J. Chem. Eng. Data **2004,** *49,* 1451−1455

Densities of Solid and Molten Salt Hydrates and Their Mixtures and Viscosities of the Molten Salts

A. Minevich, Y. Marcus,* and L. Ben-Dor

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem,
Jerusalem 91904, Israel

The densities of the salt hydrate phase-change materials (PCMs) crystalline ammonium alum (aluminum ammonium disulfate dodecahydrate), aluminum nitrate nonahydrate, and magnesium nitrate hexahydrate as well as their melts and of solid aluminum sulfate and magnesium acetate hydrates and anhydrous ammonium nitrate and sulfate were determined as a function of the temperature in the solid and liquid phases. The densities of selected mixtures of these salts were also determined as a function of the temperature. Viscosities of the corresponding molten single salts and mixtures were also determined.

---

1. Introduction

Thermal energy can be stored in and retrieved from phase-change materials (PCMs) by letting the PCM melt at a temperature a few degrees above its melting point and freeze at a few degrees below this temperature. The latent enthalpy of fusion and a small amount of sensible heat is thus stored and delivered. Among the PCMs that have been suggested, many salt hydrates have been tested and some have actually been employed for heat storage. A quantity that is of prime importance in this respect is the energy storage density (esd) of the PCM, which is the ratio of the specific latent heat to the density. PCMs having values of esd > 200 MJ m^{-3} are attractive because for a small temperature swing (above and below the melting point) they permit a larger thermal energy storage than in water, reducing costs. It is, therefore, imperative to know the density of any PCM that is suggested in order to evaluate its applicability for practical purposes. There are some additional thermophysical properties of the PCM that need to be known, such as the expansivity of the solid and of the molten PCM, the fractional volume change on melting, the viscosity of the melt, and the heat conduction of the melt and the solid PCM. The expansivity and volume change on melting are of particular importance for PCMs that are salt hydrates because the vapor space above the material should be kept to the minimum needed to allow expansion and avoid the loss of water from the molten hydrate.

In the present study, the densities of some crystalline and molten salt hydrates that have melting points above ca. 330 K and mixtures of these salt hydrates as well as the viscosities of some of the melts have been measured as a function of temperature. The hydrated salts included in this study comprise ammonium alum (aluminum ammonium disulfate dodecahydrate), aluminum sulfate, aluminum nitrate, magnesium nitrate, nickel nitrate, and magnesium acetate. In addition, anhydrous ammonium nitrate and sulfate were also used in mixtures with some salt hydrates.

2. Experimental Section

2.1. Procedures. A high-temperature (≤470 K) Julabo MD immersion circulator, equipped with flexible tubing usable up to this temperature and a silicone oil circulating fluid, was employed. Glass vessels permitting circulation of the oil in the jacket encircling a cylindrical measuring space and a well for the temperature probe were constructed. The temperature was measured with a computerized digital thermometer (Ertco-Hart, model 850C) provided with the necessary software. Temperature readings were taken as a function of time, stored, manipulated algebraically, and presented graphically in an automatic manner. Temperatures in the measuring space could be maintained at a steady value within 0.1 K and read with that probable uncertainty.

Densities of solid salts were determined pycnometrically with dodecane as a displacement liquid. The pycnometer had a nominal volume of $V = 3.5 \times 10^{-5}$ m^3, was provided via a ground glass joint with a calibrated 2.2-mm i.d. capillary that was 200 mm long, and could be immersed in a thermostated bath. The actual volume of the pycnometer to the calibration mark was measured using dodecane as the calibrating liquid. Its density from (294 to 393) K,

$$d_{\mathrm{dod}}/\mathrm{kg\ m^{-3}} = -27744.46 + 209.44(T/\mathrm{K}) - 0.384664(T/\mathrm{K})^2 \quad (1)$$

