THERMODYNAMIC MODELLING OF THE EQUILIBRIA IN LAKE BARINGO, KENYA

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Abstract

The equilibria that control the composition of a lake is presented using lake Baringo, Kenya, as an example. Lake Baringo (0°37′N, 36°05′E) lies very close to the equator in the Baringo basin in the Eastern Rift Valley, Kenya. Water from the lake was analysed chemically using standard analytical techniques to obtain the stoichiometric concentrations of the major anions and cations. However, this does not indicate how the components are distributed amongst possible species. The speciation calculation was performed using the available equililbrium constants for all the metal – ligand and proton – ligand species identified. At pH 8 the composition of the water of lake Baringo was Ca^{2+} (58.88%); $CaCO_3$ (41.12%); Mg^{2+} (97.33%); $MgCO_3$(2.88%); HCO_3^- (98.27%) and SO_4^{2-} (99.88%). Sulphate forms very weak complexes of calcium and magnesium and was excluded from the model. $MgHCO_3^+$, $CaHCO_3^+$ and $MgSO_4$ were found to be minor species.

Key words: Speciation, thermodynamic modelling

1.0   Introduction

Modelling of the speciation provides an attractive alternative to the often difficult and tedious analytical techniques in speciation studies. All that is required is an extensive data-bank of all conceivable stability constants for a system. This paper reports the use of thermodynamic data to calculate the probable speciation of the major anions and cations present in Lake Baringo, Kenya

Lake Baringo (0°37′N, 36°05′E) lies very close to the equator in the Baringo Basin in the Eastern Rift Valley, Kenya. The lake is roughly 21 kilometres long and 8 kilometres wide with a mean depth of 1.6 metres. It provides a source of fish for the nearby population. The lake has an area of about 130 square kilometres but is variable according to lake levels. Results from previous studies on Lake Baringo (Beadle, 1932, Jenkins 1936, Talling and Talling 1965 and Kallqvist 1980) gave the major species as bicarbonate, chloride, sodium, magnesium and calcium ions while (Alala, 1981) showed no significant heavy metal levels.

Under normal conditions, Lake Baringo, has low alkalinity, but with less rain, the lake has become more saline with an average conductivity of 660µS cm^{-1} while the pH varies between 8.9 and 10.5 (Odada and Olago, 2002). A parallel analysis (Ochieng et.al., 2007) of heavy metals in water and surface sediments in five Rift Valley lakes in Kenya did find some increase in the level of metals due to anthropogenic activities especially in Lake Nakuru.

The analytical data obtained for Lake Baringo however, does not indicate how the components are distributed amongst possible (complex) species. This is achieved *via* speciation calculation that assumes that the system is in equilibrium, that requires the equilibrium constants for all metal-ligand and proton-ligand species at the correct ionic strength and temperature and that accurately defines all the species formed. The speciation calculation was done by Species program (Pettit and Powell, 1999). It calculates and displays speciation curves given the total concentration of reactants and overall stability constants of the complexes considered. It was limited to six components and unable to handle solubility data.

For an aqueous solution phase of a natural water system, the actual composition is given by a set of concentrations. The simplest thermodynamic model for a natural water system is an aqueous solution, which is not subject to physico-chemical reactions with any solid or gaseous phase. Such a system is an idealisation in that water itself and all solutes have some finite escaping tendency, however small. An aqueous solution of electrolyte in a laboratory maintained at constant temperature and exposed to atmospheric pressure represents a common arrangement for studying chemical equilibria. Thermodynamic data obtained from such experimental system can be used to interpret the behaviour of real or model system of a more complex character, e.g. a natural water system (Stumm and Morgan, 1981).

2.0   Materials and methods

Water from the lake, was analysed chemically using standard analytical techniques to provide the data to calculate the probable speciation of the major anions and cations present. The procedure followed for the collection and handling of water samples was adopted from those recommended by Ahlers *et al.* (1990) with some modifications. New polythene bottles were used in the sampling process. Sampling was carried out twice in February and July to capture dry season and long rains respectively.

The bottles were first washed with detergent to remove grease then soaked in 2 mol dm^{-3} HNO_3 for a minimum of four days. A further soaking for about 24 hours in distilled deionized water followed this. Finally, the bottles were rinsed thoroughly with distilled deionized water. After cleaning, the bottles were filled with leaching solution of 0.01mol dm^{-3} analytical grade nitric acid, placed in a separate plastic bag and sealed. The sample bottles were transported in sealed plastic bags taking considerable care to avoid exposure to dust.

