Ammonium Dinitramide−Water: Interaction and Properties

Niklas Wingborg*

Swedish Defence Research Agency, FOI, Grindsjön Research Centre, SE-147 25 Tumba, Sweden

The interaction between ammonium dinitramide (ADN) and water was experimentally investigated by determining the solid−liquid phase diagram for the system ADN−water and by measuring its critical relative humidity at 25 °C. Additionally, the density of aqueous ADN solutions of different compositions were measured in the temperature range from (5 to 85) °C. The properties of ADN were compared to ammonium nitrate (AN), and the results show that ADN is more hygroscopic than AN. The density data show that aqueous ADN solutions behave as an ideal solution, with a partial molar volume independent of the composition. This made it possible to determine the molar volume and the density of pure ADN in the liquid state as well as the volumetric contraction of molten ADN on solidification and cooling.

Introduction

Ammonium dinitramide (ADN), $NH_4N(NO_2)_2$, is a relatively newly discovered inorganic solid salt, mainly intended as an oxidizer in solid rocket propellants.[1−3] Some of the properties of ADN are presented in Table 1, and an overview of different synthetic routes for its preparation have been described by Venkatachalam et al.[4] Similar to ammonium nitrate (AN), NH_4NO_3, ADN is hygroscopic and readily soluble in water. The hygroscopic properties are of importance to determine how ADN should be stored and handled. The interaction between ADN and water and the physical properties of ADN in the liquid state are also of fundamental importance. The latter has partially been studied theoretically using molecular dynamics calculations.[5] This work focused on the interaction between ADN and water by measuring some of its physical properties. A few of the preliminary results have previously been published in a proceeding paper.[6] Data for AN was used in this study as a comparison and to check the reliability of the measurement procedures. The results obtained are useful to increase the understanding of ADN and as a help in the development of ADN-based propellants.

Experimental Section

Materials. The following chemicals were used in the experimental work. They were used as received with no further purification: ammonium dinitramide (ADN), $NH_4N(NO_2)_2$, (lot no. 2002-7034 Eurenco Bofors, Sweden) and ammonium nitrate (AN), NH_4NO_3, (No. 09891 Sigma-Aldrich, Sweden).

HPLC-grade water (no. 07-421802 Tamro MedLab, Sweden) was used in the preparation of the aqueous solutions and in the calibration of the analytical apparatus.

Methods. The solubility of ADN and AN in water was determined by preparing saturated solutions in test tubes at constant temperatures. The temperature was controlled using a thermostat bath. After equilibrium was achieved, liquid samples (∼30 mg of ADN solution and ∼10 mg of AN solution, respectively) were withdrawn using a syringe. The samples were weighed prior to dilution in 1 L of water. The concentration of ADN and AN in the liquid phase were then determined by measuring the UV absorption at 284 and 201 nm, respectively, using a Perkin-Elmer Lambda-40 UV/VIS spectrophotometer. All the reported solubility data are average values based on at least three separate measurements.

Table 1. Properties of ADN

density at ambient temperature, ρ	1.81 g·cm^{-3} [7]
melting point	91.5 °C[8]
molecular weight, M	124.06 g·mol^{-1}
oxygen balance[a]	+25.79 %
heat of formation	−148 kJ·mol^{-1} [3]
heat of combustion[b]	424 kJ·mol^{-1}

[a] Weight percent of excess oxygen calculated as described in ref 9. [b] Calculated as described in ref 10.

DSC measurements were performed using a Mettler Toledo DSC30 with liquid nitrogen cooling. The measuring cell was purged with nitrogen (50 mL·min^{-1}) and the sample weight was approximately 3 mg. The temperature was adjusted using a three-point calibration with indium (ME-29749 Mettler-Toledo, Sweden), water, and anhydrous, high purity *n*-octane (no. 29,698-8 Sigma-Aldrich, Sweden). All reported temperatures are average values of two measurements, deviating at the most by 0.4 °C.