was obtained from literature data.[1,2] The pycnometer volume changed linearly with the temperature (within 7×10^{-9} m^3): $V_{\mathrm{pyc}}(T)/\mathrm{m}^3 = 2.4353 \times 10^{-5} + 3.05 \times 10^{-8}(T/\mathrm{K})$ on both heating and cooling. The density of a solidified and ground melt was determined by placing a weighed amount, m_{salt}, of the solid salt in the pycnometer, adding dodecane to the mark, and heating to the desired temperature in the bath. When steady conditions were attained, the excess dodecane over the mark was removed with a capillary pipet, and the pycnometer with contents was reweighed, yielding the weight of the dodecane (m_{dod}). The density of the solid salt is then

$$d_{\mathrm{salt}}(T) = \frac{m_{\mathrm{salt}}}{V_{\mathrm{pyc}}(T) - (m_{\mathrm{dod}}/d_{\mathrm{dod}}(T))} \quad (2)$$

The estimated uncertainty in the densities of the solids is 0.2 kg m^{-3}.

Densities of molten salts were measured by an Archimedean sinker method and were employed for molten

---

* Corresponding author. E-mail: ymarcus@vms.huji.ac.il. Phone: +972-2-6585341. Fax: +972-2-6585319.

10.1021/je049849b CCC: $27.50

Table 1. Density Coefficients (Equation 4) of Single-Salt Hydrates and Their Expansivities, α, over a Temperature Range, Δ*T*

salt	ΔT/K	a	b	$10^3(\alpha/\text{K}^{-1})$
$(NH_4)_2SO_4$, solid	298−333	1917.9 ± 3.0	0.505	0.287
NH_4NO_3, solid	298−318	1767.9 ± 3.0	0.268 ± 0.040	0.159
$NH_4Al(SO_4)_2{\cdot}12H_2O$, solid	298−328	1690.2 ± 4.0	0.158 ± 0.045	0.096
$NH_4Al(SO_4)_2{\cdot}12H_2O$, melt	353^a−378	1695.2 ± 5.3	0.852 ± 0.060	0.616
$Al(NO_3)_3{\cdot}9H_2O$, solid	298−333	1930.4 ± 3.0	0.686 ± 0.040	0.400
$Al(NO_3)_3{\cdot}9H_2O$, melt	338^a−368	1920.2 ± 3.0	0.947 ± 0.040	0.597
$Al_2(SO_4)_3{\cdot}nH_2O$, solid	298−333	1848.7 ± 3.0	0.248 ± 0.040	0.140
$Mg(NO_3)_2{\cdot}6H_2O$, solid	298−328	1756.3 ± 3.0	0.40 ± 0.07	0.245
$Mg(NO_3)_2{\cdot}6H_2O$, melt	358^a−376	1873.6 ± 9.2	0.96 ± 0.10	0.631
$Mg(CH_3CO_2)_2{\cdot}4H_2O$, solid	298−333	1549.6 ± 2.0	0.35 ± 0.04	0.243

[a] Undercooled.

salts and mixtures. A Mettler electronic balance (capacity 0.051 kg) for weighing under the balance pan was equipped with a thin gold chain supporting a sealed glass sinker weighted with lead shot. The volume of the sinker was determined as a function of the temperature by means of its weight loss when immersed in dodecane and was found to be $V_{\text{sink}}(T)/\text{m}^3 = 1.6823 \times 10^{-6} + 4.2 \times 10^{-10}(T/\text{K})$ in the range of (310 to 390) K. About 0.020 kg of ground salt crystallites was placed in the cavity of a jacketed glass vessel, through which the fluid from the thermostat bath was circulated, and melted at ~10 K above the melting point. Because a film of solid salt formed at the open surface, a layer of dodecane was put on top of the melt, and the sinker was immersed to the same height in the chain corresponding to its volume in dodecane alone. The density of the melt is obtained from the difference in weight, Δw_{sink}/kg, of the sinker in air and immersed in the melt:

$$d_{\text{melt}}/(\text{kg m}^{-3}) = \frac{\Delta w_{\text{sink}}}{V_{\text{sink}}(T)} \tag{3}$$

The estimated uncertainty in the densities of the melts is 0.5 kg m^{-3}.

