"Electrolytic Aqueous Samples Activity Coefficients Estimation, Using Ion-Selective Electrodes: Samples Collected from Musi river at Nagole, Hasmathpet, Lake Peripheral and Musi River, Pilaipally, Ghatkesar (Mandal) of Hyderabad"

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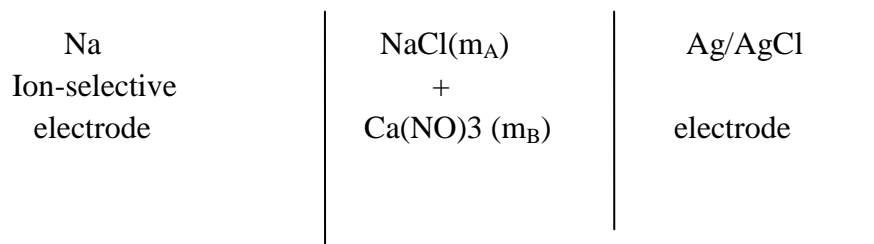Department of Chemistry, Govt.City Degree College, Nayapul, Hyderabad.

ABSTRACT

Electromotive force valuated on $NaCl$-$Ca(NO_3)_2$-H_2O system with a cell consisting of Na^+ion-selective electrode and Ag/AgCl electrode. Pitzer equations were applied for analysis of data. Electrolytic aqueous samples collected from Musi River at Nagole, Hasmathpet, Lake Peripheral and Musi River, Pilaipally, Ghatkesar (Mandal) of Hyderabad were subjected estimation of activity coefficients of using ion-selective electrodes. Aqueous electrolyte fluids thermodynamic properties i.e., activity coefficients, TDS, SAR and SAR(td) their play an important role in understanding the behaviour of water from different sources which are useful in Oceanography, Geo-chemistry, Petroleum drilling, different sources of waters such as Polluted water, Industrial waste water and also Biological fluids.
Key Words: Activity, Activity coefficient, Ion-selective electrodes and Pitzer parameters.

INTRODUCTION

Aqueous electrolyte solutions and their thermodynamic properties play an important role in understanding the behavior of natural water such as sea and lake water, biological fluids, environmental pollution waters, industrial solutions and petroleum drilling fluids[1-4]. The widely studied thermodynamic properties of these single and multi component electrolyte solutions are activities, activity coefficients[5-7]. The environmental water such as lake waters, river waters[8] etc., are found to be multi component electrolyte mixtures. Now-a-days these environmental waters are heavily polluted and are causing a lot of health problems to the people and plants on using these waters. Natural water's composition worked out to know the different parameters like chemical nature, ions, dissolved substances and their properties and other pollutants present. With this view, data has been obtained on the composition and properties of environmental waters from 3 (Three) different places i.e. Musi river at Nagole, Hasmathpet, Lake Peripheral and Musi River, Pilaipally, Ghatkesar (Mandal) of Hyderabad.

The cell consisted of Na-ion selective electrode (Elico, ENA) and an Ag/AgCl electrode[9-10] immersed in a mixture of aqueous $NaCl$ and $Ca(NO_3)_2$ solution placed in a double-walled glass vessel whose temperature was maintained within $\pm 0.01^o$. The cell arrangement was

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Na Ion-selective electrode	NaCl(m_A) + Ca(NO)3 (m_B)	Ag/AgCl electrode	

Deionised, double-distilled water was used for preparation of all stock solutions. NaCl (Merck) and Ca(NO$_3$)$_2$ (s.d. Chemicals) both analytical grade were utilized for experiments without any further purification and drying. The stock solutions of NaCl were standardized volumetrically. AgNO$_3$ and Ca(NO$_3$)$_2$ solutions were standardized volumetrically using EDTA. All solutions were prepared by weight. Weight Burettes were used for carrying out titrations and also for making dilute solutions. The electrodes were connected to a high-impedence ($\approx 10^{12}\Omega$) unit gain amplifier. The output of this amplifier was measured by a Keithley DMM 191 electrometer/multimeter. emf measurements are accurate up to 0.01 mV. The electrodes were first standardized at each of the ionic strengths studied. at every ionic strength a set of four experiments was carried out. As first step, in the double-walled glass cell, NaCl solution was taken and conductance water was added for successive portions. The potential difference was noted after each addition and equilibration. This set of results was used to calibrate the electrodes.