The critical relative humidity of ADN was determined by measuring the relative humidity above a saturated aqueous ADN solution confined in a 100 mL Erlenmeyer flask, using a Rotronic A1 hygrometer. All measurements were performed at a constant temperature of 25.0 °C with the flask submerged in a thermostat bath. The hygrometer was calibrated with a saturated aqueous solution of $Mg(NO_3)_2$ (no. 63087 Sigma-Aldrich, Sweden). To check the calibration at slightly higher relative humidity, a saturated aqueous solution of NaBr (no. 71330 Sigma-Aldrich, Sweden) was used. The reported values were read after equilibration of the relative humidity in the flask was achieved.

A Mettler Toledo DE40 density meter was used to determine the density of aqueous solutions of ADN and AN, respectively. The solutions were prepared at different concentrations in steps of 0.05 molar fractions. The maximum concentration of each salt was determined by their solubility at room temperature. Calibration of the density meter was done using water. All reported densities are the average of at least two measurements deviating less than $2 \cdot 10^{-4}$ g·cm^{-3}.

* E-mail: niklas.wingborg@foi.se. Fax: +46 8 5550 3949.

10.1021/je0600698 CCC: $30.25
Published on Web 08/10/2006

Table 2. Solubility of ADN in Water at Different Temperatures

temperature (°C)	solubility (wt %)[a]
−15.0	58.3 (0.2)
−10.0	62.7 (0.2)
0.0	69.3 (0.1)
20.0	78.1 (0.1)

[a] The values within parentheses are the experimental standard deviation.

Table 3. Data for the Liquidus Line on the Water-Rich Side in the Phase Diagram in Figure 2[a]

w_{ADN}	T_2 (°C)	w_{ADN}	T_2 (°C)
0.000	0.0	0.171	−3.1
0.049	0.4	0.251	−4.5
0.090	−1.2	0.300	−5.6
0.136	−2.2	0.403	−8.7

[a] Compositions are given in weight fraction ADN (w_{ADN}).

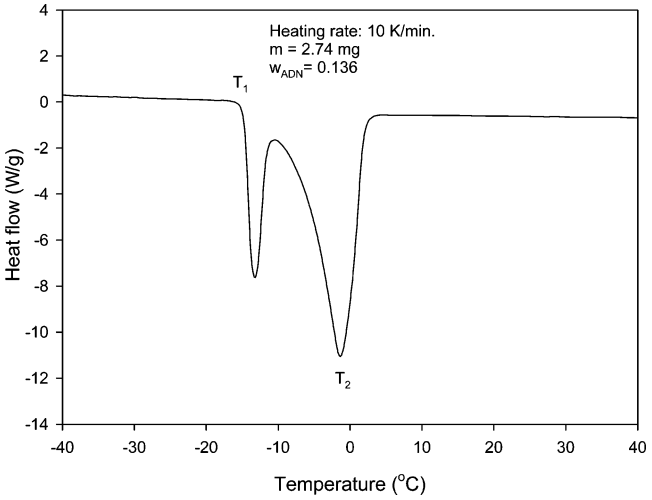

Figure 1. Typical DSC thermogram on an ADN−water mixture.

Results and Discussion

Solubility of ADN in Water. Table 2 shows the solubility of ADN in water at different temperatures. Measurements below −15 °C were prevented due to freezing of the aqueous ADN solution. The measurement procedure was checked by measuring the solubility of AN in water at 20.0 °C and was found to be 65.6 wt %, with a standard deviation of 0.3 %. This is in good agreement with literature data (65.5 %),[10] thus showing the reliability of the technique used. As shown, the solubility of ADN in water is considerably higher as compared to AN.

Phase Diagram for the System ADN−Water. To determine the phase diagram of the system ADN−water, the solubility data in Table 2 was complemented by DSC measurements on aqueous ADN solutions of different compositions. Figure 1 shows the result from a typical DSC measurement where the onset of the first endothermic melting peak, T_1, corresponds to the eutectic melting of ADN−water, and the peak temperature of the second peak, T_2, corresponds to the final melting of water in contact with the solution.[11]

With increasing weight fraction ADN (w_{ADN}), the second peak was shifted to lower temperatures until gradually merging with the first peak. Thus, at $w_{ADN} > 0.4$ the peak temperature, T_2, could not be determined. The onset of the first peak, T_1, was not altered by the composition, and the average of the eutectic melting point was found to be −15.3 °C, with a standard deviation less than 0.2 °C. The results are shown in Table 3 and in Figure 2, where the melting point of pure ADN is taken from Löbbecke et al.[8] (Table 1). From the phase diagram, the eutectic composition was found to be $w_{ADN} = 0.58$, which corresponds to a mole fraction (x_{ADN}) equal to 0.167. The reported eutectic composition for the system AN−water is $w_{AN} = 0.428$ ($x_{AN} = 0.144$) with a melting point in the range of (−16.7 to −16.8) °C.[12,13]