Viscosities of salt melts were measured with a Funlab (Spain) Plus L rotating spindle viscosimeter equipped with several stainless steel spindles for measurements in the range of (30 to 20 000) mPa·s. A jacketed glass container, permitting the thermostating fluid from the high-temperature circulator to flow in its jacket and having a thermometer well and a cylindrical space for the sample in which the spindle rotated, was employed. The instrument was tested with aqueous glycerol mixtures of known viscosity. About 0.020 kg of salt crystals was placed in the sample well of the jacketed vessel and heated by the thermostating fluid to ~10 K above the melting point. Spindles and rates of rotation (in rpm) were selected for each measurement range as required. The estimated uncertainty in the viscosities of the melts is 0.1 mPa·s, except when $\eta > 60$, when it is 1 mPa·s.

2.2. Materials. Ammonium nitrate NH_4NO_3 (AnalaR) was used as received and was used only in mixtures so that it was not melted alone. Ammonium sulfate $(NH_4)_2SO_4$ (Mallinckrodt) was used as received, and it too was used only in mixtures so that it was not melted alone. Ammonium alum $NH_4Al(SO_4)_2{\cdot}12H_2O$ (Baker's Analyzed) was ground into smaller crystals before being melted. Its water content was determined by EDTA (back) titration and was found to be (12.10 ± 0.03)/mol salt. The X-ray diffraction pattern of $NH_4Al(SO_4)_2{\cdot}12H_2O$ agreed well with the literature.[3] Aluminum nitrate nonahydrate $Al(NO_3)_3{\cdot}9H_2O$ (Fluka) was used as received. Its water content was determined by EDTA (back) titration and was found to be slightly below 9 mol/mol aluminum in one batch and slightly more than 9 mol/mol salt in another batch, determined from its mass after drying in a vacuum oven at 333 K, and (9.18 ± 0.02) mol/mol salt, determined by EDTA (back) titration. The X-ray diffraction pattern of $Al(NO_3)_3{\cdot}9H_2O$ agreed well with the literature.[4] Aluminum sulfate hydrate $Al_2(SO_4)_3{\cdot}nH_2O$, with n being nominally 16 and 18 in two preparations (Baker's Analyzed), actually contained (16.3 ± 0.1) mol water/mol salt as obtained by EDTA titration of the metal content. No systematic differences between samples from the two batches were noted. The diffraction pattern agreed with that in the literature of nominally $Al_2(SO_4)_3{\cdot}17H_2O$.[5] Magnesium nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$ (Baker's Analyzed), had a water content of (6.02 ± 0.01) mol/mol salt, as determined by EDTA and by Karl Fischer titrations. The X-ray diffraction pattern of $Mg(NO_3)_2{\cdot}6H_2O$ agreed well with the literature.[6] Magnesium acetate tetrahydrate $Mg(CH_3CO_2)_2{\cdot}4H_2O$ (Merck) had a water content of (4.00 ± 0.02) mol/mol salt, as determined by EDTA titration. Several samples of the latter were tested for their water loss in a vacuum oven at 318 K and were indeed found to lose practically 4.0 mol water/mol of salt. The X-ray diffraction pattern of $Mg(CH_3CO_2)_2{\cdot}4H_2O$ agreed well with the literature.[7] Nickel nitrate hexahydrate $Ni(NO_3)_2{\cdot}6H_2O$ (Baker's Analyzed) was found by EDTA titration (back titration with zinc sulfate of excess EDTA) to have 6.0 ± 0.1 mol water/mol salt. The X-ray diffraction pattern of $Ni(NO_3)_2{\cdot}6H_2O$ agreed well with the literature.[8] Dodecane (Humphrey Chem. Co.) was used as a density calibration liquid. Glycerol (Sigma) was used, diluted with triply distilled water, as a viscosity calibration fluid.

Mixtures were prepared on a mass basis for specified mole fractions x of the components. In view of the uncertainties in the water content of the salt hydrates reported above, the uncertainties in the mole fractions are estimated to be ≤0.002.

