Chapter 5

Investigations on the Physical, Chemical and Electrochemical Properties of Ammonium Dinitramide (ADN)

Part of the results from this chapter has been published:


THE PRESENT chapter is centered on the investigations on the purity of ADN by spectral, thermal and chemical methods, moisture absorption at different relative humidities, solubility in various organic solvents at different temperatures. The decomposition of aqueous solutions of ADN in neutral and acid media is also studied. The rate constant \( k \) and half-life \( t_{1/2} \) for the decomposition of ADN in aqueous \( H_2SO_4 \) are determined. The redox chemistry of dinitramide is investigated for the aqueous solutions of potassium dinitramide (KDN) and dinitramidic acid (DNA). The cyclic voltammograms of KDN and DNA are recorded either in 0.1M \( KNO_3 \) or 0.1M \( KCl \) solution and the redox processes at different potentials are studied. A mechanism for the electrochemical reduction and oxidation process of the dinitramide ion is proposed. The results obtained from the above studies are presented.
5.1. Determination of Purity of Ammonium dinitramide (ADN)

Detailed studies were conducted on different batches of ADN samples and their purity was evaluated by different methods. The reaction course in the ADN synthesis i.e., the formation of intermediate and final products was monitored using analytical methods.

As there was no direct procedure for estimating the purity of ADN, different techniques were tried. Two approaches, viz., conventional chemical analysis and instrumental techniques (spectral and thermal) were employed for the purpose. The instrumental techniques used in the present study were UV spectroscopy, differential scanning calorimetry (DSC) and ion-chromatography (IC). The results obtained from all the methods were compared and the purity was evaluated. This section describes the various methods adopted and the results obtained in the purity determination of ADN.

5.2. Chemical Methods of Analysis

The chemical methods employed to estimate the purity of ADN are described in the following sections.

5.2.1. Oxidation

The dinitramide anion is stable due to resonance stabilization and it has strong oxidizing properties. The oxidizing properties of ADN (e.g., oxidation of iodide ion, ferrous ion, etc.,) could not be used for the estimation of ADN due to the poor stability of dinitramidic acid formed under the conditions of the experiment. Moreover, the formed byproduct ammonium nitrate is interfering with the results.

5.2.2. Kjeldahl Method

Estimation of nitrogen by direct Kjeldahl' distillation gives results corresponding to the nitrogen of ammonium ion (NH\(_4^+\)) only and not for the dinitramide ion.
A further attempt to estimate total nitrogen by digestion with concentrated sulphuric acid prior to Kjeldahl's distillation gave erratic results due to non-stoichiometric decomposition of ADN. Kjeldahl's method adopted after reduction of the nitro (−NO₂) groups to amine (−NH₂) gave values corresponding to two nitrogen. When the experiment was repeated with potassium dinitramide (KDN), values corresponding to only one nitrogen were obtained. The results showed that the two −NO₂ groups were not estimatable by the procedure.

Since none of the above procedures resulted in reflecting the total nitrogen content of the sample, other approaches to establish the purity of ADN were attempted.

5.3. Ion-chromatography (IC) and Non-aqueous Titrimetry

Direct non-aqueous titrimetric procedure was employed for the estimation of ammonium ion in ADN. Dimethyl formamide (DMF) as solvent, tetrabutyl ammonium hydroxide (TBAH) in toluene/methanol as titrant and thymol blue as indicator was used. The presence of any other ammonium salts viz., ammonium sulphate, ammonium nitrate etc., could interfere in the estimation. Hence a separate estimation of the ammonium nitrate/ammonium sulphate by ion chromatography was carried out and necessary corrections were made to evaluate the purity of ADN. ADN containing different amounts of AN (the major impurity) was used in the present study. The samples are referred to as ADN I to V (discussed later).

IC is an analytical technique extensively used for the separation and detection of ionic species [1,2]. Anionic impurities such as NO₃⁻, SO₄²⁻ and Cl⁻ can be detected by ion chromatography. Ammonium nitrate is a byproduct in the synthesis of ADN. It is also a possible decomposition product of ADN. In the analysis of ADN samples, the concentration of ammonium nitrate is estimated using IC technique. The experimental details for the measurement are explained in chapter 2, section 2.2.1.
5.3.1. Calibration for Nitrate Ions in IC

The calibration was done for the identification of nitrate ions. Different concentrations of standard solutions of KNO₃ (2,5,10 ppm) were prepared. A calibration graph of peak area versus concentration of NO₃⁻ was made. From the calibration graph the concentration of NO₃⁻ in the sample was measured. A calibration plot is shown in Figure 5.1.