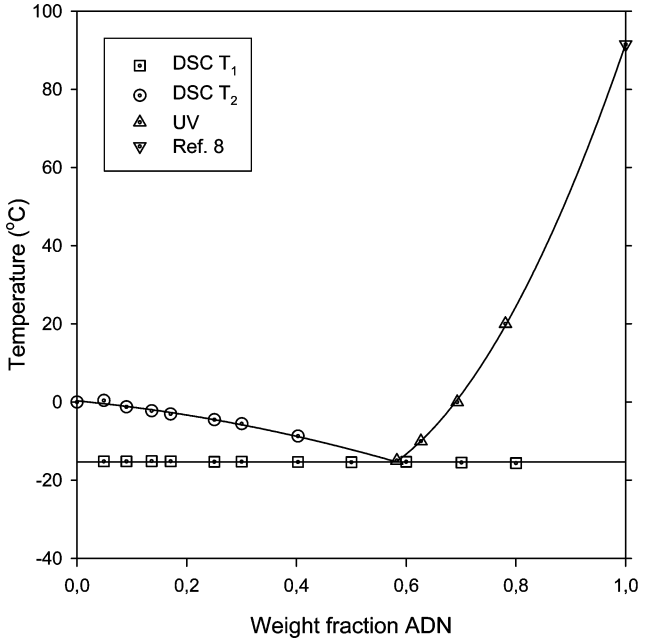

Figure 2. Solid-liquid phase diagram for the system ADN−water. The curved lines are fitted quadratic polynomials. The different symbols indicate the experimental methods and reference used.

Table 4. Critical Relative Humidity (%) at 25.0 °C

	exptl data	lit. data[10]	corrected exptl data
$Mg(NO_3)_2$	52.8	52.9	52.9
ADN	55.1		55.2
NaBr	57.5	57.6	57.6

Critical Relative Humidity. The results from the critical relative humidity measurements are shown in Table 4. As can be seen, the measured values were approximately 0.2 % lower as compared to the literature data. The experimental data were thus accordingly adjusted, and the critical relative humidity for ADN was determined to be 55.2 % at 25.0 °C. This means that the relative humidity must be below 55.2 % to prevent ADN from absorbing moisture from the atmosphere. This is lower than the corresponding value for AN, which is reported to be 61.9 % at 25.0 °C.[10]

Molar Volumes and Liquid Densities. Table 5 presents the results from the density measurements at 25.0 °C on aqueous ADN and AN solutions, respectively.

The volume (V) of a binary aqueous salt solution can be calculated according to

$$V = n_w V_w^\circ + n_s V_s^\circ \quad (1)$$

where V° is the partial molar volume, which in general depends on the composition of the solution, and n is the number of moles of water and salt respectively, as indicated by the subscript w and s. The mean molar volume of the solution is, $\bar{V}^\circ = V/(n_w + n_s)$ which, in combination with eq 1, can be rewritten as

$$\bar{V}^\circ = V_w^\circ + x_s(V_s^\circ - V_w^\circ) \quad (2)$$

By using the results from the density measurements in Table 5, the mean molar volume of the solutions were calculated as $\bar{V}^\circ = \bar{M}/\rho$, where $\bar{M} = x_w M_w + x_s M_s$. The results are shown in

Table 5. Densities (ρ) of Aqueous ADN and AN Solutions at Different Compositions at 25.0 °C[a]

w_{ADN}	x_{ADN}	ρ_{ADN/H_2O} / g·cm^{-3}	w_{AN}	x_{AN}	ρ_{AN/H_2O} / g·cm^{-3}
0.00000	0.00000	0.9970	0.00000	0.00000	0.9970
0.26581	0.04995	1.1224	0.18946	0.04998	1.0759
0.43414	0.10024	1.2156	0.33046	0.09998	1.1396
0.54737	0.14938	1.2867	0.43920	0.14985	1.1922
0.63191	0.19955	1.3446	0.52612	0.19992	1.2366
0.69628	0.24976	1.3916	0.59724	0.25023	1.2746
0.74682	0.29989	1.4306	0.65587	0.30018	1.3073
0.78836	0.35105	1.4642			

[a] Compositions given in both weight (w) and mole (x) fractions.

