Densities of nitrate hydrates used as phase change materials

Vladimír Danielik, Dominika Szendreiová

Institute of Inorganic Chemistry, Technology and Materials,
Faculty of Chemical and Food Technology STU in Bratislava,
Radlinského 9, 812 37 Bratislava, Slovak Republic
vladimir.danielik@stuba.sk

Abstract: Temperature dependency of densities of the liquid system magnesium nitrate hexahydrate — zinc nitrate hexahydrate was measured. Densities of liquid mixtures were experimentally measured at different temperatures by a method using submersible corpuscle. Based on the obtained data, temperature dependence on the density was obtained. A model describing the density in the whole concentration range very well was created.

Keywords: phase change materials, density, density of liquids, zinc nitrate, magnesium nitrate

Introduction

One of the main disadvantages of renewable energy is its non-constant production. To make renewable energy the primary source of energy worldwide, it is necessary to develop and implement effective methods of energy storage. Thermal solar energy can be stored as latent heat, which is the heat consumed in changing the physical state of materials (enthalpy of fusion). Therefore, change of state from solid to liquid is applied in devices for heat storage. Systems using latent heat energy transmission are known as phase change materials (PCMs).

Among the important physical properties of PCMs belongs: (i) phase transition temperature, crucial for PCM material selection for a given application; (ii) sufficiently high phase transition enthalpy, the amount of energy absorb when changing the phase; (iii) the number of cycles of phase transition of the storage media required for the system. Good thermal conductivity is desired and as small as possible or no supercooling. When selecting PCM, technical requirements for a suitable design have to be considered. To ensure the longest construction material life, it has to meet certain criteria: PCM phase change volume should be minimized, the storage material has to be chemically stable and non-toxic in the environment. Storage media have to be compatible with the construction materials, it is therefore necessary to verify their corrosion properties, which are important for long-term durability in cyclic processes particularly at elevated temperatures. In economic terms low price of PCM materials is important to compete with other means of energy storage. Easy recycling is important for environmental protection. To choose an optimal material for PCM systems, all these properties should be taken into account. Nitrate hydrates belong among materials that meet the states requirements (Mehling and Cabeza, 2008; Hhan et al., 2016).

This work focuses on the volume change connected with the phase transformation in the liquid system magnesium nitrate hexahydrate — zinc nitrate hexahydrate. Temperature dependence of the volume changes of the liquid phase was also investigated.

Experimental

The following chemicals were used: magnesium nitrate hexahydrate (99+ %, Acros Organics); zinc nitrate hexahydrate (p.a., Lachema).

A method including a submersible corpuscle was used for density determination. Laboratory scales Radwag AS 60/220.X2 with a mounted "KIT 85 for determination of densities of solids and liquids" were used, which allow weighing with the accuracy of 0.02 mg. The amount of chemical corresponding to ca 400 ml of liquid was placed in a closed flask placed in a thermostat filled with the glycol liquid Shell EasyCare Premium Antifreeze with the boiling point of 139 °C. Temperature dependence of the submersible corpuscle volume was calibrated using tabulated values of water density (Frostburg, 2017; Wikipedia, 2017). The calibration was done at the temperatures of 20 °C, 40 °C, 60 °C and 80 °C.

The experimental procedure was as follows: Submersible corpuscle was weighed in air at room temperature and placed into a flask with the melted chemical heated to the chosen temperature for 20 minutes. The hold time was sufficient to heat the whole corpuscle; then, the corpuscle was pulled out from the solution, the solution was poured into

the measuring container and the submersible corpuscle was placed into this container and weighed in the solution. At the same time, temperature of the solution was recorded by a thermometer with the accuracy of 0.1 °C. The density was calculated as follows:

$$\rho(t) = \frac{m_{air} - m_{sol}}{V_{c,t}} \quad (1)$$

Tab. 1. Experimentally obtained densities of the liquid phase.

