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Thermodynamic Modelling of Nitric Acid and Selected Metal Nitrate Systems on Sampled Fish Pond Waters of Kisii University

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Abstract: Surface waters consist of a complex mixture of ions and solutes which interact in a complex manner under different thermodynamic conditions. This study explored thermodynamic behavior of nitric acid/nitrous acid- selected nitrate-water systems on some fish ponds using Mixed-Solvent Electrolyte, MSE, which was applied to calculate phase equilibria, speciation, and their effect on dissolved oxygen, dissolved nitrogen and concentration of nitrates in the pond waters. In particular, solubilities and chemical speciation we analyzed for various nitrogen-containing systems. The model reproduced the speciation, solubility, and Vapor–Liquid Equilibrium (VLE) data in the nitric acid + water system at ground temperature and pressure and was therefore used to predict the effects of chemical speciation, temperature, and concentrations of various acid, base, and salt components on the formation of competing solid phases over wide ranges of temperature and concentration in water. The water samples were obtained directly from four University fish ponds labeled as Migingo, Mfangano, Ringiti and Remba Islands. A sample of water was collected from each pond. The four samples were then analyzed of their concentrations of dissolved oxygen (DO), total nitrogen (TN), nitrates and nitrites, pH and electrical conductivity. The results were used to validate the model. The findings established that there is an inverse relationship between the amount of nitrates in water and the levels of dissolved oxygen. The higher the amount of nitrates the lower the amount of DO in the pond water. A pressure of about 1 atmosphere and temperature range 20-27°C favor most particle interactions resulting in higher levels of concentration of NO_3^- ions in pond water. This research also established that variation of water temp should not exceed ±5 within the day for optimal concentrations of competing particles in solution. The systems that were analyzed in this work include the $HNO_3/HNO_2/NO_2$+ water mixtures in the full composition range that covers $xHNO_3$ from 0 to 1 and, more generally, xNO_2 from 0 to 1. Further, a model was established for the nitrate salt systems, involving the Li^+, Na^+, Ca^{2+}, and Mg^{2+} cations, encountered in the fish pond waters. Rather than focusing on particular processes, the current work provided a comprehensive treatment on the basis of the available experimental thermodynamic data for such systems. These results provided a thermodynamic foundation to explain natural variations in salt concentrations and predict mineral equilibria in the pond waters. Validation of the model was achieved through VLE, pH, solubilities and conductivity measurements.

Keywords: Coefficient, Molality, Phase, Mixed-Solvent Electrolyte, Dissolved Oxygen, Total Nitrogen

1. Introduction

Water is one of the most wonderful not yet completely understood combinations on earth. It possesses a complex of anomalous properties distinguishing it from all other substances [1]. Chemically pure water should be considered an extremely complex substance consisting of atoms of various isotopes of hydrogen and oxygen, which can form up to 18 isotope varieties of water [2]. Under natural conditions, water corresponding to the known H_2O formula is not found in a pure form [3]. Almost all known chemical elements occur in natural water [2]. A deep understanding of water chemistry is therefore eminent. In this study, a thermodynamic approach to investigation of the interactions and effects of ions present in water was done to serve a strong basis for understanding part of the chemistry of water. In particular a Mixed-Solvent Electrolyte (MSE) model was applied to inorganic ions ($NH4^+$, NO_2^-, and NO_3^-) under varying thermodynamic conditions. The model has been used to determine speciation of Hg (II) in atmospheric waters and not on the transformation of HgO to Hg (II), which had been studied extensively [4-7].

Understanding the chemistry of cloud and fog water is critical in determining the fate and transport of mercury in the atmosphere; since metal complexion can determine what reactions a metal may undergo (8). Previous studies show that nitric and nitrous acid end in water bodies as soluble nitrates (9, 10). The presence of nitrate ions in water mass encourages the growth of algae. This eventually leads to reduction of oxygen content in water [11-13]. As result aquatic animals suffocate and even die [14].

