Electrical Conductivity and Phase Transitions of Calcium Nitrate + Ammonium Nitrate + Water Mixtures[†]

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The electrical conductivity of liquid $x\mathrm{Ca(NO_3)_2}\cdot z\mathrm{H_2O} + (1 - x)\mathrm{NH_4NO_3}$ mixtures was measured as a function of temperature over the whole composition range, where $0.3 < x < 1.0$ and $2.5 < z < 8.0$. A new assessment and experimental confirmation of quasi-crystal theory of molten salts was made using electrical conductivity measurements as a suitable tool to show the difference between aqueous solutions and aqueous molten salt systems. Also, the influence of the electrolyte and water concentration on transport properties of the mixture was investigated. Because of possible applications of such systems for the heat transfer and energy storage, differential scanning calorimetry (DSC) was used to investigate the phase equilibrium in calcium nitrate tetrahydrate + ammonium nitrate mixtures. Prior to these measurements, thermal properties of pure calcium nitrate tetrahydrate and ammonium nitrate were reinvestigated: new experimental results were obtained because of existing literature discrepancies on pure components.

Introduction

Calcium nitrate tetrahydrate and its mixtures with some other inorganic salts and organic compounds have a high latent heat of fusion and low melting point and have been considered to be phase-change materials (PCMs) for thermal energy storage.[1] The effects of increased absorbance with increased temperature and the high latent heat of fusion of the PCM are proposed for simultaneous control of the temperature and insulation in solar heat storage systems protecting the solar-heated greenhouses from overheating.[2,3] These melts have been used as reaction media, and also some mixtures show a thermochromic effect if cobalt(II) halide is added in the solvent. The complexation reaction of cobalt(II) ions with halide ions in pure calcium nitrate tetrahydrate,[4] calcium nitrate tetrahydrate + ammonium nitrate,[5−7] calcium nitrate tetrahydrate + acetamide,[8,9] and ammonium nitrate + acetamide[10] were investigated earlier. In all of these melts the formation of complexes $[\mathrm{Co(NO_3)_4}]^{2-}$, $[\mathrm{Co(NO_3)_2X_2}]^{2-}$, and $[\mathrm{CoX_4}]^{2-}$ have been postulated, and their stability and resolved species spectra have been determined. In this paper, our research was extended to the transport and thermal properties of the calcium nitrate + ammonium nitrate + water mixture. Thus, additional data on mixed low temperature inorganic solvents which are proposed as a suitable PCM were provided.

Experimental Section

All used commercial chemicals were pro analysi products. Ammonium nitrate (Merck) was dried at 353.15 K. Calcium nitrate tetrahydrate (Merck) was recrystallized and analyzed for water content, and then the water/calcium nitrate mole ratio was adjusted to the appropriate concentration of water by drying or the addition of water. The mixtures for the electrical conductivity measurements were prepared by melting together appropriate amounts of calcium nitrate tetrahydrate and ammonium nitrate or calcium nitrate tetrahydrate, ammonium nitrate, and water, dried by prolonged heating at 353.15 K. The electrical conductivity measurements were carried out in a Pyrex cell with platinum electrodes in the temperature range (298.15 to 353.15) K on a conductivity meter Jenco 3107. The conductivity cell was thermostatted, and the temperature was kept constant to ± 0.1 K. Temperature and conductivity data acquisitions were made by a personal computer connected to a conductivity meter. The experimental cell was calibrated with standard 0.1000 mol $\mathrm{dm^{-3}}$ KCl solution by the same experimental procedure. The resulting cell constant amounted to 0.8737 $\mathrm{cm^{-1}}$, and it was checked from time to time to control any possible evolution. The estimated uncertainty for electrical conductivity was ± 0.5 %.