3. Results

3.1. Densities. The densities of single solid-salt hydrates were measured at (298−328 or 333) K. The data are shown in Table A1 in Supporting Information. They varied linearly with the temperature according to

$$d/(\text{kg m}^{-3}) = a - b{\cdot}(T/\text{K}) \tag{4}$$

and the coefficients a and b averaged for four independent runs are shown in Table 1. The densities of solidified mixtures of salt hydrate melts $\mathbf{A} + \mathbf{B}$ were generally linear with both temperature and the mole fraction of component $\mathbf{B}$, $x_{\mathbf{B}}$, according to

$$d/(\text{kg m}^{-3}) = (a_0 + a_1 x_{\mathbf{B}}) - (b_0 + b_1 x_{\mathbf{B}}){\cdot}(T/\text{K}) \tag{5}$$

and the coefficients are shown in Table 2.

Table 2. Density Coefficients (Equation 5) of Salt Hydrate Mixtures

salts **A** + **B**	$x_{\mathbf{B}}$	a_0	a_1	b_0	b_1
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + $Al_2(SO_4)_3 \cdot nH_2O$, solid	$\leq 0.376^a$	1699.4	139.2	0.205	0.0043
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + $Al_2(SO_4)_3 \cdot nH_2O$, melt	$\leq 0.376^a$	1695.2	68.5	0.852	0.0127
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + NH_4NO_3, solid	$\leq 0.6^a$	1725.0	71.2	0.277	
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + NH_4NO_3, solid	0.6 to 1.0	1573.3	194.6	0.079	0.189
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + NH_4NO_3 melt	$\leq 0.9^b$	1962.1	104.0	1.14	0.12
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$, solid	0.5	2118.9		1.403	
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$, melt	0.5	2007.5		1.304	
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + $(NH_4)_2SO_4$, solid	0.1	1753.8		0.330	
	0.3	1798.3		0.400	
	0.4	1826.0		0.454	
	0.5	1870.7		0.570	
	0.75	1933.2		0.680	
$NH_4Al(SO_4)_2 \cdot 12H_2O$ + $(NH_4)_2SO_4$, melt	$\leq 0.6^a$	1864.3	20.0	0.92	
$Mg(NO_3)_2 \cdot 6H_2O$ + $Mg(CH_3CO_2)_2.4_2O$, solid	0.20	1728.7		0.42	0.00
	0.35	1683.7		0.42	0.00
	0.50	1626.7		0.42	0.00
	0.67	1617.6		0.42	0.00
$Mg(NO_3)_2 \cdot 6H_2O$ + $Mg(CH_3CO_2)_2.4_2O$, melt	0.20	1822.5		1.06	0.00
	0.35	1831.4		1.06	0.00
	0.50	1812.5		1.06	0.00
	0.67	1787.6		1.06	0.00
$Mg(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$, solid	0.30	1921.2		0.70	
$Mg(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$, melt	0.30	2101.4		1.40	
$Mg(NO_3)_2 \cdot 6H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$, solid	$\leq 0.9^b$	1830.7	64.4	0.68	0.036
$Mg(NO_3)_2 \cdot 6H_2O$ + $Al(NO_3)_3 \cdot 9H_2O$, melt	$\leq 0.9^b$	1866.3	66.0	0.92	0.027

[a] Six mixtures. [b] Nine evenly spaced mixtures.

Table 3. Viscosity Coefficients (Equation 7) and Activation Gibbs Energy for the Viscous Flow of Mixtures of Molten Magnesium and Aluminum Nitrate Hydrates

x_{AlN}	range of T/K	a	$10^{-4}b$	$\Delta G^{\ddagger}$/kJ mol^{-1}
0.0	357−373	-1.444 ± 0.058	0.104 ± 0.002	1.99
0.1	358−378	-0.995 ± 0.121	0.088 ± 0.004	1.68
0.2	348−378	-0.730 ± 0.056	0.079 ± 0.002	1.51
0.3	341− 368	-0.614 ± 0.064	0.075 ± 0.002	1.44
0.4	353−378	-0.775 ± 0.050	0.082 ± 0.002	1.57
0.5	368−378	-0.630 ± 0.110	0.077 ± 0.004	1.47
0.6	368−378	-0.342 ± 0.020	0.067	1.28
0.7	373−378	0.435	0.041	0.78