2. Materials and Methods

2.1. Sampling

The water samples were obtained directly from four University fish ponds labeled as Migingo, Mfangano, Ringiti and Remba Islands. From every pond, five samples were collected and mixed to make a single sample. The four samples were labeled as A, B, C and D, respectively. The five samples from every fish pond were collected at the following points; inlet, outlet, the middle and the remaining two from opposite sides of a rectangular fish pond. Sampling was done two times a day (morning and evening) once in a month in the months of June, August and October.

2.2. Mixing of Samples to Attain Homogeneity

A thermostatic shaker with a temperature uncertainty of ±0.1K was used for measurement of equilibrium. The sample bottles were placed in the thermostat rotary shaker and shaken for 20 min to attain equilibrium. Each sample was then subdivided into four bottles for various analyses.

2.3. Sample Collection, Treatment and Analysis

2.3.1. Dissolved Oxygen (DO)

Dissolved Oxygen was determined according to the procedure formulated [15]. A Hand-held meter was used for collection of water from about 10 cm deep. The meter was kept in gentle motion through the water column while a reading was taken. Excessive turbulence was avoided to minimize presence of air bubbles in the water, near the measurement cell. Several minutes were allowed for the meter to stabilize. A field test was done and measurements immediately recorded in mg/l.

2.3.2. Total Nitrogen (T. N)

Direct collection using pre-cleaned plastic bottles about 200ml was carried out. The bottles were filled to just about the shoulder. Sample bottles were pre-rinsed three times with sample water before final sample collection. The collected sample bottles were refrigerated at about 1-4°C and stored in the dark. Analysis was done in 24 hours using persulphate digestion method 4500-nc [14] and automated Cadmium reduction method 4500-NO_3 [14].

2.3.3. Total Oxidized Nitrogen

About 125ml of filtered sample was collected in new pre-cleaned bottles. The bottles were pre-cleaned three times before final samples were collected in them. Filtering was done using 0.45µm pore diameter cellulose membrane/filter. Bottles were filled just below the shoulder of the bottle. Samples were then refrigerated at 1-4°C. Analysis was done within 24 hours using automated reduction method 4500-NO_3-F [14]. Filtration was done on site.

2.3.4. pH Measurements

A hand held meter was carefully kept in motion in water about 10cm below the surface. Unfiltered sample about 125ml was collected and transferred to pre-cleaned plastic bottles with a bottle cap. The sample bottles were rinsed three times with the fish pond water before the final samples were collected. Sample bottles were completely filled to avoid bubbles and refrigerated at about 1-4°C. Analysis was done within 6hrs using a combination of electrode (glass plus a reference electrode) and was calibrated against three commercial buffers in the field.

2.3.5. Electrical Conductivity

Collection was done using a hand held meter *in situ,* whereby the meter was held 10cm below the surface in a gentle motion through the water column while reading was made. About 125ml unfiltered sample was collected at around 25°C. Collected samples were put in new pre-cleaned plastic bottles with cap having Teflon liner.

2.3.6. Treatment

Refrigeration was done at 1-4°C. The container was completely filled to exclude air from the sample. Sample was analyzed within 24hrs. Conductivity was electrochemically measured without temperature compensation and was calibrated against a standard solution of potassium chloride on the field.

2.3.7. Temperature

Measured using a thermometer: Several minutes was allowed for reading to stabilize. The test was done in the field and results recorded in °C.

3. Results and Discussion

3.1. Sampling Results for June 2015

The concentrations of various dissolved particles in the pond waters for the samples taken in the month of June were determined and recorded in table 1 below. The concentration of nitrates was found to averagely range between 144.78 to 501.27 µmol/L with Remba recording the lowest and

Migingo highest. Migingo recorded the highest concentration of Total Nitrogen at averagely 288.58 µg/L at 23℃, while lowest average values of 1446.00 µg/L were recorded in Ringiti-2 fishpond at temperatures of about 28.5*°C*. The highest concentration of DO was recorded at a temperature of averagely 25*°C* at Remba fish ponds at the value of 7.89 *mg/L*. Lower values have been recorded at higher and lower temperatures.