	50 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$ + 50 wt. % $Zn(NO_3)_2 \cdot 6\ H_2O$							
Temperature (°C)	72	75	77.5	80.5	81.5			
Density (kg m^{-3})	1680.5	1674.0	1672.7	1671.2	1667.3			
	40 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$ + 60 wt. % $Zn(NO_3)_2 \cdot 6\ H_2O$							
Temperature (°C)	69	70	70.5	72	73	73	74	75.5
Density (kg m^{-3})	1711.5	1708.1	1710.5	1708.8	1707.2	1704.4	1702.7	1705.1
Temperature (°C)	77.5	78	78.5	79.5	79.5	80	81	81
Density (kg m^{-3})	1699.0	1696.4	1701.4	1699.9	1697.2	1693.9	1695.9	1693.0
	30 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$ + 70 wt. % $Zn(NO_3)_2 \cdot 6\ H_2O$							
Temperature (°C)	67	68	69	70	70	70.5	71	72
Density (kg m^{-3})	1736.4	1735.3	1734.0	1734.1	1732.5	1731.9	1731.3	1730.3
Temperature (°C)	73	73	73.5	74	74.5	75	75.5	76
Density (kg m^{-3})	1731.6	1728.4	1727.9	1730.2	1729.4	1726.3	1728.6	1726.0
	20 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$ + 80 wt. % $Zn(NO_3)_2 \cdot 6\ H_2O$							
Temperature (°C)	55	58	60	62	63	65	66.5	67
Density (kg m^{-3})	1772.7	1770.5	1765.0	1762.9	1761.7	1759.4	1758.5	1757.9
Temperature (°C)	68	69	70	72	78	82.5	83.5	
Density (kg m^{-3})	1754.8	1753.2	1751.1	1747.9	1740.3	1737.7	1739.3	
	10 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$ + 90 wt. % $Zn(NO_3)_2 \cdot 6\ H_2O$							
Temperature (°C)	51	53	55	56	57.5	58		
Density (kg m^{-3})	1802.1	1799.4	1796.7	1795.4	1793.2	1791.4		

Tab. 2. Estimated temperature of primary crystallization in the studied system.

Content of $Mg(NO_3)_2 \cdot 6\ H_2O$ [wt. %]	Temperature of primary crystallization [°C]
100	89 (Dincer and Rosen 2002, Lane 1980, Heckenkamp and Baumann 1997)
80	84,0
70	80,0
60	77,0
50	72,0
40	67,0
30	60,5
20	53,5
10	43,0
0	36 (Dincer and Rosen, 2002; Lane, 1980; Naumann and Emons, 1989) 36.4 (Abhat, 1983; Have et al., 1993)

Tab. 3. Estimated coefficient of eqn (2).

Content of $Mg(NO_3)_2 \cdot 6\ H_2O$ [wt. %]	Parameter a [kg · m^{-3}]	Parameter b [kg · m^{-3} · °C^{-1}]	Correlation coefficient r^2
50	1763 ± 17	1.172 ± 0.214	0.9087
40	1802 ± 7	1.344 ± 0.085	0.9656
30	1830 ± 3	1.388 ± 0.044	0.9849
20	1852 ± 5	1.435 ± 0.074	0.9921
10	1877 ± 4	1.469 ± 0.078	0.9890

where $\rho(t)$ is the density at temperature t; m_{air}, m_{sol} are weights of the submersible corpuscle in air and in solution, respectively; $V_{c,t}$ is the volume of the submersible corpuscle at temperature t.