The densities of melts of single salts were measured from ~10 K above the melting point down to as far as the salts remained molten, often as supercooled melts and up again. At temperatures >10 K above the melting point, bubbles of water vapor were observed in molten $NH_4Al(SO_4)_2 \cdot 12H_2O$ and $Al_2(SO_4)_3 \cdot nH_2O$ so that no further measurements were made at such temperatures. The densities of the melts are shown in Table A2 in Supporting Information. The densities were linear with temperature according to eq 4, and the coefficients are shown in Table 1. The same procedure was followed for mixtures of salts, with densities generally conforming to eq 5, the coefficients being shown in Table 2. The densities of both solid and molten binary salt hydrate mixtures are shown in Table A3 in Supporting Information.

3.2. Viscosity Measurements on Melts. The shear viscosities of the molten salt hydrates are Newtonian in behavior and do not depend on the shear rate. The viscosities of molten salt hydrate mixtures were measured at as high temperatures as consistent with the stability of the hydrates in open vessels. The viscosities are shown in Table A4 in Supporting Information. The values obeyed the Arrhenius expression

$$\eta = A \exp\left(\frac{B}{RT}\right) \tag{6}$$

or, expressed in logarithmic form

$$\log[\eta/(\mathrm{mPa \cdot s})] = a + \frac{b}{T/\mathrm{K}} \tag{7}$$

Viscosity measurements were made with molten $Mg(NO_3)_2 \cdot 6H_2O$ in the range from 373 K down to 357 K (supercooled) by gradually decreasing the temperature and letting it stabilize at a new value. As expected, the viscosity increased with decreasing temperature ($\eta = 22.7$ mPa·s at $T = 373$ K and $\eta = 29.0$ mPa·s at $T = 359$ K), obeying the relationship (eq 7) with $a = -1.444 \pm 0.058$ and $b = (1.04 \pm 0.02) \times 10^3$. The results for mixtures of $Mg(NO_3)_2·6H_2O + Al(NO_3)_3·9H_2O$ are shown in Table 3. Multiplication of b by 1000 ln(10)R yields the activation energy of the viscosity, $\Delta G^{\ddagger}$, in kJ mol^{-1}.

The viscosity of the $Mg(NO_3)_2·6H_2O + Ni(NO_3)_2·6H_2O$ (**NiN**) eutectic melt at $x_{\mathbf{NiN}} = 0.70$ was measured between (355 and 368) K in two series of experiments, with good agreement between them. The viscosity of the eutectic followed the expected Arrhenius dependence, eq 7, with $a = -0.642 \pm 0.074$ and $b = 464 \pm 17$, with an activation energy for viscous flow of $\Delta G^{\ddagger} = 1.41$ kJ mol^{-1}, which is somewhat lower than for neat $Mg(NO_3)_2·6H_2O$, 1.99 kJ mol^{-1}.

Viscosity measurements were carried out for a $Mg(NO_3)_2·6H_2O + Mg(CH_3CO_2)_2·4H_2O$ (**MgA**) mixture at $x_{\mathbf{MgA}} = 0.35$ in the range from (371 to 337) K by both increasing and decreasing the temperature. The viscosity obeyed the relationship (eq 7) with $a = -5.322 \pm 0.108$ and $b = (2.60 \pm 0.04) \times 10^3$. The activation energy for viscous flow was $\Delta G^{\ddagger} = 5.0$ kJ mol^{-1}. The viscosities were higher than those for pure magnesium nitrate at a given temperature (e.g., at 363 K $\eta = 27.2$ mPa·s for $Mg(NO_3)_2·6H_2O$ and $\eta = 66$ mPa·s for 0.65 $Mg(NO_3)_2·6H_2O$ + 0.35 $Mg(CH_3CO_2)_2·4H_2O$). However, when these mixtures were allowed to melt and recrystallize, we noted that the viscosity increased in subsequent cycles. Thus the viscosity was (83, 105, 128, and 138) mPa·s in the melt at 357 K in the first to fourth cycles.