Table 1. *Concentrations of Various Dissolved Particles in Pond waters for Samples taken in June 2015.*

Stations	NO_2^- µmol/L	TN µg/L	Temp *(°C)*	D. O *(mg/L)*	Cond. *(µC/cm)*	pH	NH_4^- µmol/L	NO_3^- µmol/L
A (Migingo)	312.35	2887.58	23.00	6.50	69.00	6.23	926.23	501.27
	312.35	2887.58	23.00	6.50	70.30	6.24	926.23	501.27
B (Mfangano)	37.22	2805.47	26.90	6.90	138.20	7.93	1073.92	409.65
	37.22	2805.47	26.00	6.10	138.00	7.87	1073.92	409.65
C1 (Ringiti-1)	35.32	1450.74	29.30	6.10	126.00	7.12	1218.54	265.86
	35.32	1450.74	28.50	6.60	126.00	7.39	1218.54	265.86
C2 (Ringiti-2)	16.95	1446.00	28.50	6.60	116.00	8.39	1154.69	287.76
	16.95	1446.00	28.50	6.60	116.00	8.39	1154.69	287.76
D1 (Remba-1)	194.24	2824.42	24.90	7.89	89.90	6.86	530.85	510.73
	194.24	2824.42	24.90	7.89	89.90	6.86	530.85	510.73
D2 (Remba-2)	12.08	1491.79	26.21	5.45	117.00	7.21	1202.38	144.78
	12.08	1491.79	26.21	5.45	117.00	7.21	1202.38	144.78

3.2. Sampling Results for August 2015

The concentrations of various dissolved particles in the samples taken in the month of August 2015 were determined and recorded in table 2 below. The concentrations of nitrates still remained the same as in the month of June. Migingo recorded the highest concentration of Total Nitrogen at averagely 2888.58 µg/L at 23*°C,* while lowest average values of 1446.00 µg/L were recorded in Ringiti-2 fishpond, at temperatures of about 28.5*°C*. The highest concentration of DO was recorded at a temperature of averagely 25*°C*at Remba fish ponds at the value of 7.89 *mg/L*. Lower values have been recorded at higher and lower temperatures. The pH values of the pond water determined to be averagely about 6.2 at Migingo, 7.9 at Mfangano7.2 at Ringiti-1,8.4 at Ringiti-2,6.9 at Remba -1 and 7.2 at Remba-2.

Table 2. *Concentrations of Various Dissolved Particles in Pond waters for Samples taken in August 2015.*

STATIONS	NO_3- µmol/L	NO_2^- µmol/L	TN µg/L	Temp *(°C)*	D. O *(mg/L)*	Cond. *(µC/cm)*	pH
A (Migingo)	501.27	312.35	2887.58	23.00	6.50	69.00	6.23
	501.27	312.35	2887.58	23.00	6.50	70.30	6.24
B (Mfangano)	409.65	37.22	2805.47	26.90	6.90	138.20	7.93
	409.65	37.22	2805.47	26.00	6.10	138.00	7.87
C1 (Ringiti-1)	265.86	35.32	1450.74	29.30	6.10	126.00	7.12
	265.86	35.32	1450.74	28.50	6.60	126.00	7.39
C2 (Ringiti-2)	287.76	16.95	1446.00	28.50	6.60	116.00	8.39
	287.76	16.95	1446.00	28.50	6.60	116.00	8.39
D1 (Remba-1)	510.73	194.24	2824.42	24.90	7.89	89.90	6.86
	510.73	194.24	2824.42	24.88	7.89	89.90	6.86
D2 (Remba-2)	144.78	12.08	1491.79	26.19	5.45	117.00	7.21
	144.78	12.08	1491.79	26.21	5.45	117.00	7.21

3.3. Sampling Results for October 2015

The concentrations of various dissolved particles in the pond waters for the samples taken in the month of October were determined and recorded in table 3 below.

