IN-SITU ELECTROCHEMICAL STUDIES TO INVESTIGATE
INTERACTIONS OF ATMOSPHERIC COMPONENTS WITH
ALKALI METAL NITRATE SOLVENTS

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ABSTRACT

The diffusion coefficient of nitrite ions was determined in 50 mol% NaNO₃-KNO₃ from cyclic voltammetric and chrono-potentiometric measurements using gold electrodes over the temperature range 250-400°C. The solubility of water was determined indirectly using cyclic voltammetry over a similar range of temperature.

INTRODUCTION

Recently the molten nitrates of sodium and potassium have been selected as potential candidates for thermal storage media in solar-thermal applications (1). This use would involve handling many thousands of tons of salt in the liquid phase at temperatures between 300-600°C. The handling, containing, and chemical reactivity of such solvents are of paramount importance in such an undertaking, particularly since these liquids would be exposed to variable atmospheric conditions. Interactions with atmospheric components are important, particularly with respect to the oxygen, water and carbon dioxide content of the atmosphere. The likelihood of interaction between these atmosphere components and the liquid nitrates is small at lower temperatures (<300°C for the binary NaNO₃-KNO₃ mixture). However, the high temperatures and the use of metallic containers will most certainly lead to decomposition of the nitrate. The presence of oxygen, carbon dioxide and water may moderate the reaction pathways available (2,3). The characterization of the reactions involving water and carbon dioxide with these nitrate melts under aerial conditions is therefore of prime importance.

Thermal decomposition of these nitrate melts is referred to in the literature (4). Nitrite (5,6) is a commonly observed product of this degradation and is often reported even when the salts have been carefully treated under inert atmosphere. The presence of oxygen in the atmosphere in contact with these salts can result in further reactions. Some studies have reportedly prepared nitrite free melts (<10⁻⁴ M NO₂⁻) at low temperature (<280°C) and in such cases Zambonin and co-workers (3,7) have studied manometrically the solubility of gases such as O₂, CO₂, H₂, and water vapor in the binary melt over the temperature range 225-270°C. Jordan and Zambonin (8,9) reported that the chemistry of oxide ion in nitrate melts was affected not only by the presence of oxygen but also by the container material such as Pyrex glass which tended to buffer the oxide content of the melt as well as introduce
silicate moieties into the system (10). Because of this and the need to work up to 600°C, we have selected alumina ware for containment of the melt and structural material for the electrodes. This will ensure inertness of the working materials. Platinum was discounted because of a suspicion of catalytic interactions with the nitrate at the higher temperature (11).

In this paper some preliminary data are reported for the nitrite solute and for water, a major component in the atmosphere. Table 1 illustrates the variations reported by previous workers for the diffusional characteristics of the nitrite ions in the binary mixture. To monitor nitrite ion changes in the melt in thermal decomposition/atmospheric reactions, it is necessary to have more precise data for this solute over a wide temperature interval.

The behavior of water in molten nitrates has been studied by numerous workers and has generated some controversy. Zambonin has investigated the solubility of this solute over a limited temperature range in NaN_3-KNO_3 using a manometric method (14). From these results and RDE experiments he reported Henrian constants, a heat of solution, and a diffusion coefficient for water at 603 K. Table 1 summarizes these previous results. The results reported here extend these data to higher temperatures.

EXPERIMENTAL

The experimental cell is shown in Figure 1. Figure 2 shows detail of the individual electrodes. The reference electrode was

$$\text{Ag|AgNO}_3 \, 0.07\text{m, KNO}_3-\text{NaN}_3 | \text{glass membrane}$$

which was enclosed in a sodium-β alumina tube containing the binary mixture. This ensured that the melt in the main compartment did not come into contact with Pyrex glass. The gold counter electrode was contained in a separate alumina tube. The working electrode was a gold flag mounted on a gold wire sealed into alumina. The surface areas of the working electrodes were measured by the method of Wolfe and Caton (15). The agreement between the measured and geometric areas was better than 10%.

The melts were prepared either by vacuum fusion of the ultrapure salts or from P_2O_5 dried ACS grade salts which were then dried up to 200°C under vacuum, melted under pure oxygen, evacuated, and subsequently filtered. The latter material was almost transparent.

Water was added in the form of LiNO_3·3H_2O or by saturating argon gas at a known partial pressure. ACS grade sodium nitrite, dried over P_2O_5 under vacuum, was added in the pilot ion studies.

Cyclic voltammetry and chronopotentiometry were made using a PAR 175 universal generator, a PAR 174A polarographic unit, a 373
potentiostat, and either a Plotamatic X-Y recorder or a Bascom-Turner microprocessor controlled data logger.