Table 6. Results from the Regression Analysis[a]

	ADN	AN
r^2	0.99995	0.99975
$V_w^\bullet$/cm^3·mol^{-1}	17.98 (0.03)	17.98 (0.04)
$V_s^\bullet$/cm^3·mol^{-1}	74.08 (0.17)	51.23 (0.24)
ρ_s/g·cm^{-3}	1.675 (0.004)	1.562 (0.007)

[a] $V_w^\bullet$ and $V_s^\bullet$ are the molar volumes for water and the salts, respectively; ρ_s is the density of the salts in the liquid state; and r^2 is the linear correlation coefficient. All properties at 25.0 °C. The values within parentheses are the standard deviation.

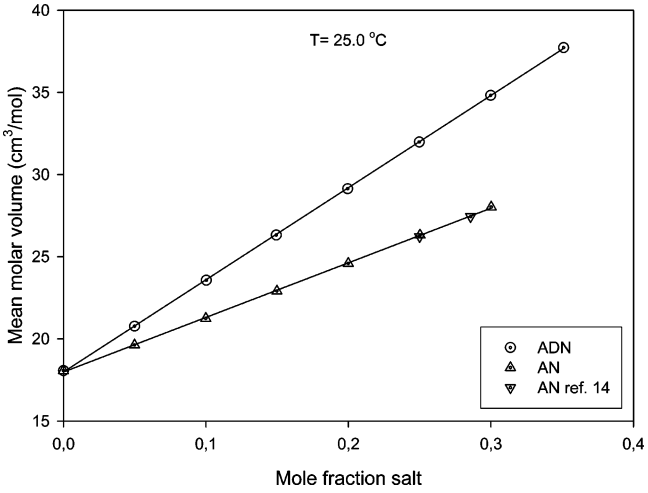

Figure 3. Mean molar volume for aqueous ADN and AN solutions as a function of the mole fraction of respective salt at 25.0 °C.

Figure 3, where the mean molar volumes are shown as a function of the mole fraction (x) of the respective salt. Density data of aqueous AN solutions found in the literature[14] were used as comparison, as seen in Figure 3, showing good agreement.

The results in Figure 3 show linear relationships; thus, linear equations were fitted to the data. The density data of aqueous AN solutions found in the literature[14] was however not used in the linear regression analysis. Excellent linear correlations were found as seen in Figure 3 and in Table 6 by their correlation coefficients (r^2) close to unity. From this analysis it seems that the partial molar volumes ($V°$) are independent of the composition and thus equal to the molar volumes of the pure substances ($V^\bullet$). This shows that aqueous solutions of ADN and AN, in this respect, can be considered as ideal solutions. Equation 2 was thus rewritten as eq 3, and the molar volumes of pure water, ADN, and AN were calculated. The results are shown in Table 6 together with the corresponding densities of ADN and AN in the liquid state, calculated as $\rho_s = V_s^\bullet/M_s$:

$$\bar{V}° = V_w^\bullet + x_s(V_s^\bullet - V_w^\bullet) \tag{3}$$

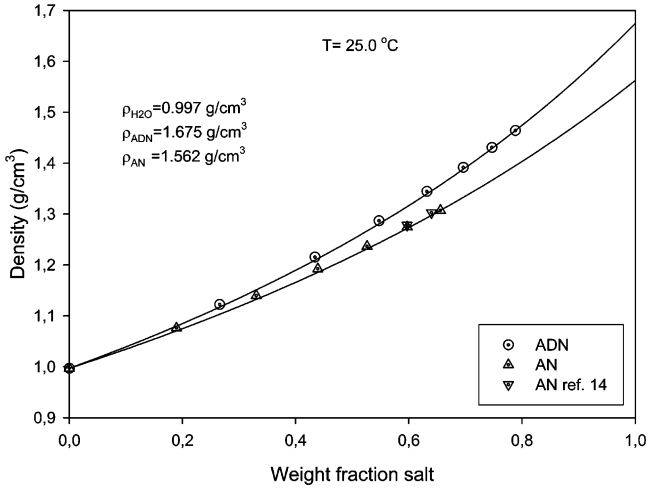

Figure 4. Density of aqueous ADN and AN solutions at 25.0 °C as a function of weight fraction of respective salt. Solid lines: calculated values using eq 4. Dots: experimental data from Table 5 and ref 14.