Temperature dependence of density was treated by the well-known expression:

$$\rho = a - b \cdot t \qquad (2)$$

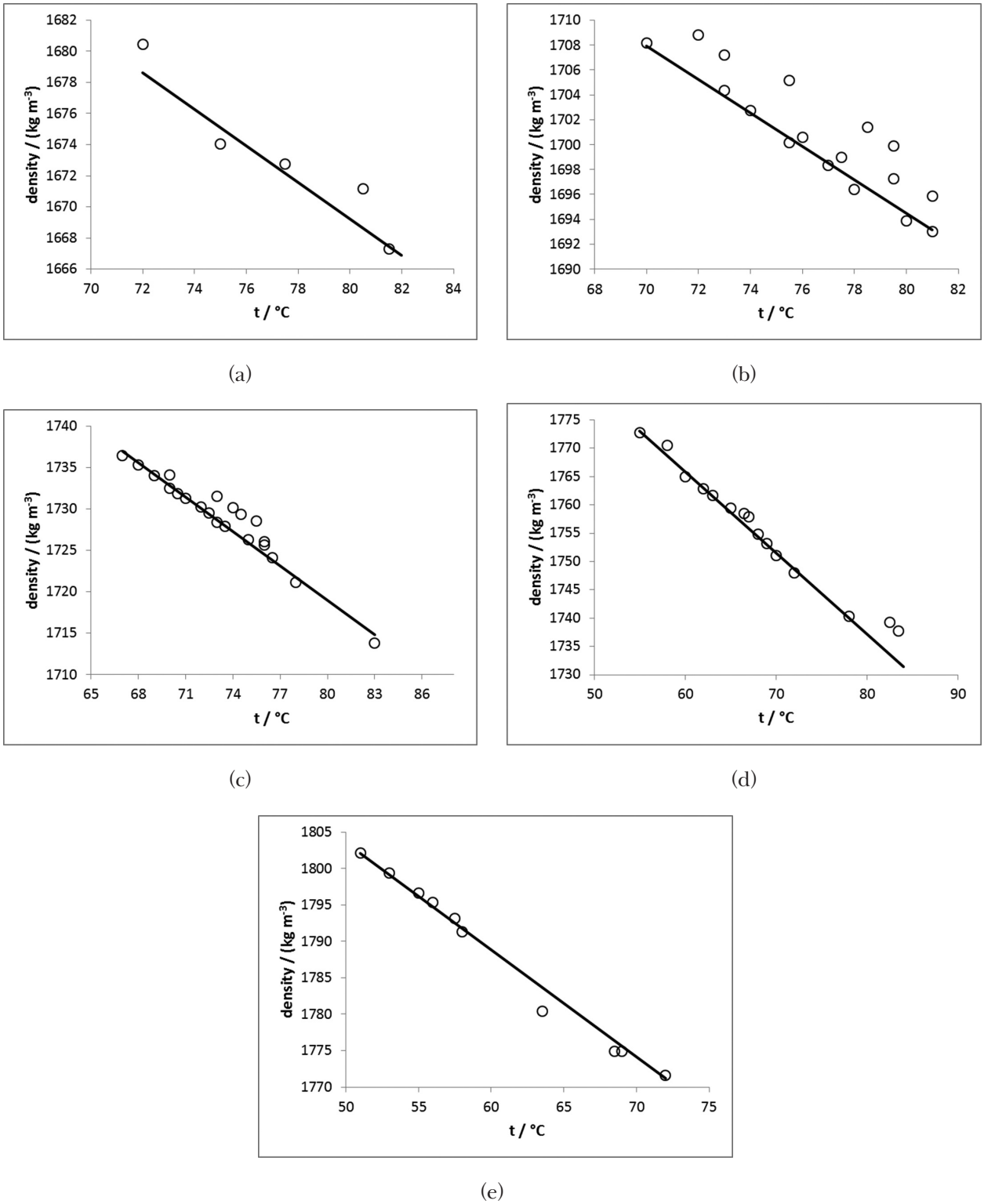

Fig. 1. Comparison of experimentally obtained and calculated densities of the system $Mg(NO_3)_2 \cdot 6\ H_2O + Zn(NO_3)_2 \cdot 6\ H_2O$. (a): 50 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$; (b): 40 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$; (c): 30 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$; (d): 20 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$; (e): 10 wt. % $Mg(NO_3)_2 \cdot 6\ H_2O$. Circles: exp. data; full line: calculated data based on coefficients presented in Table 3.

where t is the temperature in °C and a, b are empirical parameters obtained by linear regression analysis (least square method).