In the second set, NaCl solution was taken in the cell and Ca(NO$_3$)$_2$ solution was added in successive aliquots.

Third set was started with Ca(NO$_3$)$_2$ solution and portions of NaCl solution added subsequently. The overlapping portion between the second and third sets was used to test the reproducibility and accuracy of the measurements.

During fourth set, emfs were measured with Ca(NO$_3$)$_2$ solution after adding conductance water in portions. This set of results was used to calculated the selectivity coefficient of Na-Ion-selective electrode toward Ca^{2+} ion in Ca(NO$_3$)$_2$ solution. The solubility of Ca(NO$_3$)$_2$ in water is low. Therefore, the experiments could be carried out up to a maximum ionic strength of 3.0 mol kg^{-1} only, in order to avoid the precipitation of salts after the addition of NaCl solution.

Results and Discussion

Equations for emf claculation of Na$^+$ ion-selective electrode vs Ag/AgCl electrode in NaCl-Ca(NO$_3$)$_2$-H$_2$O as follows:

$$E = E_o + k \log (a_{Na} \, a_{Cl} + K a^{1/2}_{Ca} \, a_{Cl}) \qquad (1)$$

Where, k is Nernst slope = $(RT/F) \ln 10$ which is the and E_o is the emf due to the NaCl solution at unit activity. The selectivity coefficient (K) values were in the range 10^{-5} to 10^{-4} at the ionic strengths studied, and hence $Ka^{1/2}{}_{Ca}$, a_{Cl} term in eqn. (1) could be neglected. As $a_{Na} = (m_A + 2m_B)\gamma_+$ and $a_{Cl} = m_A\gamma_-$, eqn. (1) could be rearranged as

$$\gamma^2{}_{\pm} = [1/(m_{Na}m_{Cl})]\ 10^{\ (E-Eo)/k} \qquad (2)$$

Hence, the mean activity coefficients ($\gamma_{\pm}$) of NaCl could be determined by substituting the emfs of the cell with NaCl + Ca(NO$_3$)$_2$ mixture, i.e. E in eqn. (2). The experimental mean ionic activity coefficients of NaCl in aqueous NaCl + Ca(NO$_3$)$_2$ system were determined at different values of the ionic strength fractions (y_B) of Ca(NO$_3$)$_2$, where $y_B = 3m_B/(m_A + 3m_B)$.

The data given in table-1 one Musi river at Nagole, Hasmathpet second Lake Peripheral and third Musi River, Pilaipally, Ghatkesar (Mandal) of Hyderabad.

This data shows that all these waters are slightly basic because there pH is in the range 7.9 to 8.7 the water is quite contaminated and has a lot of dissolved substances because the total dissolved solids (TDS) in these waters is in the range 700 to 1700mg/ litre the conductance in the range of 1100 to 2800 µmho, indicating the presence of considerable amounts of dissolved ionic substances or electrolytes in these waters.

Table -1: Composition of Environmental Fluids

S. No.	Place of Waters	Bulk properties			Ionic Composition (moles/litre)				
					Cations			Anions	
		pH	Conductivity	TDS	Na$^+$		Ca^{2+}	NO$_3^-$	Cl$^-$
1.	Musi river near Nagole	8.2	1559	976	0.00457		0.00167 (67)	0.00016 (10)	0.00725 (257)
2.	Hasmathpet lake (Peripheral)	8.7	1320	810	0.00674		0.00187 (75)	0.00010 (6.0)	0.00821 (291)
3	Musi river near Pilaipally, Ghatkesar	8.3	2170	1306	0.01109		0.00187 (75)	0.00010 (6.0)	0.01090 (388)