The value of the molar volume for AN was compared to literature data (50.93 and 51.69 at (20 and 30) °C, respectively)[15] showing good agreement. The calculated molar volume of water was in both systems less than 0.5 % lower than the molar volume of pure water, calculated as $V_w^\bullet = M_w/\rho_w$, using literature density data for water (0.9970 g·cm^{-3} at 25.0 °C).[10]

As a consequence of an ideal solution there is no ΔV on mixing and the volume of a binary aqueous salt solution is $V = V_w + V_s$, which can be rewritten as

$$\frac{1}{\rho} = \frac{w_w}{\rho_w} + \frac{w_s}{\rho_s} \tag{4}$$

By using eq 4, the density of aqueous solutions of ADN and AN respectively were calculated using the values of the liquid densities in Table 6 and the density of pure water at 25.0 °C (0.9970 g·cm^{-3}).[10] The calculated densities (shown in Figure 4 as solid lines) were found to deviate, at the most, with −0.5 % and −0.6 % for the aqueous ADN and AN solutions, respectively, as compared to the experimental data shown in Table 5.

To determine the molar volume and the liquid density of ADN at other temperatures, the density of the aqueous ADN solutions were measured between (5 and 85) °C. Measurements at higher temperatures were prevented by bubble formation in the density meter. The results are shown in Table 7.

The molar volumes and the liquid densities were then determined by using the same procedure as above and the data in Table 7. The results are shown in Table 8 and in Figure 5. At all temperatures the solutions were close to ideal, as indicated by correlation coefficients close to unity. The maximum deviation of the molar volume of water in Table 8 was found at 5.0 °C and was approximately 0.7 % lower than the literature value for pure water.

The results in Table 8 can be used to calculate the density of aqueous ADN solutions at different compositions, at temperatures between (5 and 85) °C. At temperatures above 25 °C, the accuracy will be better than 0.5 % thanks to the better agreement with ideal behavior, as shown by the higher correlation coefficient (r^2) in Table 8. By extrapolating the liquid density in Figure 5 to higher temperature, the liquid density of ADN at 100 °C was estimated to be 1.61 g·cm^{-3}. This is 11 % lower than the density of solid ADN at ambient conditions, as shown in Table 1. Thus, pure molten ADN at 100 °C will, on

Table 7. Densities (g·cm^{-3}) of Aqueous ADN Solutions at Different Compositions (w_{ADN}) and Temperatures[a]

w_{ADN}	5.0 °C	15.0 °C	35.0 °C	45.0 °C	55.0 °C	65.0 °C	75.0 °C	85.0 °C
0.00000	1.0000	0.9991	0.9940	0.9902	0.9857	0.9806	0.9749	0.9686
0.26581	1.1324	1.1277	1.1168	1.1106	1.1043	1.0973	1.0905	1.0829
0.43414	1.2284	1.2224	1.2091	1.2018	1.1948	1.1870	1.1795	1.1713
0.54737	1.3008	1.2940	1.2796	1.2717	1.2644	1.2562	1.2488	1.2405
0.63191	1.3596	1.3523	1.3373	1.3290	1.3217	1.3133	1.3058	1.2974
0.69628	1.4072	1.3995	1.3842	1.3758	1.3684	1.3599	1.3525	1.3442
0.74682	1.4464	1.4387	1.4232	1.4147	1.4073	1.3988	1.3914	1.3833
0.78836	*b*	1.4723	1.4565	1.4482	1.4405	1.4323	1.4246	1.4165

[a] Density data at 25.0 °C are shown in Table 5. [b] Not measured due to freezing of sample.