Measurements on the $NH_4Al(SO_4)_2·12H_2O + Al_2(SO_4)_3·nH_2O$ (**AlS**) molten mixture (at $x_{\mathbf{AlS}} = 0.30$) starting at 373 K had to be discontinued because of the corrosion of the stainless steel spindle of the viscosimeter.

4. Discussion

As mentioned in the Introduction, the fractional expansion of a PCM on melting is an important quantity in the design of the thermal-energy storage device. When the density of molten $NH_4Al(SO_4)_2·12H_2O$ is compared with the density of $NH_4Al(SO_4)_2·12H_2O$ crystals, both extrapolated to the melting point ($T_m = 364$ K), the density decrease on melting is -24.8 kg m^{-3}, or the expansion on melting is $\Delta_{fus}V/V_{solid} = 1.6\%$. This value is small but reasonable. When the density of molten $Mg(NO_3)_2·6H_2O$ is compared with the density of $Mg(NO_3)_2·6H_2O$ crystals, both extrapolated to $T_m = 362$ K, the density decrease on melting is -85.4 kg m^{-3}, or the expansion on melting is $\Delta_{fus}V/V_{solid} = 5.3\%$. Such a value is expected. For the eutectic $NH_4Al(SO_4)_2·12H_2O + Al_2(SO_4)_3·nH_2O$ at $x_{\mathbf{AlS}} = 0.28$ and the melting point $T_m = 350$ K, the density of the solid is 1665.3, and that of the melt is 1440.4 kg m^{-3}. The density decrease on melting is -224.9 kg m^{-3}, and the volume increase on melting is rather large, 14.5%. At the melting point of the equimolar mixture of $NH_4Al(SO_4)_2·12H_2O$ and $Al(NO_3)_3·9H_2O$ $T_m = 346$ K, the difference in density between the solid and the melt is $1633.3 - 1556.1 = 77.2$ kg m^{-3} (i.e., an expansion of 4.7%). Mixtures of $Mg(NO_3)_2·6H_2O + Ni(NO_3)_2·6H_2O$ at the eutectic composition of 30 mol % **NiN** have a density of 1682 kg m^{-3} for the solid and 1621 kg m^{-3} for the melt, both extrapolated to $T_m = 343$ K. The density decrease on melting of this eutectic is 61 kg m^{-3}, corresponding to $\Delta_{fus}V/V_{solid} = 3.6\%$. The densities for the eutectic composition of molten $Mg(NO_3)_2·6H_2O + Mg(CH_3CO_2)_2·4H_2O$ (**MgA**) mixtures ($x_{\mathbf{MgA}} = 0.35$) are below those for the mixtures with a somewhat higher magnesium acetate content ($x_{\mathbf{MgA}} = 0.40$). When the density of equimolar $Mg(NO_3)_2·6H_2O + Mg(CH_3CO_2)_2·4H_2O$ melts and crystals are compared, both extrapolated to the melting point (341 K), the density decrease on melting is 65.1 kg m^{-3}, or the expansion on melting is $\Delta_{fus}V/V_{solid} = 4.3\%$. Such a value is, again, expected.

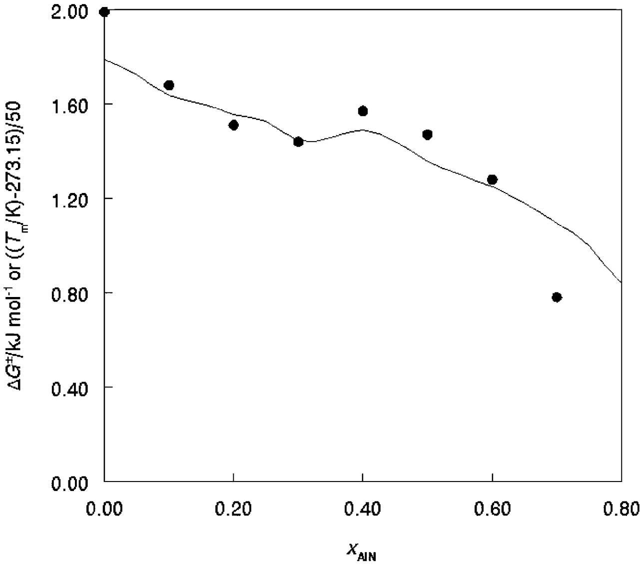

Figure 1. Activation Gibbs energy for viscous flow (●) and the solid−liquid phase diagram of mixtures of $Mg(NO_3)_2·6H_2O + Al(NO_3)_3·9H_2O$ (−).

