Wang et al [9] is used to verify the simulation validity, as also illustrated in Table 4. The average deviation between modelled and experimental data is higher with this mixture.

The reason for the discrepancies between simulated and literature results can be due to the formation of a $4KNO_3 \cdot Ca(NO_3)_2$ complex, which can affect the validity of the $K/Ca//NO_3$ binary parameters [9]. Anyway, the temperature trend as a function of the composition is also in this case well fitted.

It is very interesting to note that replacing sodium nitrate with potassium nitrate it is possible to decrease the liquidus temperatures in the low melting zones of about 30°C. Given the high price expected with KNO_3 it can be concluded that the addition of this nitrate leads to limited favourable impact on the mixtures properties.

In both cases, given the large low melting zone, below 450K, presented by both ternaries, a relative large set of compounds can be selected and evaluated for CSP applications, especially, given the lithium high cost, to be used as HTF.

TABLE 4. Comparison between simulated and experimental liquidus temperatures for the two ternary mixtures

$NaNO_3$ (mol%)	KNO_3 (mol%)	$LiNO_3$ (mol%)	$Ca(NO_3)_2$ (mol%)	T liquidus model	T liquidus Experimental (K)	Literature
50		40	10	440	458	DSC This work
43.3		42.4	14.3	454	447	[10]
43.1		40.5	16.4	453	448	[10]
42		43	15	454	447	[10]
	59.1	32.1	8.8	460	402	DSC This work
					391	[9]
	57.6	32.9	9.5	460	390	[9]
	54.5	39.9	5.6	390	405	[9]

CONCLUSIONS

Several potentially favorable nitrate/nitrite mixtures are proposed as low melting materials for CSP applications but very few experimental data are present about this topic. The main reason is the difficult and time necessary to obtain proper experimental results. This work represents the follow up of previous papers dedicated to the calculation of fitting parameters for binary mixtures. Since it is of special scientific and practical interest the investigation about multicomponent systems, those results were to be used to simulate more complicated phase diagrams.

In this work two promising simple ternaries were studied, namely $LiNO_3/NaNO_3/Ca(NO_3)_2$ and $LiNO_3/KNO_3/Ca(NO_3)_2$, and their liquidus surfaces were modelled. Although a worst fitting was obtained with the latter ternary, the temperatures trend was confirmed in both cases, thus providing a very useful predictive tool to localize low freezing materials.

The next planned step is to use the above mentioned binary fitting parameters to simulate, with the same procedure, more complex systems, reciprocal ternaries and quaternary or quinary mixtures.

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