RESULTS

Melt Purity. The initial state of the solvents used in these experiments was examined voltammetrically. The measurements showed the initial nitrite ion content to be about $\approx 2 \times 10^{-3}$ molal when the vacuum melting procedure was used. Melting under oxygen reduced this nitrite ion content to approximately $0.3-0.7 \times 10^{-3}$ molal. Figure 3 shows a typical background for the oxygen treated melt. The effect of oxygen is probably to oxidize organic residues which otherwise reduce nitrate to nitrite. These results are higher than those reported by Goeting and Ketelaar (5), but the temperature (which is thought to play a significant role) was somewhat higher (250-350°C) in our case. The remaining background between $\approx +0.400$V to $-1.00$V AgAgI (0.07m) showed current densities less than 150 $\mu$A-cm$^{-2}$ at a scan rate of 100 mV-sec$^{-1}$.

Nitrite Ion as Solute. The assessment of the nitrite ion content of the melts required a knowledge of the diffusion characteristics of nitrite ions. The data in the literature are inconsistent. Pilot ion additions of nitrite were made at each temperature to enable suitable background corrections to be made. The measurements were made in decreasing order of temperature followed by reheating to 375°C and then cooling to the lowest temperature in the initial cycle (275°C). Cyclic voltammetric measurements (Figure 4) at several differing scan rates and chronopotentiometric measurements (Figure 5) at several current densities were made at each temperature plateau.

The results were analyzed assuming the nitrite ion oxidation to be reversible (12), viz.,

$$\mathrm{NO}_2^- \rightleftharpoons \mathrm{NO}_2(g) + e.$$ 

The number of electrons involved in this process was confirmed from the ratio of $i_p/\omega^{1/2}/i_r^{1/2}$ at each temperature. The cyclic voltammetric and chronopotentiometric data which was obtained were found to agree with the Randles-Sevcik and Sand equations, respectively, for each concentration and temperature employed. The mean values of $i_p/\omega^{1/2}$C and $i_r^{1/2}/C$ and their standard deviations were used to evaluate the diffusion coefficient at each temperature. These results are combined in the form of an Arrhenius plot given in Figure 6. Using a least square procedure these data were fitted to a straight line expressed by

$$\ln D = -6.427 - 2.921T^{-1}$$

from which the activation energy for diffusion of the nitrite ion was found to be 5.8 kcal-mol$^{-1}$. This value is typical for diffusional processes in molten nitrates (16). Table 2 shows typical diffusion coefficients calculated from the above equation (1) and compares these
values with those reported in the literature. Our results are consistent with those of Zambonin (9) and have been confirmed by recent pulse polarographic measurement at a gold electrode (17). The inconsistency of the literature data calculated from chronopotentiometric measurements may arise from the serial oxidation of the platinum electrodes and nitrite ions (7).

The maximum nitrite content which was reached after several additions (1.07 x 10^{-2} molal) was readily reduced to the original background concentration at 300°C in our experimental cell by NO_2 gas purging (5).

Water Solute. Two kinds of experiments have been carried out for water:

(1) Use of argon saturated with known water vapor pressures, as the water source.

(2) Use of lithium nitrate trihydrate as the source of water.

The rapid quantitative uptake and removal of water from this melt has been demonstrated by following the cathodic reduction peak associated with water.

Zambonin (14) reported a single datum for the diffusion coefficient of water based upon RDE measurements. By observing the cyclic voltammograms (Figure 7) at different temperatures for a constant water partial pressure, an activation energy was obtained (Figure 8) which is made up of a contribution from the heat of solution and an activation energy for diffusion of water. Using a heat of solution determined from manometric data by Zambonin and co-workers (14), the diffusional contribution to this total activation energy has been calculated. A value of 4.4 kcal mol^{-1} was obtained. From this result and the single diffusion coefficient given by Zambonin (14), Henry's law constants for water solubility up to 350°C were calculated. Table 3 compares solubility data derived from cyclic voltammetric results with those reported by Zambonin. The agreement is satisfactory, considering the different techniques employed.

In an attempt to substantiate the diffusion coefficient for water reported by Zambonin, additions of LiNO_3 trihydrate were made to both open and closed experimental cells, measuring the cathodic peak at a function of time after each addition. Figure 9 shows two typical results. From an extrapolation of the line to t=0, a value of \( \text{i_o} \) was found, from which the diffusion coefficient for water was calculated (18). Table 4 shows the results and compares them with those calculated by the previous method. The reasonable agreement between the results lends confidence to the procedures and the data so obtained. It is intended to measure these properties more precisely using a combination of rotating disc and stationary electrode measurements to resolve, simultaneously, the concentration and diffusion coefficient of these species.
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TABLE 1. DATA RELATING TO NITRITE AND WATER IN BINARY NaNO₃-KNO₃

| Species | E(V) | $10^5D$ cm²sec⁻¹ | Temp. °K | Method | Ref. |
|---------|------|----------------|----------|--------|------|
| NO₂⁻ | $E_{\frac{NO_2^-}{NO_2^-}} = -0.44$ | 5.2 | 571 | Chronopotentiometry | 12 |
| | $E_{\frac{1}{2}} = -0.44$ | 0.525 | 502 | Rotating Disc Electrode | 19 |
| | 2.4 ± 0.7 | 523 | Chronopotentiometry | 13 |
| H₂O | $E_{\frac{1}{2}} = -1.19$ | 1.9 | 502 | Rotating Disc Electrode | 14 |