Reproducibility of the experiments was checked by six measurements of water density at 21 °C. The measured density values were in the range of (997.7 — 998.6) kg m^{-3} with the average value of (997.98 ± 0.33) kg m^{-3}, which is in agreement with the tabulated value of 997.995 kg m^{-3} (Frostburg, 2017). Based on the standard deviation of the average value, the uncertainty of the measured value is 0.04 %.

Results and Discussion

Experimentally measured values of the liquid phase density are summarized in Table 1. These values were usually measured at the temperatures of up to 80 °C. When the content of magnesium nitrate hexahydrate was higher than 50 wt. % (melting temperature above 80 °C), the solution solidified on the surface of the submersible corpuscle and the density experiment had to be stopped. The estimated melting temperatures of all measured compositions of the system are presented in Table 2 (temperatures were estimated during the measurement, when crystallization on the submersible corpuscle was observed.).

Correlation coefficients of eqn. (2) are listed in Table 3 showing that eqn. (2) describes the temperature dependence well and thus it can be used also for extrapolation in a reasonable range. Comparison of the experimental and the calculated data is shown in Fig. 1.

Based on the data published in this work, an approximation of densities in the system $Mg(NO_3)_2 \cdot 6\ H_2O$ — $Zn(NO_3)_2 \cdot 6\ H_2O$ can be done. Data on temperature dependence of pure components density (Danielik and Bogárová, 2017) were also taken into account. Eqn. (2) can be divided into two terms: (i) hypothetical density of liquid phase at 0 °C (parameter a); (ii) temperature dependence (parameter b) related with the coefficient of thermal volume expansion.

Molar volumes of the hypothetical liquid phase at 0 °C were compared with the prediction of additivity of molar volumes (dotted line) in Fig. 2. As it can be seen, the system behavior is quite far from ideality, differences can be expressed in form of excess molar volume:

$$V_m = \sum x_i V^0_{m,i} + \Delta V^E \qquad (3)$$

$$\Delta V^E = x_1 x_2 \left(A x_1 + B\right) \qquad (4)$$

where V_m is the molar volume of the mixture, $V^0_{m,i}$ is the molar volume of pure component i in the mixture, ΔV^E is the excess molar volume, x_i is the mole fraction of component i (subscripts 1, 2 denote $Mg(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, respectively) and A, B are parameters obtained by regression analysis:

$A = (19.355 \pm 6.648) \cdot 10^{-6}$ m^3 mol^{-1};
$B = (-28.195 \pm 2.402) \cdot 10^{-6}$ m^3 mol^{-1}

Molar volumes of the hypothetic liquid state at 0 °C compared with the calculated ones are shown in Fig. 2.

Parameter b of eqn. (2) depends on the molar composition of the system by a second order polynomial (Fig. 3) (coefficients were determined by the least square method):

$$b = B_0 x_1^2 + B_1 x_1 + B_2 \qquad (5)$$

where x is the mole fraction of $Mg(NO_3)_2 \cdot 6H_2O$; $r^2 = 0.998$ and:

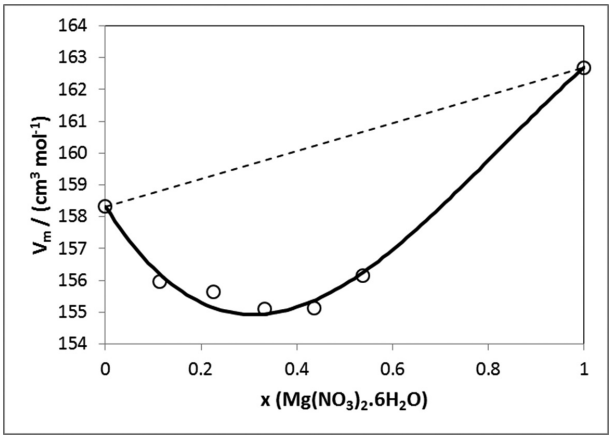

Fig. 2. Molar volume of the hypothetical liquid phase at 0 °C; (full line): calculated; (dotted line): ideal behavior (additivity of molar volumes).