![Calibration Graph](image)

**Figure 5.1:** IC calibration plot for nitrate ion

5.3.2. Detection of Anionic Species in IC

The presence of Cl⁻, NO₃⁻ and SO₄²⁻ can easily be identified in a single isocratical run by IC. Figure 5.2 shows the IC chromatogram for a known concentration of mixtures of Cl⁻, NO₃⁻ and SO₄²⁻ ions. The peaks at 1.26, 2.15 and 3.60 min. is due to chloride, nitrate and sulphate ion respectively.
5.3.3. Analysis of $\text{NO}_3^-$ and $\text{N}_3\text{O}_4^-$ ions in ADN

About 200mg of ADN was dissolved in distilled water and made upto 100ml. 20 ml of the solution was diluted to 100ml and injected into the IC column and the chromatogram was recorded.
A typical IC spectrum of ADN given in Figure 5.3 shows a peak at 2.49 min corresponding to the nitrate ion and the peak area for the same was measured. No peaks corresponding to any other impurities were observed. The broad peak at 35 min was due to the dinitramide ion of ADN. The concentration of ammonium nitrate obtained from IC for different batches of ADN was included in Table 5.1. The total ammonium ion content of ADN was estimated by non-aqueous titrimetry and the concentration of AN is estimated by IC method. The purity of ADN was calculated by subtracting the AN content from the total ammonium content. The obtained results are summarized in Table 5.1.

**Table 5.1**: Purity values obtained by IC combined with non-aqueous titrimetry

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ammonium nitrate(^a) (%)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN I</td>
<td>0.65</td>
<td>98.6</td>
</tr>
<tr>
<td>ADN II</td>
<td>1.7</td>
<td>98.0</td>
</tr>
<tr>
<td>ADN III</td>
<td>1.5</td>
<td>96.9</td>
</tr>
<tr>
<td>ADN IV</td>
<td>2.0</td>
<td>97.8</td>
</tr>
<tr>
<td>ADN V</td>
<td>1.5</td>
<td>97.0</td>
</tr>
</tbody>
</table>

\(^a\) by Ion chromatography

As seen from Table 5.1, the purity values vary from 97 to 98.6% for different batches of ADN.

### 5.4. Analysis of ADN by UV method

UV spectroscopy was used for process monitoring i.e., to follow the conversion of reactants to dinitramidic acid and also for the purity analysis of ADN \(^{3,4}\). Quantitative analysis by UV spectroscopy is based on Beer-Lambert's law. The details of which are given in chapter 2, section 2.6.1.

All the experiments were carried out in aqueous medium using distilled water. The prepared aqueous solutions were sensitive to light;
hence they were stored in amber coloured flasks. Absorbance measurements were conducted immediately after preparation of the solution. The concentration of the sample was taken such that the absorbance was within the range of 0.2 to 0.8. The concentration corresponding to the absorbance of unknown ADN solution was obtained from the calibration graph. The percentage purity of ADN was calculated as follows:

\[
\text{% purity} = \left( \frac{C_1}{C_2} \right) \times 100
\]

where \( C_1 \) is the concentration of ADN obtained from the calibration graph and \( C_2 \) is the concentration of the ADN taken. The calculated % purity of different samples of ADN is given in Table 5.2.

**Table 5.2: Purity values obtained by UV method**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>By UV</td>
</tr>
<tr>
<td>ADN I</td>
<td>98.2</td>
</tr>
<tr>
<td>ADN II</td>
<td>98.1</td>
</tr>
<tr>
<td>ADN III</td>
<td>98.8</td>
</tr>
<tr>
<td>ADN IV</td>
<td>99.1</td>
</tr>
<tr>
<td>ADN V</td>
<td>97.9</td>
</tr>
</tbody>
</table>

The purity values obtained by UV varies from 98 to 99% as seen from Table 5.2.

5.4.1. **Effect of AN on the Absorption Spectrum of ADN**

In order to quickly estimate ADN in the process solution which is a mixture of ADN and AN, it is necessary to study the effect of AN concentration in the mixture on the purity of ADN. AN being the major impurity/byproduct in the synthesis of ADN, its influence on the absorption spectrum of ADN is studied by UV spectroscopy. Figure 5.4 shows the absorption spectrum of ADN and AN in water. Two absorption maxima at
212 and 284nm are observed for ADN and one absorption maximum at 302nm is observed for AN.