The temperatures of phase transitions of pure calcium nitrate tetrahydrate, ammonium nitrate, and their mixtures were measured with a TA Instruments Q20 differential scanning calorimeter. Samples of ≈ 25 mg were contained in aluminum crucibles and well-sealed. Experiments were conducted at a heating and cooling rate between 5 $\mathrm{K\cdot min^{-1}}$ and if necessary 2.5 $\mathrm{K\cdot min^{-1}}$. The temperature scale and sensitivity were subsequently checked with standard materials. The uncertainty of temperature determination was within ± 1 K.

Results and Discussion

Electrical Conductivity. The electrical conductivity was determined at different temperatures for the systems $x\mathrm{Ca(NO_3)_2}\cdot z\mathrm{H_2O} + (1 - x)\mathrm{NH_4NO_3}$ with different mole ratios of $\mathrm{Ca(NO_3)_2\cdot 4H_2O}$, x, and different amounts of water content, z. Conductivity measurements of these liquid mixtures were performed for the first time, although their density data were reported earlier.[11] The conductivity of $x\mathrm{Ca(NO_3)_2}\cdot z\mathrm{H_2O} + (1 - x)\mathrm{NH_4NO_3}$ liquid mixtures was measured in the composition range $0.3 < x < 1.0$ and $2.5 < z < 8.0$.

In Figure 1 the experimental conductivity isotherms at six different temperatures for the systems with $z = 4.0$ were plotted

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[†] Part of the "Josef M. G. Barthel Festschrift".

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10.1021/je900927a

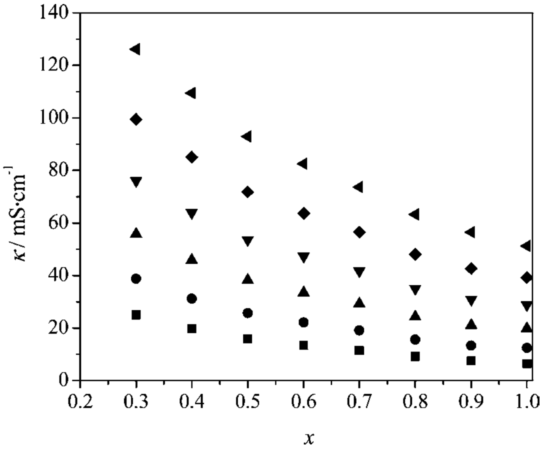

Figure 1. Electrical conductivity isotherms of $x\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O} + (1 - x)\text{NH}_4\text{NO}_3$ at different temperatures: left-pointing triangle, 353.15 K; ◆, 343.15 K; ▼, 333.15 K; ▲, 323.15 K; ●, 313.15 K; ■, 303.15 K.

Table 1. Coefficients of the Equation $\kappa/\text{mS}\cdot\text{cm}^{-1} = a - b(T/\text{K}) + c(T/\text{K})^2$ of Liquid $x\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O} + (1 - x)\text{NH}_4\text{NO}_3$ in the Temperature Range (298.15 to 353.15) K

x	a	b	$c\cdot 10^{-3}$	correlation
1.0	546.3	4.079	7.58	0.99931
0.9	779.2	5.571	9.98	0.99993
0.8	852.5	6.098	10.94	0.99998
0.7	898.9	6.511	11.82	0.99994
0.6	943.8	6.892	12.61	0.99995
0.5	1057.4	7.707	14.09	0.99994
0.4	1206.9	8.818	16.17	0.99996
0.3	1134.3	8.537	16.09	0.99983

against the mole fraction x. Electrical conductivity decreases with the increase of $\text{Ca(NO}_3)_2$ concentration, with significantly larger changes in the ammonium nitrate-rich region.

The experimental conductivity, κ, was well-represented by the following equation:

$$\kappa/\text{mS}\cdot\text{cm}^{-1} = a - b(T/\text{K}) + c(T/\text{K})^2 \qquad (1)$$

where κ is specific conductivity, T is the absolute temperature, and a, b, and c are coefficients determined by the least-squares method. All coefficients are listed in Table 1.