The densities of molten $Mg(NO_3)_2·6H_2O + Al(NO_3)_3·9H_2O$ (**AlN**) were determined by Ramana et al.[11] at $0.9 \geq x_{\mathbf{AlN}} \geq 0.4$ over a relatively small temperature range. Their values were (3.2 ± 0.2)% lower than ours, but their aluminum nitrate preparation had a $H_2O:Al(NO_3)_3$ ratio of 10.03 whereas ours had a ratio of 9.2 ± 0.2. No other data for comparison with the melt densities of the salt hydrates and their mixtures studied here could be found.

The densities of independent mixtures of crystals are expected to be the averages of the densities of the two solid salts weighted by their respective mass fractions. In such cases, there is no need to measure the densities of the solidified mixtures. However, if the components form solid solutions when crystallized from the mixed melt or form a compound when mixed and melted together, then this expectation is not met. Thus, the densities of solidified molten $Mg(NO_3)_2·6H_2O + Mg(CH_3CO_2)_2·4H_2O$ mixtures were *not* the weighted means of those of the components. This can be ascribed to the formation of a crystalline compound between the components.[9] Also, for $NH_4Al(SO_4)_2·12H_2O + (NH_4)_2SO_4$ mixtures the densities do lie above the mass fraction-weighted composition, where in this case no compound formation was detected but solid solution formation is likely.

The expansivities of the melts, $\alpha = (dV/dT)/V = -(dd/dT)/d$ for the crystalline and molten single salts are shown in the last column of Table 1. (The value of d is taken as the mean of the values over the range of measurement.) As expected, the expansivities of the melts are considerably larger than those of the solids, the former being near 0.6×10^{-3} K^{-1} whereas the latter are generally $<0.3 \times 10^{-3}$ K^{-1}.

All the melts examined with respect to their viscosities behaved in a Newtonian manner and were (except for mixtures involving magnesium acetate) of a magnitude typical of anhydrous salts melting at a considerably higher temperature, e.g., nitrates at 480 to 600 K.[12] Previous studies of the viscosities of molten salt hydrates, however, dealt mainly with glass forming melts, so that comparisons cannot be made.

The activation energies of viscous flow, $\Delta G^{\ddagger}$, are shown in Figure 1 as a function of composition for mixtures of $Mg(NO_3)_2 \cdot 6H_2O + Al(NO_3)_3 \cdot 9H_2O$. It is noteworthy that the curve is not smooth but shows a maximum at $x_{\mathbf{AlN}} \approx 0.4$, which coincides with a kink in the solid−liquid phase diagram for mixtures of these two salt hydrates.[10] No evidence was obtained by X-ray diffraction of a new compound that crystallizes from the melt at this composition, so the common feature in the curves should be due to a restructuring in the melt.

For molten mixtures of $Mg(NO_3)_2 \cdot 6H_2O + Mg(CH_3CO_2)_2 \cdot 4H_2O$, the viscosity depends on the history of the sample in the sense that it depends on how many times the mixture has been melted and frozen again. Molten neat $Mg(CH_3CO_2)_2 \cdot 4H_2O$ tends to form a glass on cooling rather than freezing to a crystalline solid, and so do its mixtures with $Mg(NO_3)_2 \cdot 6H_2O$ with $x_{\mathbf{MgA}} > 0.80$. The hydrogen bonds that appear to exist in the material[7] rearrange themselves on melting but appear not to be able to form the crystal lattice on cooling the rather viscous melts, having a high value of $\Delta G^{\ddagger} = 5$ kJ mol^{-1} even when diluted to $x_{\mathbf{MgA}} = 0.35$. This may explain the dependence of the viscosity on the cycling through melting and solidification which may also be due to the partial loss of water from $Mg(CH_3CO_2)_2 \cdot 4H_2O$ and its hydrolysis leading to the formation of less mobile species.