![Absorption spectrum of ADN and AN](image)

**Figure 5.4:** Absorption spectrum of ADN and AN

### 5.4.1. Methods

A stock solution of AN (1M/Lit) was prepared. A known amount of the above solution was mixed with different concentration of ADN solution (from $700 \times 10^{-5}$ to $10x10^{-5}$ M/L). Different concentrations of mixtures of ADN and AN were made using distilled water and the absorption spectrum was recorded. The absorption maximum for each concentration of the ADN-AN mixtures was found out by UV spectroscopy.

### 5.4.2. Results and Discussion

Figure 5.5 shows the plot of ADN concentration versus absorption maximum for a fixed concentration of AN (1M/Lit). From Figure 5.5 it is seen that at higher concentrations of ADN, AN has very little effect on the absorbance of ADN at 284-285nm. At lower concentrations of ADN, the
effect of AN on the absorption maximum of ADN is predominant as the absorption maximum shows a bathochromic shift from 284nm to 300nm. The studies reveal that at concentrations of ADN higher than $5 \times 10^{-3}$ M/Lit, the absorption spectrum of ADN is least influenced by the presence of AN, and at concentrations lower than $2 \times 10^{-3}$ M/L, the presence of AN causes a bathochromic shift of the absorption maximum. This implies that 2mM/L or higher of ADN present in a solution of AN (1M/Lit), can be easily quantified by the method.

![Figure 5.5: Effect of AN on the absorption spectrum of ADN](image)

5.5. Purity Determination of ADN by DSC

Differential scanning calorimetry (DSC) is a thermal analysis technique used to detect and measure heat changes associated with physical transitions (viz., melting, glass transition etc.,) and chemical reactions [5,6]. Melting of a sample is detected as an endotherm in DSC.
Experiments were conducted on a TA Instruments MDSC 2920 differential scanning calorimeter in sealed aluminium pans with nitrogen purged at a flow rate of 50mL/min. The heating rate employed was 1°C/min and a sample mass of 2mg was used.

5.5.1. Qualitative Evaluation

A preliminary DSC analysis of all the samples of ADN are conducted at 5°C/min. Figure 5.6 shows the melting endotherms for different batches of ADN having different purity levels.

![DSC melting curves of ADN samples of different purity levels](image)

**Figure 5.6:** DSC melting curves of ADN samples of different purity levels

A sharp endotherm was observed for ADN with 98.1% purity, while other samples with purity 96.8 and 95.5% show a broad endotherm. The shape of the melting endotherm and the temperature range of melting process is an indication of the purity. Broad endotherms are indicative of low purity and sharp endotherms indicate high purity.
5.5.2. Quantitative Evaluation

Samples showing sharp melting endotherms are subjected to the 'Purity Analysis' method by DSC [7,8]. The sharp melting endotherm sample was subjected to the purity analysis using Van't Hoff's equation given in 5.1.

\[ T_s = T_o - \frac{R}{\Delta H_f} \cdot \frac{T}{X} \cdot \frac{1}{F} \]  
...............(5.1)

where, 'Ts' is sample temperature, 'To' is melting temperature of the pure sample in Kelvin, 'R' is the gas constant (8.314 J/mol.K), 'X' is mol fraction impurity. 'ΔHf' is the heat of fusion of sample (J/mol), 'F' is the fraction of total sample melted at Ts. The impurity level is determined from the slope of a plot of Ts Versus 1/F. A typical purity plot of ADN is given in Figure 5.7.

![Figure 5.7: Purity plot of ammonium dinitramide (ADN) at 1°C/min](image-url)
The purity plot in Figure 5.7 shows the melting point of ADN as 92°C. The purity of ADN is calculated by built-in purity software available with the TA thermal analyzer. Purity plot is obtained by plotting temperature versus heat flow. The purity value obtained from DSC for the sample is 98.10%. The purity values obtained from DSC for different samples of ADN are given in Table 5.3. The method is applicable for samples with purity >98mol %.

The purity of ADN determined by UV, chemical and DSC method is compared and found to agree with each other as seen in Table 5.3. The purity values obtained by UV are slightly higher than those obtained by DSC and chemical methods.