Using our experimental values, the electrical conductivity of all $x\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O} + (1 - x)\text{NH}_4\text{NO}_3$ is presented in Figure 2 as a function of temperature. From Figure 2 it can be seen that specific conductivity decreases with the increase of $\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O}$ mole fraction at constant temperature. The reason for the specific conductivity decrease with the increase of the calcium nitrate mole ratio in the systems with constant water content may be discussed in the terms of quasi-crystal theory of aqueous molten salts. In such melts, water concentration is not sufficient to occupy all coordination sites of each ion. Hence, small cations with higher charge are preferentially hydrated, because of strong ion−dipole interactions. In our case, only Ca^{2+} ions are hydrated, increasing the effective ionic radius and decreasing the conductivity of the ion. The same trend was observed earlier in a similar $\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ system.[12] The fact that only small divalent cations are hydrated in the systems containing both divalent and univalent cations is also observed elsewhere.[13,14] Also, the specific conductivity of all systems in Figure 2 increases with the increase of temperature as expected.

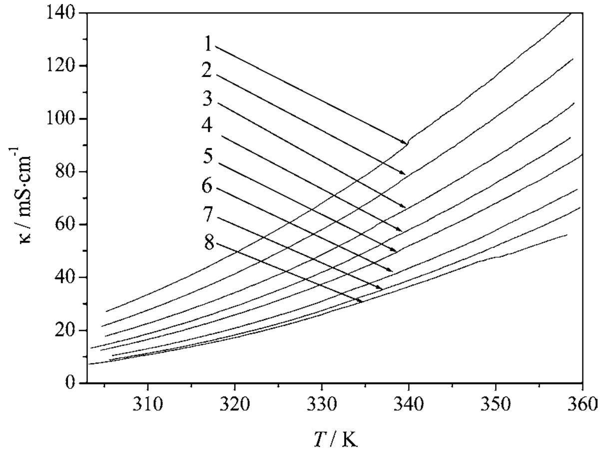

Figure 2. Electrical conductivity of $x\text{Ca(NO}_3)_2\cdot 4\text{H}_2\text{O} + (1 - x)\text{NH}_4\text{NO}_3$ vs temperature: **1**, $x = 0.3$; **2**, $x = 0.4$; **3**, $x = 0.5$; **4**, $x = 0.6$; **5**, $x = 0.7$; **6**, $x = 0.8$; **7**, $x = 0.9$; **8**, $x = 1.0$.

Table 2. Coefficients of the Equation $\kappa/\text{mS}\cdot\text{cm}^{-1} = a - b(T/\text{K}) + c(T/\text{K})^2$ of Liquid $0.5\text{Ca(NO}_3)_2\cdot z\text{H}_2\text{O} + 0.5\text{NH}_4\text{NO}_3$ in the Temperature Range (298.15 to 353.15) K

z	a	b	$c\cdot 10^{-3}$	correlation
2.5	1016.6	6.833	11.53	0.99997
3.0	1085.1	7.494	12.97	0.99994
4.0	1057.4	7.707	14.09	0.99994
5.0	835.7	6.724	13.45	0.99974
6.0	154.2	2.762	8.01	0.99980
7.0	−70.39	1.504	6.53	0.99993
8.0	7189.3	52.10	94.68	0.99997

Because of strong interactions between ions and water, it was essential to investigate the influence of water on transport properties in the mixture. Varying the calcium nitrate tetrahydrate mole fraction x in the system, the water concentration was not kept constant. Hence, electrical conductivity measurements were performed at different temperatures in the system $0.5\text{Ca(NO}_3)_2\cdot z\text{H}_2\text{O} + 0.5\text{NH}_4\text{NO}_3$, where the mole ratio of the salts was constant and the water content z was different. Experimental values were fitted using eq 1, and the results are presented in Table 2.

The variation of specific conductivity in $0.5\text{Ca(NO}_3)_2\cdot z\text{H}_2\text{O} + 0.5\text{NH}_4\text{NO}_3$ with temperature is presented in Figure 3. As it can be seen from Figure 3, the specific conductivity increases with an increase in temperature as expected. However, in the system with high water content, $0.5\text{Ca(NO}_3)_2\cdot 8\text{H}_2\text{O} + 0.5\text{NH}_4\text{NO}_3$, this change of the conductivity is more evident compared to the other systems where $z < 8$.