Further analysis has revealed that the ionic species predominantly present in these waters are Na$^+$, Ca^{2+} as cations and NO$_3^-$, Cl$^-$ as anions. The concentrations of all these ions in each two sets of waters selected are listed in Table-1 These ionic species correspond to about 60 to 90% of the total dissolved solids. The remaining is due to the organic matter and non-ionizable substances such as pesticides, phenols,

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detergents, organic solvents, etc. The electrolytes which are present to a total of about 60 to 90% constitute a major portion of the dissolved solids in these waters. In general water is a good solvent for ionic substances and is a poor solvent for organic matter. It is considered that, water collected from different environmental sources will have different electrolytes components. These dissolved ions play a vital role and cause major effects (health hazards) when used as (i) drinking water for cattle and village laborers, and (ii) irrigation water for crops.

When the environment water or an aqueous solution is exposed to atmosphere, the carbondioxide (gas) from the atmospheric air is dissolved in the water, resulting in the formation of bicarbonate (HCO_3^-) and (CO_3^{2-}) ions in water. Then, an equilibrium is established between the dissolved CO_2, HCO_3^- ion and CO_3^{2-} ion in solution.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$
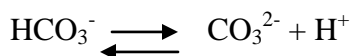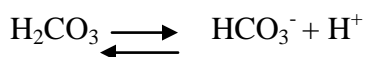
The acid dissociation constant and pK^a values of carbonic acid are given below.

Carbonic acid: $Ka_1 = 4.3 \times 10^{-7}$: $pK^a_1 = 6.37$

$$Ka_2 = 5.6 \times 10^{-11} : pK^a_2 = 10.25$$

From these dissociations constants it could be calculated that at a P^H less than 4.4 only free CO_2 is present. Between a pH of 4.3 and 6.3, CO_2 is replaced by HCO_3^- ion until at a pH of 8.3 essentially no free CO_2 remains. Between pH of 8.3 and 12 certain fraction of HCO_3^- is gradually converted into CO_3^{2-}. At pH of 12 or above the hydroxide ion begins to form the two environmental waters studied in the present work are having the pH close to 8.3. Thus, all the dissolved carbon dioxide is mostly in the form of the bicarbonate ion[11].

In the present work the activity coefficients of the dissolved ions and the corresponding electrolytes in the 2 (two) selected environmental waters will be calculated using the Pitzer equations. A computer programme in Fortan/Basic has been developed for calculating the activity coefficients of the 2 cations and 2 anions in these multielectrolyte environmental fluid.

These ionic activity coefficients (γ_+ and γ_- values) have been used to estimate the mean ionic activity coefficient ($\gamma_\pm$) values of the 4 electrolytes that are possible (2 x 2 = 4) for these cations and anions[12]. These activity coefficient values are listed in Tables (2) (3) and (4) Table-2 the $\gamma_\pm$ values in the water of Musi river at Nagole, Hasmathpet, Table-3 are of Lake Peripheral and Table-4 are related to Musi River, Pilaipally, Ghatkesar (Mandal) of Hyderabad.

However, the United States Public Health Drinking Water Standards[13] (USPHS) are shown in table-5. By Comparing Table-1 and Table-5 it was found that all untreated waters collected from lakes and nalah in different parts of Hyderabad are NOT desirable for drinking because: (1) total dissolved solids (TDS), (2) specific conductances, (3) chloride ion concentration, (4) nitrate ion concentration and (5) Ca^{2+}ion concentration, etc., exceed the permissible limits by considerable amounts. Therefore, these waters are to be treated appropriately before using them as drinking water (with respect of electrolyte concentrations). The activity coefficients of the Involved ions and salts which are listed in Tables 2-4 are quite useful in designing and optimizing the treatment processes.