Table 5.3: Comparison of obtained purity values by different methods

<table>
<thead>
<tr>
<th>Sample</th>
<th>Purity (%)</th>
<th>By Chemical method</th>
<th>By UV</th>
<th>By DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN I</td>
<td>98.6</td>
<td>98.2</td>
<td>98.0</td>
<td></td>
</tr>
<tr>
<td>ADN II</td>
<td>98.0</td>
<td>98.1</td>
<td>97.8</td>
<td></td>
</tr>
<tr>
<td>ADN III</td>
<td>96.9</td>
<td>98.8</td>
<td>96.9</td>
<td></td>
</tr>
<tr>
<td>ADN IV</td>
<td>97.8</td>
<td>99.1</td>
<td>96.8</td>
<td></td>
</tr>
<tr>
<td>ADN V</td>
<td>97.0</td>
<td>97.9</td>
<td>96.2</td>
<td></td>
</tr>
</tbody>
</table>

5.6. Decomposition of ADN in Neutral and Aqueous Acidic solutions

ADN is stable to base, and slowly decomposes in neutral and acid medium. The aqueous solutions of ADN undergo decomposition in presence of light. Very dilute solutions of ADN in water are quite stable to decomposition, while concentrated solutions are less stable. The decomposition of ADN in neutral and acidic solutions is studied and the results obtained from the study are presented in this section.
5.7. Experimental

5.7.1. Materials

Ammonium dinitramide (ADN) was prepared according to the procedure explained in chapter 3, section 3.2.2. The purity of ADN used in the study is >98%.

Con. H₂SO₄ (Qualigens, Mumbai) was used as received. Distilled water was used to prepare respective solutions of ADN.

5.7.2. Methods

Different concentrations of aqueous solutions of ADN were made with distilled water and kept in plain and amber coloured bottles. They were analyzed by UV spectroscopy for the change in absorption at 284nm over a period of days. From the results, the extent of decomposition of ADN was determined.

To the solutions of different concentration of ADN, known concentration of sulphuric acid solution was added. The combined solution was kept in a constant temperature bath of desired temperature. Samples were withdrawn at regular intervals, diluted and the absorbance at 284nm was measured by UV spectroscopy. From the absorbance values, the extent of decomposition of ADN was calculated.

5.8. Results and Discussion

5.8.1. Decomposition of Aqueous Solutions of ADN

Figure 5.8 shows the concentration of ADN versus time plots for the decomposition of aqueous solutions of ADN kept in plain and amber coloured bottles.
It is seen from Figure 5.8, that the decomposition of aqueous ADN solutions kept in plain bottles is slow up to 160hrs and is accelerated after 200hrs. This is due to the formation of dinitramidic acid or HNO₃ (the products of ADN decomposition) which catalyses further decomposition of the remaining ADN. The catalyzing effect is clearly seen as the concentration of ADN decrease rapidly at about 750hrs. The decomposition of higher concentration of ADN is more compared to lower concentration.

Figure 5.8 also shows the concentration versus time plot for the aqueous solutions of ADN kept in amber bottles. Unlike, the solutions kept in plain bottles, the solutions in amber coloured bottles do not show appreciable decrease in their concentrations even after 750hrs. The results indicate that the aqueous solutions of ADN are sensitive to visible light and undergo photochemical decomposition, the products formed in the decomposition, further catalyzes the decomposition of the remaining ADN.
5.8.2. Decomposition of Aqueous Acidic Solutions of ADN

ADN decomposes slowly in aqueous acid medium and it is stable to base \(^9\). The decay of ADN was measured at temperatures between 30 to 75°C in aqueous sulphuric acid solutions. The molar concentrations of sulphuric acid used in the study are from 6.3M to 10M. The decomposition of ADN was monitored by measuring the absorbance at 284nm at different time intervals.

Table 5.4: Decomposition of ADN in aqueous sulphuric acid

<table>
<thead>
<tr>
<th>Acid concentration</th>
<th>Temperature ( (^\circ \text{C}) )</th>
<th>Rate constant ( (\text{min}^{-1}) )</th>
<th>Half life ( (t_{1/2}, \text{min.}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3M</td>
<td>30</td>
<td>No comp.</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0003</td>
<td>2310.5</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.0005</td>
<td>1386.3</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.0030</td>
<td>231.1</td>
</tr>
<tr>
<td>8.1M</td>
<td>30</td>
<td>No comp.</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0048</td>
<td>144.4</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.0194</td>
<td>35.7</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.1291</td>
<td>5.4</td>
</tr>
<tr>
<td>10M</td>
<td>30</td>
<td>0.0057</td>
<td>121.6</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0230</td>
<td>30.1</td>
</tr>
<tr>
<td>11M(^a)</td>
<td>30</td>
<td>0.0074</td>
<td>93.0</td>
</tr>
<tr>
<td>12M(^a)</td>
<td>30</td>
<td>0.0252</td>
<td>28.0</td>
</tr>
<tr>
<td>13M(^a)</td>
<td>30</td>
<td>0.3350</td>
<td>2.1</td>
</tr>
</tbody>
</table>