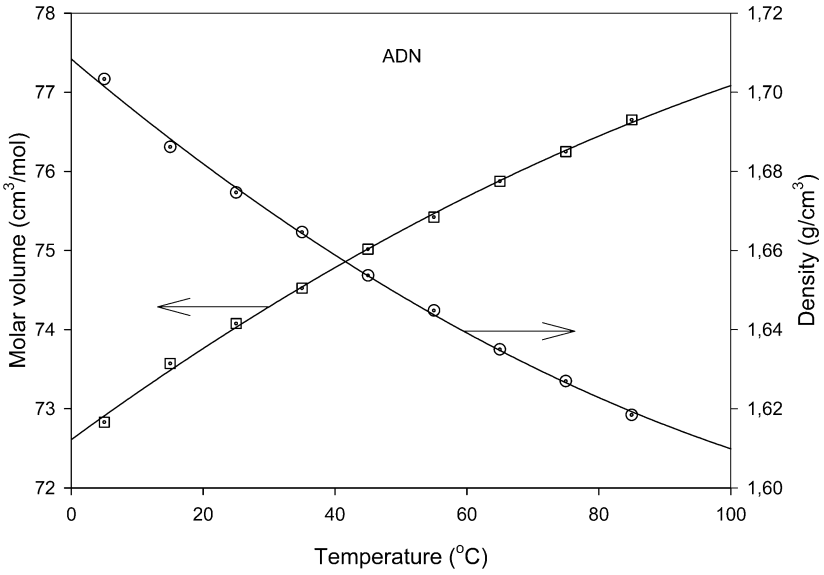

Figure 5. Molar volume and density of ADN in the liquid state as a function of temperature. The lines are fitted quadratic polynomials.

Table 8. Molar Volumes for Water ($V_w^{\bullet}$) and ADN ($V_{ADN}^{\bullet}$) and Density of ADN (ρ_{ADN}) in the Liquid State at Different Temperatures. r^2 Is the Linear Correlation Coefficient

T		$V_w^{\bullet}$ [a,b]	$V_w^{\bullet}$ [c]	$V_{ADN}^{\bullet}$ [b]	ρ_{ADN}
°C	r^2	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	g·cm^{-3}
5.0	0.99983	17.89 (0.06)	18.02	72.83 (0.33)	1.703 (0.008)
15.0	0.99991	17.91 (0.05)	18.03	73.57 (0.22)	1.686 (0.005)
25.0	0.99995	17.98 (0.03)	18.07	74.08 (0.17)	1.675 (0.004)
35.0	0.99997	18.06 (0.03)	18.12	74.52 (0.13)	1.665 (0.003)
45.0	0.99999	18.15 (0.02)	18.19	75.02 (0.08)	1.654 (0.002)
55.0	0.99999	18.25 (0.01)	18.28	75.42 (0.06)	1.645 (0.001)
65.0	1.00000	18.37 (0.01)	18.37	75.88 (0.03)	1.635 (0.001)
75.0	1.00000	18.48 (0.01)	18.48	76.25 (0.03)	1.627 (0.001)
85.0	1.00000	18.62 (0.01)	18.60	76.65 (0.04)	1.618 (0.001)

[a] Calculated using the density data of the aqueous ADN solutions. [b] The standard deviation is given within the parentheses. [c] Calculated as $V_w^{\bullet} = M_w/\rho_w$ using literature density data for water.[10]

crystallization and cooling to ambient temperature, shrink by 11 %.

Conclusions

ADN is more hygroscopic than AN, as shown by its higher solubility in water (ADN 78.1 % and AN 65.5 % at 20.0 °C) and its lower critical relative humidity (ADN 55.2 % and AN 61.9 % at 25.0 °C). Hence, to prevent ADN from absorbing moisture during handling, storing, and processing, the relative humidity in the atmosphere must be below 55 %. ADN−water forms a eutectic mixture at 58 % ADN, with a melting point of −15.3 °C. The partial molar volume of ADN in aqueous solutions is independent of the composition and thus equal to the molar volume of pure ADN. Thus, in this respect, an aqueous ADN solution can be considered as an ideal solution. The molar volume of ADN and its corresponding density in the liquid state was determined between (5 and 85) °C and was at 25.0 °C 74.08 g·mol^{-1} and 1.675 g·cm^{-3}, respectively. As a consequence of an ideal solution, the density of aqueous ADN solutions at different compositions can easily be calculated with good accuracy, deviating at the most by 0.5 % at 25.0 °C. At higher temperatures the deviation is lower. By extrapolating the density of pure ADN in the liquid state to higher temperatures, the shrinkage on solidification and cooling of ADN from 100 °C to room temperature was estimated to be 11 %.