On reaching the sampling area, all the bottles were filled partially at least twice and shaken before emptying. Subsequently bottles were filled by hand-dipping (hand protected by wearing plastic hand gloves) empty bottles beneath the water surface. After sampling the bottles were capped and immediately wrapped in polythene bags and later transported to the laboratory.

Samples were drawn from six randomly selected sites along the shore in order to provide a range in water composition. From each site, four aliquots of 500 ml each was withdrawn. Filtration was done as soon as the samples were brought to the laboratory. The filters were first leached with distilled deionized water. Filtration through 0.45 μm nominal pore size membrane filters (Nalgene) was done directly into the acid-cleaned polythene bottles. By convection, whatever passes through the filters is taken to be soluble.

After filtration two 500 ml bottles from each site were preserved for later analysis by the addition of 1 ml concentrated nitric acid per 500 ml of water and kept frozen. The remaining two bottles also stored frozen were left unacidified for the analysis of anions. 2-4 ml of chloroform were added to samples stored for the analysis of nitrite and nitrate to retard bacterial decomposition.

A variety of methods and procedures routinely used in the analysis of natural waters were used, as there were many parameters to be determined. These have a common theme: they involve a physical phenomenon or relationship and its application via appropriate instrumentation. Techniques using these phenomena include potentiometry, voltammetry and spectromery. These were adopted from various standard textbooks of analytical chemistry (Colterman, 1978, Marr 1983,

Braun, 1982, Vogel, 1961, Midgley 1991 and Linder *et al.,* 1984). Analytical grade reagents (BDH Analar grade) were used in all preparation of reagents using deionised water.

Atomic Absorption Spectrophotometer (901 GBC Scientific Equipment Pty Ltd) was used to determine the levels of iron, calcium, manganese and magnesium. Sodium and potassium were determined by flame photometer (Corning 400) using butane as fuel with air as oxidant. Sulphate and phosphorus were analysed at 530 nm and 426 nm respectively using spectronic 20 spetrometer (Bauch and Lamb). For each element a calibration curve was obtained by drawing a graph of absorbance against the corresponding concentrations of working standard solutions. In most cases, the curves were found to be linear in the concentration ranges used for each element. The reproducibility of each instrument for each element analysed was tested. A standard concentration for each element was analysed four times and a mean absorbance calculated in each case.

The carbonate and bicarbonate concentrations were determined by titrimetric procedures. Fluoride and nitrate were determined using the respective ion selective electrodes. The determination of lead, copper and cadmium were done by stripping voltammetry and concentrations determined by standard addition. A typical instrument setting was: Differential pulse polarography, purging time, 180 seconds; equilibration time, 10 seconds; deposition time, 60 seconds and scan range from -1.00 to -.0.15 V (versus Ag/AgCl reference electrode).

3.0   Results and discussions

The results of the analysis of the lake are presented in Table 1. The 95% confidence limits for the concentrations were calculated on a sample size of six (n=6). The number of significant figures quoted specify the estimate of the precision of the results and the uncertainty in the last figures have been emphasised by having them as subscripts.

The average water temperature of Lake Baringo was moderately high (29°C). This high temperature might facilitate rapid decomposition of organic materials in the lake. The conductivity mean value for the lake water was 793 μS cm^{-1}. High conductivity implies the lake has become more saline (Odada and Olago, 2002). The conductivity of most freshwaters ranges from 10 to 1000 μS cm^{-1} but may exceed 1000 μS cm^{-1} in polluted waters.

The mean pH value of 8.2 was recorded for the lake. This means that the lake can be classified as fresh water lake, which depending on other variables, can be suitable for human consumption. The pH of most natural waters is between 6.0 and 8.5 and therefore it falls within the World Health Organisation (WHO)

recommended values (Meybeck 1990). Lower values can occur in dilute waters high in organic content and higher values in eutrophic water, groundwater, brines and salt lakes. A pH value of 8.2 therefore places Lake Baringo near the alkaline limits for human consumption.

The electroneutrality principle, Σ(cation charges) = Σ(anion charges), must hold, however a discrepancy was observed in this relationship and the analytical data because organic matter was not included in the analysis. Oxidative decomposition of organic matter will be very rapid at 29°C. Thus although the conjugate bases of simple molecules such as carboxylic acids, amino acids and peptides will contribute to the anion charge, their lifetime will be short. However, the refractory end products of organic oxidation, humic and fulvic acids will persist and will contribute to anion charge.