Table 3. *Concentrations of Various Dissolved Particles in Pond waters for Samples taken in the month of October.*

Stations	NO_3- µmol/L	NO_2^- µmol/L	TN µg/L	Temp (°C)	D. O (mg/L)	Cond. (µC/cm)	pH
A (Migingo)	511.00	312.60	2888.55	23.10	6.47	71.00	6.22
	511.30	312.60	2888.56	23.00	6.44	71.10	6.21
B (Mfangano)	409.65	37.22	2805.47	26.90	6.90	138.20	7.93
	409.63	37.20	2805.52	26.00	6.15	138.00	7.86
C1 (Ringiti-1)	265.85	35.32	1450.70	29.33	6.10	126.00	7.13
	265.86	35.30	1450.75	28.50	6.60	126.00	7.38
C2 (Ringiti-2)	287.75	16.94	1446.00	28.52	6.60	116.00	8.40
	287.77	16.94	1446.00	28.50	6.60	116.00	8.39
D1 (Remba-1)	510.73	194.24	2824.44	24.90	7.89	89.90	6.88

Stations	NO_3- µmol/L	NO_2^- µmol/L	TN µg/L	Temp (°C)	D. O (mg/L)	Cond. (µC/cm)	pH
	510.72	194.26	2824.42	24.90	7.89	89.90	6.87
D2 (Remba-2)	144.80	12.08	1491.79	26.21	5.45	117.00	7.21
	144.77	12.08	1491.78	26.19	5.44	116.90	7.20

The concentration of nitrates was found to averagely range between 144.79 to 511.15 µmol/L with Remba recording the lowest and

Migingo highest. Migingo recorded the highest concentration of Total Nitrogen at averagely 2888.56 µg/L at 23.1*°C,* while lowest average values of 1446.00 µg/L were recorded in Ringiti-2 fishpond at temperatures of about 28.5*°C*. The highest concentration of DO was recorded at a temperature of averagely 25*°C* at Remba fish ponds at the value of 7.89 mg/L. Lower values have been recorded at higher and lower temperatures. The measured pH values were determined to range from 6.2 at Migingo to 8.4 at Ringiti-2.

The results reveal that, although the amounts of each dissolved particle were determined at random temperatures, the values register minimal variations for the three sets of sampling done twice a day in each case. Even within a day, the measured quantities did not show appreciable variations. This means that the concentrations of various dissolved particle in Kisii University fish are almost constant even within the span of three seasons in a year when the sampling was done. This implies that the ponds are very conducive for fish keeping.

3.4. Variation of NO_3^- Against DO

Figure 1 below shows a curve that compares the effect of dissolved nitrates on the amount of DO in fish pond waters. The amounts of DO were determined at different times of the day in three different seasons; the correspondent concentrations of nitrates were also determined and the results mapped in the graph above. The results indicated that, the higher the amount of nitrates the lower the amount of DO in the pond water. This could be affiliated to temperature and pressure changes.

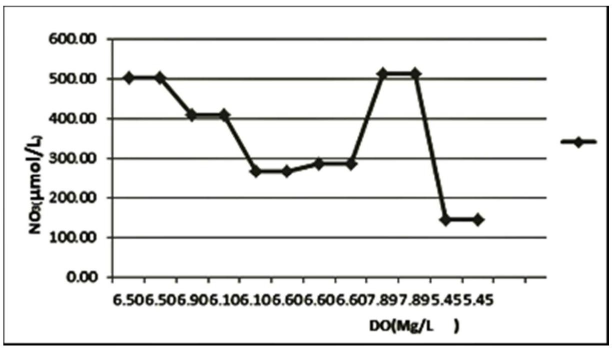

Figure 1. *Profile for variation of NO_3^- against DO.*

3.5. Variation of Temperature Against DO

The curve captures the amounts of DO at different temperatures at pressure of 1 atm (figure 2). These were average values taken in three different seasons of sampling. The profile reveals that a slight change in temperature has a huge impact on the amount of dissolved oxygen.-Higher temperatures diminish amount of DO and hence reduce its availability in water. Optimal temperatures for high concentration of DO are between 25-30°C.