Table -2: Activity Coefficients of Ions and Electrolytes in Water of Musi River at Nagole (I=0.01608)

Cations →	Na^+	Ca^{2+}
Anions ↓	γ_{Na} =0.8755	γ_{Ca} = 0.5770
NO_3^- γ_{NO3} = 0.8855	γ_{NaNO3} = 0.8805	$\gamma_{Ca(NO3)2}$ =0.7677
Cl^- γ_{Cl} = 0.8867	γ_{NaCl}= 0.8811	γ_{CaCl2} =0.7684

Table-3: Activity Coefficients of Ions and Electrolytes in Water of Hasmathpet Lake Peripheral (I=0.01969)

Cations →	Na^+	Ca^{2+}
Anions ↓	γ_{Na}=0.8368	γ_{Ca} = 0.5532
NO_3^- γ_{NO3} = 0.8761	γ_{NaNO3}= 0.8699	$\gamma_{Ca(NO3)2}$=0.7516
Cl^- γ_{Cl} = 0.8780	γ_{NaCl}= 0.8709	γ_{CaCl2}=0.7527

Table 4: Activity Coefficients of Ions and Electrolytes in Water of Musi River Pilaipally, Ghatkesar (Mandal) (I=0.02348)

Cations →	Na^+	Ca^{2+}
Anions ↓	γ_{Na}=0.8572	γ_{Ca} = 0.5186

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NO_3^- $\gamma_{NO3} = 0.8649$	$\gamma_{NaNO3}= 0.8610$	$\gamma_{Ca(NO3)2}=0.7293$
Cl^- $\gamma_{Cl} = 0.8678$	$\gamma_{NaCl}= 0.8625$	$\gamma_{CaCl2}=0.7310$

Table-5
USA domestic water supply standards

ION /PROPERTY	maximum permissible limit

Calcium	100 mg/litre
Magnesium	30 mg/litre
Chloride	250 mg/litre
Sulphate	250 mg/litre
Nitrate	6.3 mg/litre
Total Dissolved Solids	500 mg/litre
P^H	6.0 to 8.5
Conductance	300 μmho cm^{-1}

By comparing the relative Na^+ ion concentration and total concentration of Ca^{2+} ions in the lake and nalah waters collected was determined to know the usefulness of the water for agriculture purposes. (cf. Table -1). This sodium hazard could be estimated using the parameter 'sodium absorption ratio (SAR)' which is defined as

$$SAR = \frac{Na^+}{\sqrt{(Ca^{++} + Mg^{++})/2}}$$

Using the appropriate activity coefficients the thermodynamic value of SAR can be defined as

$$SAR(td) = \frac{[Na^+] \cdot \gamma_{Na+}}{\sqrt{([Ca^{2+}]\gamma_{Ca2+} + [Mg^{++}]\gamma_{Mg2+})/2}}$$

In present work, estimated activity coefficient values listed in the Tables 2-4 were used to calculated the simple SAR values and SAR (td) values of samples collected. The values are listed in Table-5

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Table -5: The SAR and SAR (td) values

Sl. No.	Water	Concentrations of Ions an Activity Coefficients (γ)	SAR	SAR (td)
1.	Musi river at Nagole	Na = 0.00457 : γ = 0.8755	0.079	0.090
		Ca = 0.00334 : γ = 0.5770		
3.	Hasmathpet Lake Peripheral	Na = 0.00674 : γ= 0.8638	0.108	0.125
		Ca = 0.00374 : γ = 0.5532		
4.	Musi River, Pilaipally, Ghatkesar (Mandal)	Na = 0.01109 : γ = 0.8572	0.188	0.223
		Ca = 0.00374 : γ = 0.5186		

For all the waters studied the SAR and SAR (td) values are less than 10 and are within the acceptable limits. However, in all the cases the SAR (td) is higher than the sample SAR value. Thus, the water quality is found to be less when the true thermodynamic SAR values [SAR (td)] are calculated as compared to the conclusions based on simple SAR values. This factory may become very crucial when the waters having high salinity or soils having high salinity are involved.

As discussed above, the activity coefficients of the dissolved ions/electrolytes are quite useful in understanding and treatment of drinking waters, agricultural waters and Biological fluids[14].

CONCLUSIONS:

Pitzer formulism made use to describe the properties of concentrated electrolyte mixtures.

Trends of activity coefficients of pure and mixed electrolyte solutions explained. The differences in activity coefficient arise due to the effect of different electrolytes are explained

Acknowledgement

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