In Figure 4, the specific conductivity of the mixture $0.5\text{Ca(NO}_3)_2\cdot z\text{H}_2\text{O} + 0.5\text{NH}_4\text{NO}_3$ at several different temper-

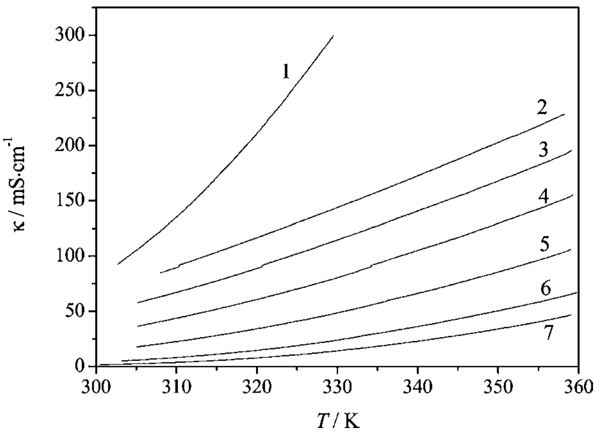

Figure 3. Electrical conductivity of $0.5\text{Ca(NO}_3)_2\cdot z\text{H}_2\text{O} - 0.5\text{NH}_4\text{NO}_3$ vs temperature: **1**, $z = 8$; **2**, $z = 7$; **3**, $z = 6$; **4**, $z = 5$; **5**, $z = 4$; **6**, $z = 3$; **7**, $z = 2.5$.

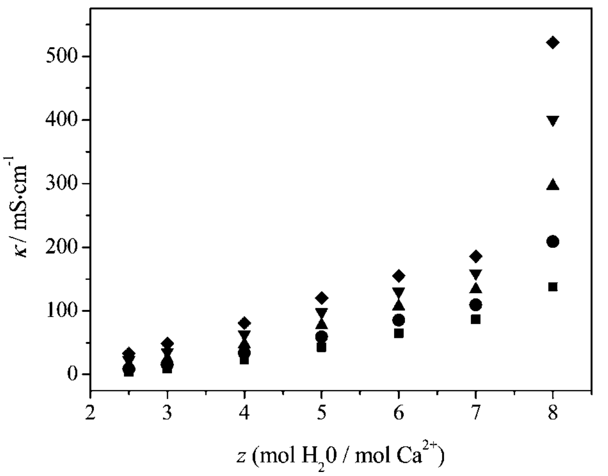

Figure 4. Variation of the specific conductivity with water concentration z in $0.5Ca(NO_3)_2 \cdot zH_2O - 0.5NH_4NO_3$ at different temperatures:◆, 343.15 K;▼, 333.15 K; ▲, 323.15 K; ●, 313.15 K; ■, 303.15 K.

atures is presented. The conductivity increases linearly up to $z = 7$, followed with the drastic increase at $z = 8$. This can be explained by the difference between the quasi-crystal structure of aqueous molten salts and aqueous solutions. In the quasi-crystal lattice only some cations are preferentially hydrated because of a low amount of water. In the case of $0.5Ca(NO_3)_2 \cdot 8H_2O - 0.5NH_4NO_3$, all ions are hydrated, breaking the quasi-crystal structure of the system and forming the aqueous solution with higher specific conductivity.

Thermal Measurements. Thermal properties of highly concentrated electrolytes and aqueous molten salts are a very rare subject of examination. Because of possible applications of such systems for heat transfer and energy storage, calorimetric measurements of pure calcium nitrate tetrahydrate and ammonium nitrate were performed. Also, existing literature data on temperatures of phase transitions are very uncertain; therefore, it seemed appropriate to perform new measurements and at the same time to assess the reliability of all existing calorimetric data on $Ca(NO_3)_2 \cdot 4H_2O$ and NH_4NO_3.