Supporting Information Available:

Densities of solid single-salt hydrates, molten single-salt hydrates, and mixtures of salt hydrates and viscosities of molten $Mg(NO_3)_2 \cdot 6H_2O$ and its mixtures. This material is available free of charge via the Internet at http://pubs acs.org.

Literature Cited

(1) Dornte, R. W.; Smyth C. P. The Dielectric Polarization of Liquids. X. The Polarization and Refraction of the Normal Paraffins. *J. Am. Chem. Soc.* **1930**, *52*, 3546−3552.

(2) Findegg, G. H. Density and Expansivity of Some Liquid Alkanes. *Monatsh. Chem.* **1970**, *101*, 1081−1088.

(3) Swanson, H. E. Standard X-ray Diffraction Powder Patterns. *Natl. Bur. Stand. Circ. 539 (U. S.)* **1956**, *6*, 10.

(4) Swanson, H. E. Standard X-ray Diffraction Powder Patterns. *Natl. Bur. Stand., Monogr. 25 (U. S.)* **1974**, *11*, 6.

(5) Cesbron, F.; Sadrzadeh, M. New Data on Alunogen. *Bull. Soc. Fr. Mineral Crystallogr.* **1973**, *96*, 385−387.

(6) Mozzi, R. L.; Bekebrede, W. R. Cell Dimensions and Space Group of Magnesium Nitrate Hexahydrate. *Acta Crystallogr.* **1961**, *14*, 1296−1297. Mozzi, R. L.; Bekebrede, W. R. *International Center for Diffraction Data*, card no. 14-0101: $Mg(NO_3)_2 \cdot 6H_2O$, monoclinic, $P2_1/c$; 2000.

(7) deWolff, A. Tech. Phys. Dienst Delft, The Netherlands, private communication in *International Center for Diffraction Data*; card no. 11-0729: α-$Mg(CH_3CO_2)_2 \cdot 4H_2O$ monoclinic, $P2_1$/a; card no. 14-0833, β-$Mg(CH_3CO_2)_2 \cdot 4H_2O$, monoclinic, $P2_1$/a; 2000.

(8) Swanson, H. E. Standard X-ray Diffraction Powder Patterns. *Natl. Bur. Stand., Monogr. 25 (U. S.)* **1974**, *12*, 26. Swanson, H. E. *International Center for Diffraction Data*; card no. 25-0577: $Ni(NO_3)_2 \cdot 6H_2O$ triclinic; 2000.

(9) Cohen, Sh.; Ben-Dor, L.; Marcus, Y. A. New Double Salt: Triacetatohexaaquo- dimagnesium Nitrate. *J. Cryst. Growth* **2003**, *254*, 151−155.

(10) Marcus, Y.; Minevich, A.; Ben-Dor, L. Solid−Liquid Phase Diagrams of Some Binary Salt Hydrate Mixtures Involving Magnesium Nitrate and Acetate, Magnesium and Aluminum Nitrates, Ammonium Alum and Sulfate, and Ammonium Alum and Aluminum Sulfate. *Thermochim. Acta* **2004**, *412*, 163−170.

(11) Ramana, K. V.; Sharma, R. C.; Gaur, H. C. Volumetric Properties of Molten Hydrated Salts. 6. Mixtures of Aluminum Nitrate Decahydrate with Hydrates of Calcium, Cadmium, Zinc, and Magnesium Nitrates. *J. Chem. Eng. Data* **1985**, *30*, 449−452.

(12) Higgs, R. W.; Litovitz, T. R. Ultrasonic Absorption and Velocity in Molten Salts. *J. Acoust. Soc. Am.* **1960**, *32*, 1108−1115.

Received for review April 15, 2004. Accepted June 9, 2004. This research was supported by a grant from the Ministry of Science Culture Sport Israel and the Forschungszentrum Juelich GMBH (KFA) within the German−Israeli Energy Research program.

JE049849B