The salt concentration is high but consistent with water loss by evaporation. Magnesuim and Calcium are low, controlled mainly by precipitation of their carbonate salts. Natural waters are dynamic systems. If a sample is returned to the laboratory for analysis, it is important to suppress photosynthesis. The photosynthetic reaction will alter the sample pH by consuming CO_2 and increasing the ratio $[CO_3^{2-}]/[HCO_3^-]$. This may promote precipitation of carbonate salts. The high $[HCO_3^-]$ and high pH are consistent with intensive biodegradation of organic matter and photosynthetic activity. Biodegradation generates inorganic carbon, CO_2 from organic matter. Photosynthesis consumes CO_2 in the production of O_2. This process lead to the net conversion of HCO_3^- to CO_3^{2-} and hence an increase in pH. Sulphate tends to concentrate in the water because its Ca and Mg salts are reasonably soluble.

Table 1: The concentration in mg L^{-1} of the selected water variables

			WHO	**EC**
pH	**8.2**		**6.5**	**8.5**
	February, 2007	July, 2007		
Na^+	307±3.3	280.0±34.0	200	175
K^+	15.3±3.0	16.0±2.0		
Ca^{2+}	1.1±0.1	4.0±1.6		
Mg^{2+}	3.0±0.3	3.04±0.2		
CO_3^{2-}	139.3±2.5	154.3±5.0		
HCO_3^-	429.1±16.0	448.5±9.0		
PO_4^{3-}	0.56±0.04	0.43±0.06		
SO_4^{2-}	29.2±1.8	20.5±2.8	40	25
NO_2^-	0.08±0.02	0.20±0.02		
NO_3^-	0.08±0.03	0.09±0.02	45	50

F$^-$	2.22±0.09	3.9±0.05	1.5	1.5
Cl$^-$	49.3±6.8	59.2±2.9	250	250
DOC	4.3±6.8	4.1±0.8		
COD	nd	18.2±8.1		
Cu^{2+}	0.008		1	0.1
Pb^{2+}	0.002		0.05	0.05

The thermodynamic data obtained was used to calculate, using the Species computer program (Pettit and Powell, 1999), the probable speciation of the major anions and cations present in lake Baringo, Kenya. The objective of the calculations in the Species program was to determine the most probable chemical model of a system. The program could accept up to six mass balance equations, run on an IBM compartible PC, it had a very simple user interface and a proper graphical output. The results showed a relatively low concentration of lead and copper and these were not included in the species calculations. Lead and copper are also likely to be solublized by polydentate weak acids ligands which form chelated complexes. The organic ligands were undifferentiated in the DOC.

The concentration of the species in equilibrium is defined in terms of an equilibrium constant:

$$[M_p L_q H_r] = [M]^p [L]^q [H]^r \beta_{pqr}$$

Further, the concentrations of the species in equilibrium are constrained by the law of mass action. For a three component system of a metal ion M, a ligand L and hydrogen ion H$^+$ with concentrations [M], [L] and [H] (ionic charges are omitted for the sake of generality) the expressions for the mass-balance equations are:

$$T_M = [M] + p \sum \beta_{pqr} [M]^p [L]^q [H]^r$$

$$T_L = [L] + q \sum \beta_{pqr} [M]^p [L]^q [H]^r$$

$$T_H = [H] + r \sum \beta_{pqr} [M]^p [L]^q [H]^r$$

T_M, T_L and T_H are the concentrations in total of metal, ligand and proton respectively. Three component system would give three non-linear equations with [M], [L] and $[M_p L_q H_r]$ as the only unknowns if the hydrogen ion concentration obtained from the measurement of pH is known.

Using the mass balance equations, the stability constants and the total concentration value of each component were used as input data for the Species program. In the calculations Species program progressively estimates equilibrium

concentrations until all mass balance equations are satisfied. The output may be plotted as percentage versus pH.

In extremely dilute aqueous solutions, such as most rivers and lakes, the major dissolved species can be looked upon as individual free ions. A chemical analysis of such water reported in terms of concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- etc. may provide an entirely satisfactory model of the internal economy of the system. When one considers all the possible binary complexes that might occur in a natural water containing many dissolved elements, the complication seem at first to be overwhelming. However, no complexes need to be considered between cations and chloride ions or between K^+ and HCO_3^- or CO_3^{2-} . Alkali metal complexes with OH^- , Cl^- and NO_3^- are very weak and thermodynamic data for these complexes are highly uncertain. But K^+ interacts with SO_4^{2-}; Na^+, Ca^{2+} and Mg^{2+} interact with each of the anions SO_4^{2-}, HCO_3^- and CO_3^{2-}. The OH^- interactions may be neglected because of the generally low concentrations of OH^- (Stumm and Morgan (1981).