\(^a\) literature value (ref. 9)

Table 5.4 gives the rate constant and half-life for the decomposition of ADN at different acid concentrations and temperatures. The rate constants were generated by the first-order analysis of the absorbance-time data. As is it seen from Table 5.4, no decomposition was observed at 30°C in 6.3 and 8.1M sulphuric acid even after few days. Appreciable
decomposition was observed at temperatures between 50 and 75°C. In 10M sulphuric acid, decomposition was observed even at 30°C. As expected, the rate constants show an increase as the temperature increases. Table 5.4 also shows the results obtained for a higher concentration of sulphuric acid solutions. The decomposition of ADN is very rapid in 10-12M sulphuric acid with a half-life ranging from 2-90min. The half-life for the decomposition of ADN in different concentrations of aqueous sulphuric acid solutions decreases as the temperature is increased. The results indicate that the rate of acid catalyzed decomposition of ADN increases directly with acidity.

5.9. Moisture Absorption Studies on Ammonium Dinitramide (ADN)

ADN is a moisture sensitive, hygroscopic powder and should be handled below a relative humidity (R.H) of 50% [10]. The evaluation of extent of moisture absorption of ADN is important for its use in propellants. The extent of moisture absorption of ADN at relative humidities of 62% and 74% was studied. The time taken for equilibrium was found out from the absorption curve. The absorption rate constants were calculated. Two grades of ADN i.e. fine and coarse have been subjected to this study and the results obtained were discussed.

5.10. Experimental

5.10.1. Materials

Ammonium dinitramide (ADN) with purity > 98% was used. It is a pale yellow hygroscopic powder with a melting point of 92°C. It is twice recrystallized from ethylacetate, kept in a dark coloured bottle and stored in a desiccator.

ADN (coarse) with a particle size of 200-300μm was prepared by an emulsion crystallization process (chapter 3, section 3.15). The particle size of ADN (fine) is 30-40μm.
Sodium nitrate (NaNO\textsubscript{3}) and ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}) (CDH, Mumbai) were used as received.

5.10.2. Methods

For maintaining a constant humidity of 62% and 74%, a saturated water solution of ammonium nitrate or a saturated solution of sodium nitrate was prepared\textsuperscript{[11]}. The prepared solutions were transferred to a desiccator and kept closed till the air in the desiccator gets equilibrated with the required relative humidity. The percentage humidity was monitored using a digital thermohygrometer.

Moisture absorption of ADN was studied by keeping weighed quantities of ADN in the desiccator and recording the increase in weight at different time intervals.

5.11. Results and Discussion

The extent of moisture uptake of ADN (coarse) and ADN (fine) is studied under a relative humidity of 62% and 74%. Weighed quantities of ADN were taken in a petridish and kept inside a glass desiccator containing the respective saturated solutions. The samples were taken at different time intervals and the increase in weight was recorded. Figure 5.9 shows the plot of time versus % moisture uptake of ADN at a relative humidity of 62%.
As seen from Figure 5.9, the moisture absorption curve for both fine and coarse ADN showed a steep increase till 50hrs. After that the moisture uptake was relatively slow and reaches equilibrium. The time taken for equilibrium is 164 hrs and 182 hrs for ADN (coarse) and ADN (fine) respectively.

Figure 5.10: Hygroscopicity of ADN at 74% R.H
Figure 5.10 shows the plot of time versus % moisture uptake of ADN at a relative humidity of 74%. The moisture uptake was steep till 100hrs and reaches equilibrium. The time taken for equilibrium is 324 hrs and 375 hrs for ADN (coarse) and ADN (fine) respectively. The equilibrium time taken for ADN (coarse) and ADN (fine) at 74% R.H is twice as that at 62% R.H.

5.11.1. Determination of Absorption Rate Constants

The absorption rate constants for the moisture absorption of ADN at 62% & 74% R.H were calculated based on the equation given in 5.2.

\[-\ln(1-A) = Kt + c\] ...........(5.2)

where, ‘t’ is absorption time, ‘K’ is absorption rate constant and A= q/t/qe, ‘q’ is amount absorbed at time ‘t’ and ‘qe’ is amount absorbed at equilibrium. A plot of −ln(1-A) versus time t, gives a straight line for all the cases. From the slope of the curve, the adsorption rate constants were determined. The plots of −ln(1-A) versus t are given in Figure 5.11

![Figure 5.11: Rate constant plots for the moisture absorption of ADN](image)
The calculated rate constants along with correlation coefficients for ADN (coarse & fine) at 62% & 74% R.H are given in Table 5.5.