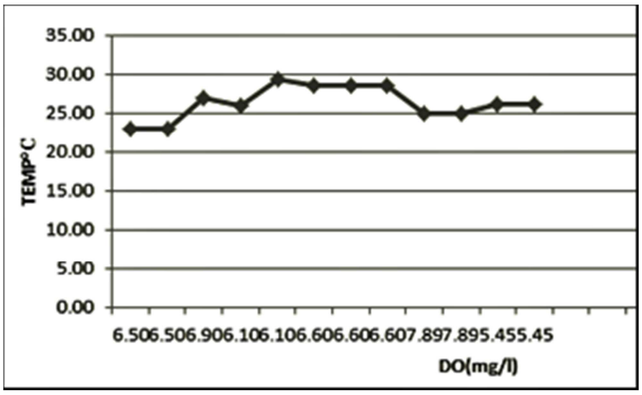

Figure 2. *Profile for variation of Temperature against DO.*

3.6. Variation of Total Nitrogen Against Temperature

The amounts of total nitrogen in the pond waters were determined at random temperatures and the spread was developed. The profile revealed that low temperatures do not favor presence of nitrogen in pond water (figure 3). A temperature range of between 26-30°C registers highest concentration of nitrogen in water.

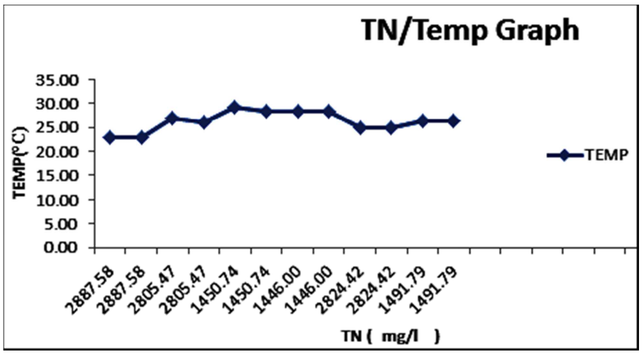

Figure 3. *Profile for variation of Temperature against TN.*

3.7. Variation of TN Against NO^-_3 Ions

From the recorded values of concentrations of total nitrogen and nitrates in the pond waters, there was no clear relationship between total nitrogen and amount of dissolved nitrates in water (figure 4). However the highest concentration of nitrates was recorded when total nitrogen was highest in pond water.

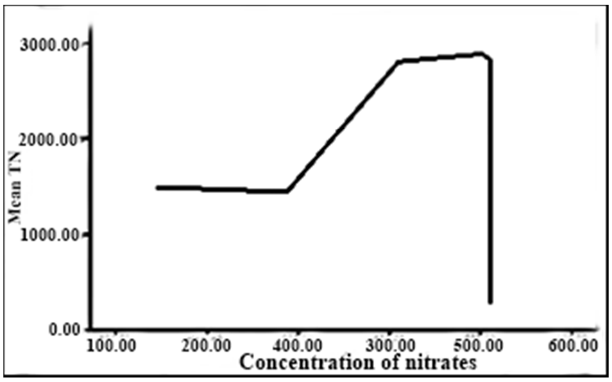

Figure 4. *Profile for variation of TN against NO3.*

3.8. Variation of pH Against (NO^-_3)

Similarly, relationships between pH and concentrations of nitrates and conductivity and concentrations of nitrates were equally analyzed as shown in figures 5 and 6 respectively. Optimal values of nitrate concentrations of about150-250mg/l provide a neutral pH environment. Values between 300-480mg/l provide an alkaline pH but values beyond 500mg/l cause acidic conditions in water. This could be due low DO.