The corresponding thermograms yielded the temperature change of each thermal event upon heating and cooling. However, as supercooling was observed on nearly all cooling curves, the values reported here were taken from heating cycles only.

The melting temperature of pure $Ca(NO_3)_2 \cdot 4H_2O$ was reported earlier as a temperature range, (312.15 to 320) K[15] and (313.15 to 315.15) K.[16] The phase transitions of two modifications of calcium nitrate tetrahydrate were not observed by these authors. In this narrow temperature range two thermal events are merged. The characteristic differential scanning calorimetry (DSC) heating thermogram of pure $Ca(NO_3)_2 \cdot 4H_2O$ obtained by us (heating rate 5 K·min^{-1}) is presented in Figure 5. Only one endothermic peak characteristic for solid/liquid phase transition is observed, and the melting temperature determined is 316.95 K. During the cooling, the exothermic peak was not observed because of the supercooling effect.

The temperature determined in Figure 5 resulted actually from the superposition of two effects, and several phase equilibria take place over the narrow temperature range. For this reason, we performed a more detailed investigation by running DSC scans at a smaller heating rate ($v = 2.5$ K·min^{-1}). In Figure 6 two separated peaks can be observed, ascribing the presence of two different α and β modifications of calcium nitrate tetrahydrate.

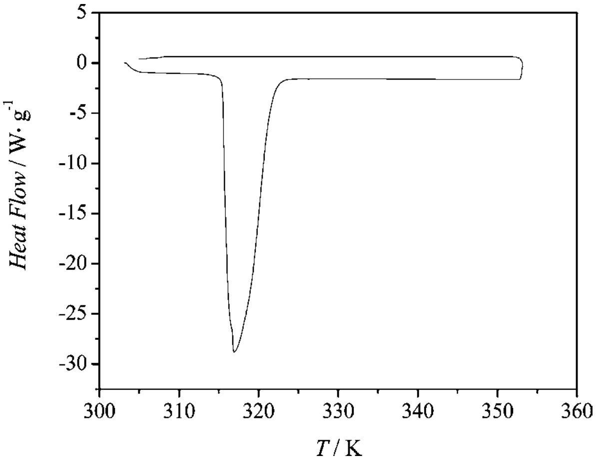

Figure 5. DSC thermogram of calcium nitrate tetrahydrate, $v = 5$ K·min^{-1}.

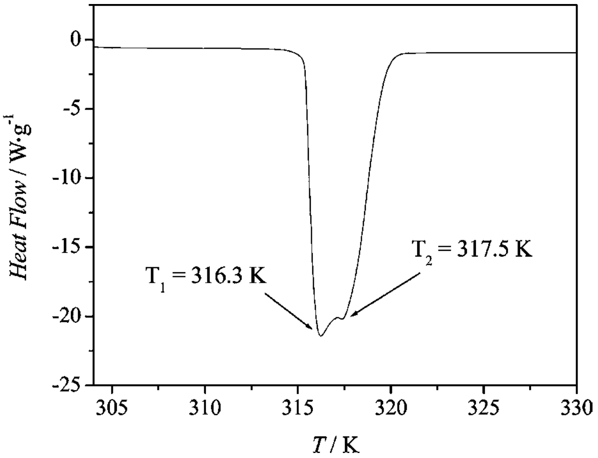

Figure 6. DSC thermogram of calcium nitrate tetrahydrate, $v = 2.5$ K·min^{-1}.