The important dissolved species may therefore include: K^+, KSO_4^- Na^+, $NaCO_3^-$, $NaHCO_3$, $NaSO_4^-$ Ca^{2+}, $CaHCO_3^+$, $CaCO_3$, $CaSO_4$, Mg^{2+}, $MgHCO_3^+$, $MgCO_3$, $MgSO_4$ HCO_3^-, CO_3^{2-}, SO_4^{2-} .The concentrations of the most important species as determined in Lake Baringo (see Table 2) together with the literature values of the stability constants (Table 3) for the major inorganic species most likely to be in solution were fed into the program Species modified to include up to six components simultaneously.

Table 2: Concentrations (mM) of the most important species in Lake-Baringo

	Feb. 2007	July, 2007
Na^+	1.3	1.2
K^+	0.39	0.41
Ca^{2+}	0.028	0.10
Mg^{2+}	0.12	0.12
CO_3^{2-}	2.3	2.6
SO_4^{2-}	0.3	0.21

The reliability of such species calculations in modelling relies heavily on the thermodynamic data available. It follows that very careful judgement is needed in selecting the stability constants available. Much of these are reported at different ionic strengths and temperatures.

Table 3: Stability constants (log K_{ML} values) for the important metal-inorganic ligand systems at 25°C

Ligand	Ca^{2+}	Mg^{2+}	H$^+$
CO$_3^{2-}$	4.44[a]	2.984[c]	9.95[b]
HCO$_3^-$	1.14[a]	1.066[c]	
SO$_4^{2-}$	1.39[d]	2.47[f]	1.10[e]

[a]Kallqvist (1980] [b]Guyader (1983) [c]Maya (1982) [d]Siebert (1977) [e]Graggs (1979) [f]Khoe (1988)

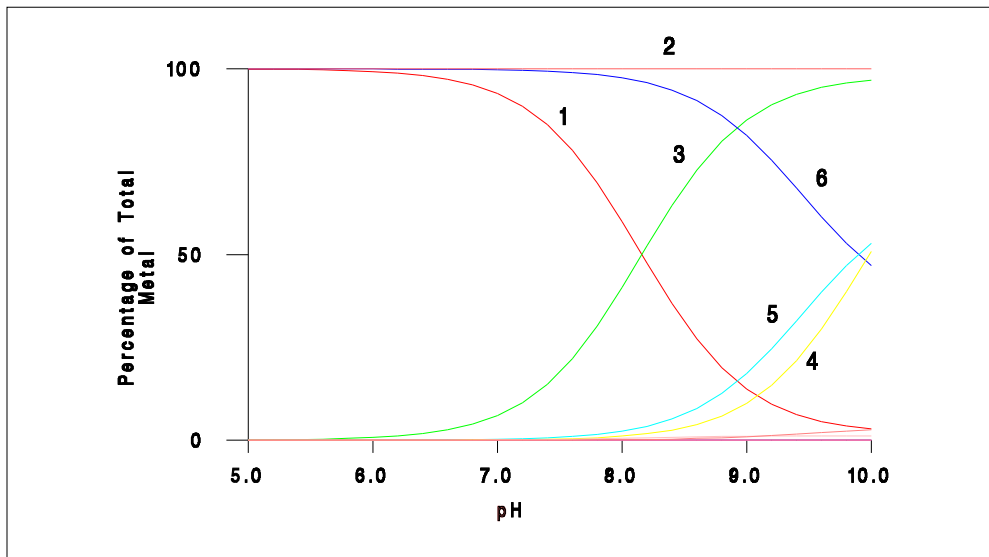The species distribution curves of the major complexes are shown in Figure 1.

Figure 1: The species distribution curves of the major complexes

where 1= Ca^{2+} 2= SO$_4^{2-}$ 3= CaCO$_3$

4= CO$_3^{2-}$ 5= MgCO$_3$ 6= Mg^{2+}

4.0 Conclusion

Sulphate forms very weak complexes of calcium and magnesium and it can be safely excluded from the model. $MgHCO_3^+$, $CaHCO_3^+$ and $MgSO_4$ were also found to be minor species. At pH 8 therefore the composition of the water is as shown in Table 4.

Table 4: Percentage Composition at pH 8

Component	Total Analytical Concentration /mM	Dominant Species pH 8
Ca^{2+}	0.028	$CaCO_3$ (41.12%) Ca^{2+} (58.88%)
Mg^{2+}	0.12	Mg^{2+} (97.33%) $MgCO_3$ (2.88%) $MgSO_4$ (0.29%)
CO_3^{2-}	2.3	HCO_3^- (98.27%)
SO_4^{2-}	0.3	SO_4^{2-} (99.88%)

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