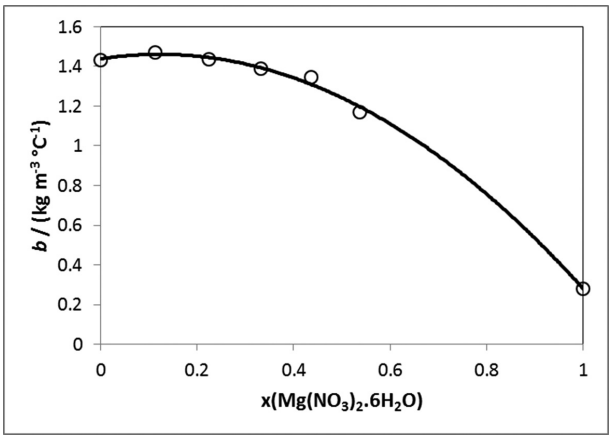

Fig. 3. Composition dependence of parameter b of eqn. (2); (full line): eqn. (5).

$$B_0 = (-1.355 \pm 0.084)\ \text{kg m}^{-3}\ ^\circ\text{C}^{-1},$$
$$B_1 = (0.3769 \pm 0.0895)\ \text{kg m}^{-3}\ ^\circ\text{C}^{-1},$$
$$B_2 = (1.438 \pm 0.018)\ \text{kg m}^{-3}\ ^\circ\text{C}^{-1}$$

An approximation of the density can be calculated from these dependencies at any composition in a reasonable range of temperatures.

Conclusion

Densities of the liquid system $Mg(NO_3)_2 \cdot 6\ H_2O$ – $Zn(NO_3)_2 \cdot 6\ H_2O$ were determined experimentally up to 30 °C overheat. Reasonable experimental data were obtained up to 50 wt. % of magnesium nitrate hexahydrate. The used method was not suitable for the determination of the density above ca 80 °C due the solidification of the solution on the surface of the submersible corpuscle.
An empirical model describing the density in the whole concentration range was proposed based on the molar volumes of pure components. Standard deviation of the model is 4 kg m^{-3}.

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References

Abhat A (1983) Low temperature latent heat thermal energy storage: heat storage materials, Solar Energy 30: 313–332.
Danielik V, Bogárová E (2017) Densities of selected phase change materials in liquid state, Chemical Data Collections 9–10: 244–250.
Dincer I, Rosen MA (2002) Thermal energy storage, Systems and Applications, John Wiley & Sons, Chichester (England).
Frostburg (2017) http://antoine.frostburg.edu/chem/senese/javascript/water-density.html (date: 29. 9. 2017).
Hawes DW, Feldman D, Banu D (1993) Latent heat storage in building materials, Energy Buildings 20: 77–86.
Heckenkamp J, Baumann H (1997) Latentwärmespeicher, Sonderdruck aus Nachrichten 11: 1075–1081.
Khan Z, Khan Z, Ghafoor A (2016) A review of performance enhancement of PCM based latent heat storage system within the context of materials, thermal stability and compatibility, Energy Convers Manage 15: 132–158.
Lane GA (1980), Low temperature heat storage with phase change materials, Ambient Energy 1: 155–168.
Mehling H, Cabeza LF (2008) Heat and cold storage with PCM an up to date introduction into basics and applications, Springer, Berlin.
Naumann R, Emons HH (1989) Results of thermal analysis for investigation of salt hydrates as latent heat-storage materials, Thermal Analysis 35: 1009–1031.
Wikipedia (2017) https://en.wikipedia.org/wiki/Density (date: 29. 9. 2017).