Table 5.5: Calculated rate constant for the moisture absorption of ADN

<table>
<thead>
<tr>
<th>System</th>
<th>Rate constant (K, min⁻¹)</th>
<th>Correlation coefficient (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN (Coarse, 62% R.H)</td>
<td>$7.582 \times 10^{-4}$</td>
<td>0.9923</td>
</tr>
<tr>
<td>ADN (Fine, 62% R.H)</td>
<td>$7.475 \times 10^{-4}$</td>
<td>0.9909</td>
</tr>
<tr>
<td>ADN (Coarse, 74% R.H)</td>
<td>$3.488 \times 10^{-4}$</td>
<td>0.9984</td>
</tr>
<tr>
<td>ADN (Fine, 74% R.H)</td>
<td>$3.050 \times 10^{-4}$</td>
<td>0.9948</td>
</tr>
</tbody>
</table>

From Table 5.5, it is seen that the rate constant values are higher for ADN at 62% R.H and are lower at 74% R.H. This indicates that the moisture uptake for ADN is fast at 62% R.H and is slow at 74% R.H. Comparing Figures 5.9 & 5.10, it is seen that the equilibrium time is achieved fast for the ADN samples at 62% R.H (160-180 hrs) and is slow at 74% R.H (320-370 hrs).

5.12. Solubility of ADN in Different Solvents

Solubility of ADN is important in selecting a suitable solvent for the extraction, recrystallization and dissolution. Solvents such as ethyl acetate, isopropanol, acetonitrile, acetone, methanol and water are used for studying the extent of solubility of ADN.

5.13. Experimental
5.13.1. Materials

Ammonium dinitramide (ADN) with a mean particle size of 40-50μm was used.

Analytical reagent grade ethylacetate, isopropanol, acetonitrile, acetone and methanol (Qualigens, Mumbai) were distilled and dried over
molecular sieves prior to use. Distilled water was used for the solubility measurements of ADN in water.

5.13.2. Methods

1g of ADN was taken in a small Erlenmeyer flask and stored in a desiccator. 20ml graduated burette (0.1ml graduations) was filled with the respective solvent. For solubility measurements at room temperature (32°C), the solvent was slowly added with stirring to the flask containing ADN till all the ADN is dissolved. The % solubility was then calculated from the amount of solvent consumed to dissolve ADN. Experiments were repeated thrice and the mean value was taken. For the solubility measurements at temperatures other than room temperature, the flask containing ADN was kept in a bath of desired temperature and the solvent was slowly added into the flask. The flask was shaken well and the amount of solvent consumed for the complete dissolution of ADN was then measured.

5.14. Results and Discussion

The % solubility of ADN at different temperatures and in different solvents is given in Table 5.6.

Table 5.6: Solubility of ADN in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acetate</td>
<td>32</td>
<td>2.0</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>32</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>4.9</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>32</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>10.8</td>
</tr>
</tbody>
</table>
From Table 5.6 it is seen that the solubility of ADN is 420% in water, while in ethylacetate it is 2%. In polar solvents, the solubility of ADN is high. The solubility in methanol at 32°C is 90%. The % solubility of ADN in various solvents shows a decrease as the temperature is reduced. Due to the very low solubility of ADN in ethylacetate, it is proved to be a recrystallization solvent for ADN.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>% Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Methanol</td>
<td>32</td>
</tr>
<tr>
<td>Water</td>
<td>32</td>
</tr>
</tbody>
</table>

From Table 5.6 it is seen that the solubility of ADN is 420% in water, while in ethylacetate it is 2%. In polar solvents, the solubility of ADN is high. The solubility in methanol at 32°C is 90%. The % solubility of ADN in various solvents shows a decrease as the temperature is reduced. Due to the very low solubility of ADN in ethylacetate, it is proved to be a recrystallization solvent for ADN.

5.15. Cyclic Voltammetric Studies on Potassium Dinitramide and Dinitramidic acid Solutions

The redox chemistry \(^{12}\) of potassium dinitramide and dinitramidic acid solutions was studied using cyclic voltammetry (CV) in aqueous solutions of either potassium nitrate or potassium chloride. The oxidation and reduction potentials were obtained from the cyclic voltammograms. The mechanism by which the oxidation-reduction process takes place was proposed.