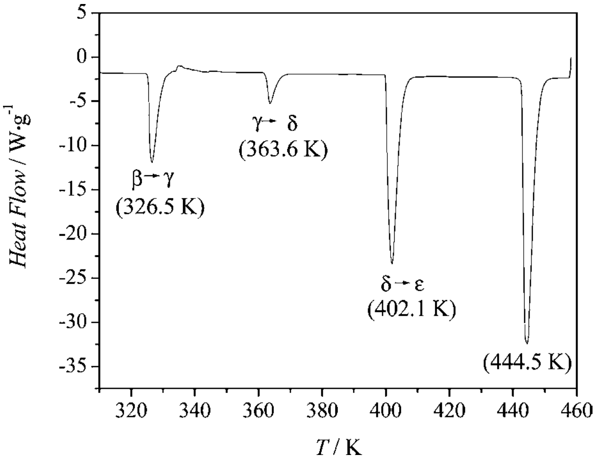

Figure 7. DSC thermogram of ammonium nitrate, $v = 5$ K·min^{-1}.

Phase transitions in ammonium nitrate were investigated by different methods and different authors earlier.[17,18] Special attention has been paid to temperatures and enthalpies of phase transitions in ammonium nitrate because of the important role of this salt in chemical industry.[19] The DSC thermogram obtained with the heating rate of 5 K·min^{-1} is presented in Figure 7.

In Figure 7 four characteristic temperatures were determined in the temperature range (303.15 to 463.15) K. Five crystal modifications of ammonium nitrate, α, β, γ, δ, and ε, are known from the literature,[17] but the first one, α, exists at lower temperatures, and it is not visible in presented figure. According

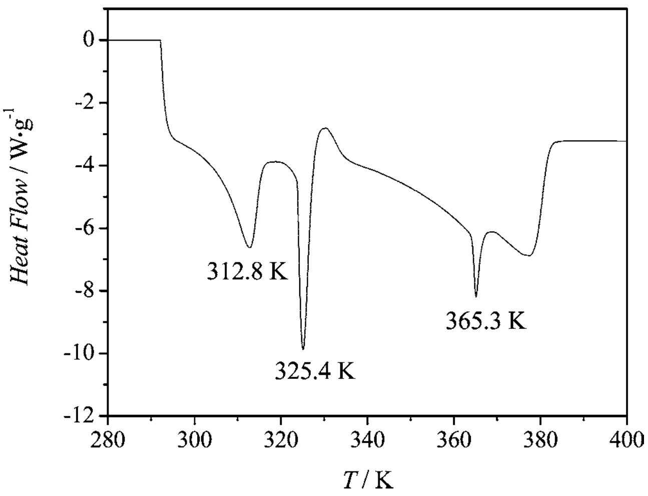

Figure 8. DSC thermogram of $0.1Ca(NO_3)_2 \cdot 4H_2O + 0.9NH_4NO_3$ binary mixture.

to available literature data,[18] the second phase transition, $\beta \rightarrow \gamma$, exists between (316.15 and 323.15) K. The corresponding temperature value presented in Figure 7 is 326.55 K. The next transformation, $\gamma \rightarrow \delta$, corresponds to a temperature of 363.65 K, and it is not predominant on the heating curve. The sharp peak at 402.05 K is characteristic for the last $\delta \rightarrow \varepsilon$ phase transformation. The melting temperature of the ε modification determined here is 444.45 K.

DSC scans were also conducted on the mixtures of calcium nitrate tetrahydrate−ammonium nitrate with different mole ratios of calcium nitrate/ammonium nitrate. All $x\mathrm{Ca(NO_3)_2 \cdot 4H_2O} + (1 - x)\mathrm{NH_4NO_3}$ mixtures where $x > 0.2$ are miscible at room temperature, and no thermal effects were observed on the heating curves. It is interesting to see a DSC thermogram of $0.1Ca(NO_3)_2 \cdot 4H_2O + 0.9NH_4NO_3$ binary mixture (Figure 8). Phase transitions presented in Figure 8 are characteristic of the pure components, and this mixture is immiscible in the whole temperature range.

Supporting Information Available:

Tables of experimental electrical conductivity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review October 31, 2009. Accepted March 22, 2010. This work was financially supported by the Ministry of Science and Environmental Protection of Republic of Serbia under contract No. 14204G and The Provincial Secretariat for Science and Technological Development of APV.

JE900927A