H₂O Solubility in Molten Nitrates

| Solvent | Temp. °C | Henry's Constant mol mol⁻¹mm⁻¹ | Range of HL | $\Delta H_{\text{soln}}$ kcal mol⁻¹ | $10^5D$ cm²sec⁻¹ | Ref. |
|---------|----------|-------------------------------|-------------|----------------------------------|-----------------|------|
| NaNO₃-KNO₃ | 227 | 176 | 20 mm | -8.4 | 1.94 | 14 |
| 50:50 mol% | 294 | 63 | 20 mm | | | 3 |
### Table 2. Comparison of Experimental and Literature Data for Nitrite Ion Diffusion Coefficients

| Method                     | Ret. | $D \times 10^6 \text{ cm}^2\text{-sec}^{-1}$ | This Paper | $x$ \text{ cm} |
|----------------------------|------|---------------------------------------------|------------|----------------|
| Rotating Disc Electrode    | 9    | $5.25 \pm 0.1$                              | 3.3        | 5.10           |
| Chronopotentiometry        | 6    | 27.5                                        | 0.0        | 2.23           |
| Chronopotentiometry        | 13   | 24.8                                        | 0.3        | 2.23           |
| Chronopotentiometry        | 12   | 5.2                                         | 0.5        | 5.71           |
| Pulse Polarography         | 17   | 9.3                                         | 0.5        | 9.9            |

$$JND = 2.427 - 2.921 \times 10^{-7} \, (\text{cm})$$
### TABLE 3. EXPERIMENTAL AND DERIVED RESULTS FOR WATER IN MOLTEN SODIUM POTASSIUM NITRATE MIXTURE (50 mol%)

| Temp. °K | P mm Hg | \(i_D/v_A^3\) cm\(^{-2}\)y\(^{-1}\)s\(^{1}\) | \(D \times 10^6\) cm\(^2\)s\(^{-1}\) | \(C \times 10^3\) mol kg\(^{-1}\) | \(K_H \times 10^4\) mol kg\(^{-1}\)mm\(^{-1}\) | \(K_H \times 10^4\) mol kg\(^{-1}\)mm\(^{-1}\) |
|----------|---------|---------------------------------|----------------------------|-----------------|-----------------|-----------------|
| 523      | 20.94   | 50.98                           | 22                         | 9.82            | 4.6             | 6.0             |
| 573      | 9.21    | 18.85                           | 32                         | 3.20            | 3.4             | -               |
| 573      | 19.35   | 36.06                           | 32                         | 6.15            | 3.1             | -               |
| 573      | 20.82   | 33.77                           | 32                         | 5.26            | 2.5             | 3.3             |
| 573      | 31.82   | 45.24                           | 32                         | 7.68            | 2.4             | -               |
| 598      | 8.04    | 5.76                            | 37                         | 0.94            | 1.1             | -               |
| 598      | 20.94   | 25.57                           | 37                         | 4.19            | 2.0             | -               |
| 623      | 20.94   | 19.34                           | 44                         | 2.96            | 1.4             | -               |

Note: Calculation based upon \(D_{H_2O} = 19 \times 10^{-6}\) cm\(^2\)sec\(^{-1}\) at 503°K and an activation energy for diffusion of 4.4 kcal mol\(^{-1}\).

### TABLE 4. DIFFUSION COEFFICIENT FOR WATER AT 300°C

|                         | \(D_{H_2O}\) cm\(^2\)sec\(^{-1}\) | Conc. LiNO\(_3\)H\(_2\)O Added |
|-------------------------|-----------------------------------|-------------------------------|
| **Open (Argon Flowing)**| 13 \times 10^{-6}                 | 4.08 \times 10^{-3} knol kg\(^{-1}\) |
| **Closed (Argon Stationary)**| 21 \times 10^{-6}                | 6.65 \times 10^{-3} mol kg\(^{-1}\) |
| **Calculated**          | 32 \times 10^{-6}                | From Zambonin's value of 19 \times 10^{-6} at 230°C (14) and our activation energy for diffusion of 4.4 kcal mol\(^{-1}\). |
Fig. 1. Electrochemical cell. Fig. 2. Individual cell components.

Fig. 3. Binary nitrate, background cycle oxygen treatment.

Area = 0.365 cm²
Scan Rate = 100 mV sec⁻¹
Temperature = 350°C
Fig. 4. Typical cyclic voltammogram for nitrite ion oxidation.
Conc. NO$_2^-$ = 1.044 x 10$^{-2}$ mol kg$^{-1}$
Area = 0.365 cm$^2$
Temperature = 375°C

Fig. 5. Typical chronopotentiogram for nitrite ion oxidation.

Fig. 6. Arrhenius plot for nitrite ion diffusion.
Fig. 7. Cyclic voltammograms for cathodic process involving water.

Temperature = 305°C; $P_{H_2O} = 20.5$ mm; Area = 0.365.

Fig. 8. Arrhenius plot for water from cyclic voltammetric data.

Fig. 9. Plot of $i_p$ as function of time after addition of LiNO$_3$H$_2$O to open and closed systems.