5.16. Experimental
5.16.1. Materials

Potassium dinitramide (KDN) was prepared by the procedure described in chapter 3; section 3.5.2 (vide infra). Dinitramidic acid (DNA) solution was obtained in the preparation of ammonium dinitramide (Chapter 3; Section 3.3.2). Analytical reagent grade KNO\(_3\) & KCl (Glaxo Limited, Mumbai) were used as received. Double distilled water was used in all experiments.
5.16.2. Methods

Electrochemical measurements were made on a EG&G Instruments -Princeton Applied Research Electrochemical Impedance Analyzer-Model No. 6310 in either potassium nitrate or potassium chloride solutions. Platinum rod was used as a counter electrode and a standard calomel electrode (SCE) as a reference electrode. Experiments were carried out in a closed glass cell.

5.17. Results and Discussions

5.17.1. Electrochemical Studies of Potassium Dinitramide

2-3 mM of KDN solution was prepared and deaerated by purging nitrogen for 5-10 minutes. The pH of this solution is 6.5. 0.1M KNO₃ solution was prepared and deaerated by purging nitrogen. Cyclic voltammogram (CV) was recorded using a Pt rod as a counter electrode and SCE as the reference electrode. Figure 5.12 shows the CV KDN at a pH of 6.5.

\[\text{Figure 5.12: CV of KDN in 0.1M KNO}_3 \text{ solution}\]
The CV shows two separate irreversible reduction peaks at -900mV and at -650mV versus SCE. These reduction processes are chemically irreversible, because the products obtained in the reaction disappear rapidly. The product of reduction reaction shows an oxidation wave at 800mV in the CV. The product of reduction is nitrite, which is confirmed by recording CV for sodium nitrite in KNO₃ solution. It shows an oxidation peak in the same region (Figure 5.13). The CV of sodium nitrite is given in Figure 5.13.

Figure 5.13: CV of sodium nitrite in KNO₃ solution

Figure 5.13 clearly shows an oxidation wave at 810mV, which is very close to the value of 800mV in the CV for KDN. Thus at a pH of 6.5, the dinitramide anion is first reduced in a two electron step to produce nitrite plus nitramidic acid (H₃N⁺(NO₂)₂). CVs were repeatedly recorded on the same KDN solution. Figure 5.14 shows the CV of KDN after repetition of several cycles.
Figure 5.14: CV of KDN in 0.1M KNO₃ (repeated cycle)

Figure 5.14 clearly revealed that the reduction peak at -650mV was retained, while the one at -900mV has disappeared at repeated cycling. The disappearance of -900mV peak on repeated cycle indicates that the CVs are influenced by the state of cleanliness of the electrode surface. This strong dependence of the ability to observe the redox processes for dinitramide on the state of cleanliness of the electrode surface indicates that the heterogeneous electron transfer process is slow and follows a diffusion control mechanism \[^{13}\]. This is confirmed by recording the CV at different scan rates \((v)\). The peak current is proportional to \(v^{1/2}\) indicating diffusion-controlled mechanism. Specifically, electrode surfaces are to be scrupulously cleaned by flaming for each recording of CV. Separate runs were carried out after cleaning the electrode in con. HNO₃ followed by heating to red hot. All the runs show the appearance of -900mV reduction peak, indicating that the surface cleanliness plays an important role in the redox process.
At different scan rates, the peak current at $-900\text{mV}$ was plotted against square root of scan rate. Figure 5.15 shows the plot of square root of scan rate versus peak current. The linear fits of the plot indicate that the reduction waves are characteristic of the delivery of dinitramide ion to the electrode via diffusion.

![Graph](attachment://graph.png)

Figure 5.15: Peak current versus $\sqrt{v}$ plot for KDN at pH 6.5

5.17.2. Electrochemical Studies of Dinitramidic acid (DNA) Solution

The reaction mixture before neutralisation in the nitration of ammonium sulphamate is the dinitramidic acid solution, its pH is around 3. Figure 5.16 shows the CV of DNA solution recorded in 0.1M KCl and 0.1M KNO₃ solutions with SCE as the reference electrode. A strong irreversible reduction peak is observed. The peak potential for the DNA solution is observed at $-310\text{mV}$ in KCl and at $-340\text{mV}$ in KNO₃ solution. The peak vanishes after repeated cycling in this case also. The reduction peak for DNA is observed at $-340\text{mV}$ as the peak potential for KDN is observed at $-650\text{mV}$. The peak shift to more positive value for DNA is due to the low pH of the solution ($<3.0$).
5.17.3. Mechanism of Redox Process of Dinitramide