Acknowledgment

The author thanks Dennis Menning at FOI for his help with the solubility measurements and Professor Charles Kappenstein at the Université de Poitiers, France, for valuable discussions.

Literature Cited

(1) Bottaro, J. C.; Penwell, P. E.; Schmitt, R. J. 1,1,3,3-Tetraoxy-1,2,3-triazapropene anion, a new oxy anion of nitrogen: the dinitramide anion and its salts. *J. Am. Chem. Soc.* **1997**, *119*, 9405−9410.

(2) Christe, K. O.; Wilson, W. W.; Petrie, M. A.; Michels, H. H.; Bottaro, J. C.; Gilardi, R. The dinitramide anion, $N(NO_2)_2^-$. *Inorg. Chem.* **1996**, *35*, 5068−5071.

(3) Östmark, H.; Bemm, U.; Langlet, A.; Sandén, R.; Wingborg, N. The properties of ammonium dinitramide (ADN): part 1, basic properties and spectroscopic data. *J. Energ. Mater.* **2000**, *18*, 123−128.

(4) Venkatachalam, S.; Santhosh, G.; Ninan, K. N. An overview on the synthetic routes and properties of ammonium dinitramide (ADN) and other dinitramide salts. *Propellants, Explos., Pyrotech.* **2004**, *29*, 178−187.

(5) Velardez, G. F.; Alavi, S.; Thompson, D. L. Molecular dynamics studies of melting and liquid properties of ammonium dinitramide. *J. Chem. Phys.* **2003**, *119*, 6698−6708.

(6) Kappenstein, C.; Batonneau, Y.; Perianu, E.-A.; Wingborg, N. Non toxic ionic liquids as hydrazine substitutes. Comparison of physico-chemical properties and evaluation of ADN and HAN. *2nd Interna-*

tional Conference on Green Propellants for Space Propulsion, Chia Laguna, Sardinia, Italy, 2004; ESA SP-557; pp 119−124.
(7) Wingborg, N.; van Zelst, M. *Comparative Study of the Properties of ADN and HNF*; Report R-00-01423-310- SE; FOA: Stockholm, Sweden, 2000.
(8) Löbbecke, S.; Krause, H. H.; Pfeil, A. Thermal analysis of ammonium dinitramide decomposition. *Propellants, Explos., Pyrotech.* **1997**, *22*, 184−188.
(9) Akhavan, J. *The Chemistry of Explosives*; The Royal Society of Chemistry: Cambridge, UK, 1998.
(10) *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press: Boca Raton, FL, 2003.
(11) Beyer, K. D. Determination of binary phase diagrams of aqueous systems that are of importance for processes in the stratosphere. *Mettler Toledo Thermal Analysis UserCom* **2003**, *18*, 9−12.
(12) Misane, L.; El Allali, S.; Kaddami, M.; Zrineh, A.; Tenu, R.; Berthet, J.; Counioux, J. J. Le système ternaire $H_2O-NH_4NO_3-Mg(NO_3)$ isothermes −25, −14, 0, 30 et 45 °C. *Thermochim. Acta* **2000**, *356*, 117−126.
(13) Ibnlfassi, A.; Kaddami, M.; El Kacemi, K. Systeme ternaire: $H_2O-Zn(NO_3)_2-NH_4NO_3$. I. Les isothermes −25 et −20 °C. *J. Therm. Anal. Calorim.* **2003**, *74*, 341−347.
(14) Sharma, R. C.; Gaur, H. C. Densities and molar volumes of the ammonium nitrate−water system. *J. Chem. Eng. Data* **1977**, *22*, 41−44.
(15) Tsekhanskaya, Y. V.; Fedotova, O. K. Partial molar volumes of ammonium nitrate−water system components. *Khim. Prom., Ser.: Azotnaya Prom.* **1979**, *4*, 7−8.

Received for review February 16, 2006. Accepted May 28, 2006. The author thanks the Swedish Armed Forces for funding this work.

JE0600698