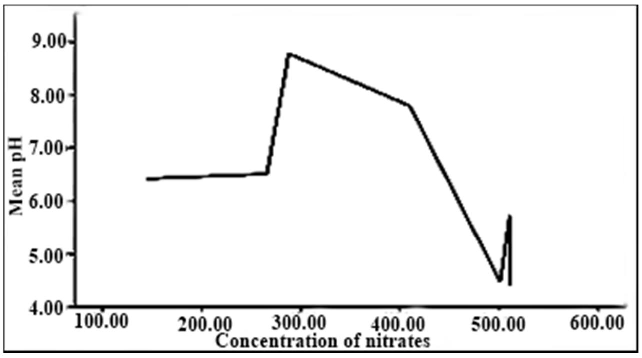

Figure 5. *Profile for variation of pH against NO_3^-.*

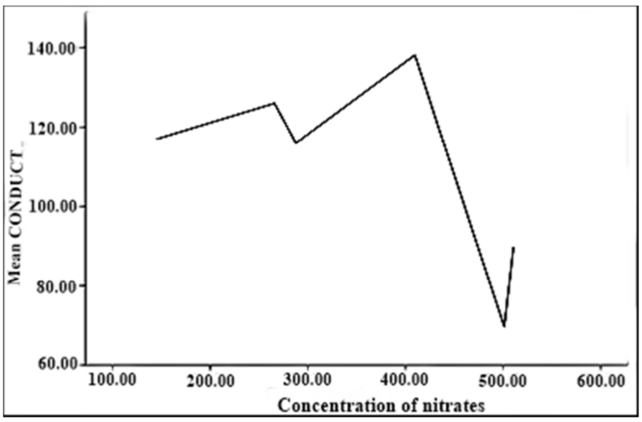

Figure 6. *Profile for variation of Conductivity against NO_3^- Concentration.*

The profile indicated that mean conductivity increases with increase in concentration of nitrates with maximum value registered at 140 units at a concentration of 415mg/l, from which it steeply falls down.

4. Conclusion

Considering the fact that MSE model is known to be very reliable, [16], it was successively validate using the measured quantities from the samples obtained from the fish ponds of Kisii University together with other data available in the literature [17, 18]. The model was also successively used to establish various trends in particle interactions in fish pond waters. It was found that there exists an inverse relationship between the amount of nitrates in water and the levels of dissolved oxygen. The higher the amount of nitrates the lower the amount of DO in the pond water. A pressure of about 1 atmosphere and temperature range 20-27°C favour most particle interactions resulting in higher levels of concentration of NO_3^- ions in pond water. Optimal temperatures for fairly balanced concentrations of the nitrate salts were established as between 20°C -23°C. Higher temperatures diminish amount of DO and hence reduce its availability in water. Elevated temp intensifies the solubility of toxic substances. This research established that variation of water temperature should not exceed ±5 within the day for optimal concentrations of competing particles in solution.

The presence of nitrate ions in water mass encourages the growth of algae. This eventually leads to reduction oxygen (O_2) content in water. Low DO slows down conversion of ammonia to NO_2^- and finally to NO_3^-. NO_2^- and NH_4^+ are toxic to fish. Optimal pH- for Optimal Amounts of nitrates was established as within 7.5-9.0 pH, weakly alkaline condition.

The model has been validated by calculations of the pH, solubilities, and VLE for Selected nitrogen-containing systems namely $Ca(NO_3)_2$, $LiNO_3$, $NaNO_3$ and HNO_3, in water, and by predicting the effects of chemical speciation, temperature, and acid/base/salt concentrations on the formation of various compounds. The model contains three contributions to the excess Gibbs free energy: a long range electrostatic interaction term represented by the Pitzer-Debye- Huckel expression, [19]) a short range interaction term expressed by the UNIQUAC model for the binary interactions between all species and middle range term of a second virial coefficient-type for the remaining ionic interactions [20]. The solution chemistry is modeled by incorporating explicit speciation calculations so that all chemical equilibria of ionic dissociation, ion pair formation, hydrolysis of metal ions, formation of metal-ligand complexes, acid-base reactions. However in this report metal-ligand complexes were not analyzed. For all types of systems and data, the model has been shown to reproduce experimental results with good accuracy.

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