The proposed mechanism of the electrochemical process is given in Scheme 5.1.

\[
\begin{align*}
\text{[O}_2\text{N}:\text{N}^\ddagger\text{NO}_2^-]^- & \quad \text{e}^- \quad \text{[O}_2\text{N}^\ddagger\text{N}:\text{NO}_2^-]^- + \text{NO}_2^- \\
2\text{H}^+ + \text{e}^- & \quad \\
\text{H}^+ + \text{HN-NO}_2^- & \quad \text{H}_2\text{N-NO}_2^- \\
& \quad \text{(Nitramidic Acid)} \\
\text{NH}_4^+ & \quad \text{[N}^\ddagger\text{H}^-]^- + \text{NO}_2^- \quad 2\text{H}^+ + \text{e}^- \\
\end{align*}
\]

Scheme 5.1: Electrochemical redox process of dinitramide anion
The first step involves a concerted electron transfer / bond cleavage in which nitrite and a radical species are formed. The dissociation of N-N bond is responsible for the chemical irreversibility of the first reduction process. The radical formed gets protonated in a rapid follow-up process to give nitramidic acid. The extent of protonation depends on the pH of the medium, since pKa for nitramidic acid is 6.5. During the process only one electron will be transferred which is consistent with the overall two-electron reduction in the first peak. The second reduction peak is believed to take place in a similar manner. A concerted electron transfer / bond cleavage event occurs, resulting in formation of nitrite and a radical product that is reduced further and protonated in rapid follow-up process. Thus, the electrochemical studies indicate that dinitramide anion undergoes two separate, kinetically complicated, two electron reduction processes to produce two molecules of nitrite and one molecule of ammonium, which depends on the pH of the medium.

5.18. Conclusions

Different techniques viz., thermal, spectroscopic and chemical methods were used for the determination of purity of ammonium dinitramide (ADN). For sharp melting samples of ADN, DSC is the simplest, fastest and most reliable method to determine the purity. The non-aqueous titrimetric procedure coupled with estimation of ammonium nitrate by ion chromatography gives results comparable to that obtained by UV and DSC methods. UV method is preferred for monitoring the course of reaction during the nitration of ammonium sulphamate. The presence of anionic impurities in ADN is accurately determined by IC. The effect of AN on the absorption spectrum of ADN is studied, the results show that at higher concentrations of ADN, AN has only little influence on the absorption spectrum, while at lower concentrations of ADN, the absorption maximum showed a bathochromic shift from 284nm to 300nm.
The decomposition of aqueous solutions of ADN kept in plain and amber coloured bottles are studied. Aqueous ADN solutions undergo decomposition in presence of light and are catalyzed by the decomposition products. However, aqueous solutions of ADN kept in amber coloured bottles do not show appreciable decomposition. The decomposition of ADN in 6.3 to 10M aqueous solutions of sulphuric acid is studied; the rate constant and half-life for the decomposition are determined. The decomposition of ADN is found to follow first order kinetics and the rate increases with acidity. At higher molar concentrations of sulphuric acid, the decomposition is very fast with half life ranging from 2-90min. The data generated at different temperatures and concentrations are summarized.

The hygroscopicity of ADN (fine) and ADN (coarse) was studied under relative humidities of 62% and 74%. The extent of moisture absorption of ADN was recorded for different time intervals and the time taken for equilibrium was found out. The equilibrium time taken is higher for ADN (fine) and ADN(coarse) at R.H 74%. The calculated rate constant for the moisture absorption is higher for ADN at 62% R.H and is lower at 74% R.H.

The solubility of ADN in various solvents was determined at different temperatures and was compared. ADN is highly soluble in polar solvents. The solubility of ADN in ethyl acetate is low, while in water the solubility is >400%. The solubility of ADN in acetonitrile, acetone, methanol and isopropanol is between 10 to 90%. At lower temperatures, the solubility of ADN is low.

The redox chemistry of dinitramide anion was studied by cyclic voltammetry (CV) methods. The CV of KDN showed two reduction peaks at -650mV and -900mV and an oxidation peak at 800mV. The product of reduction is identified as nitrite. The redox processes are very much dependent on the surface cleanliness of the electrode and the peak potentials depend on the pH of the medium. The redox process follows a diffusion-controlled mechanism.
5.19. References


