



ESTIMATION OF ACTIVITY COEFFICIENTS OF ELECTROLYTIC AQUEOUS SAMPLES USING ION-SELECTIVE ELECTRODES: SAMPLES COLLECTED FROM HUSSAIN SAGAR LAKE AND KUKATPALLY NALAH OF HYDERABAD

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ABSTRACT

Electromotive force measurements have been carried out on the system $\text{NaCl}-\text{Ca}(\text{NO}_3)_2-\text{H}_2\text{O}$ using a cell consisting of sodium ion-selective electrode and an Ag/AgCl electrode. The data are analysed using the Pitzer equations. Further, samples collected from Hussain sagar lake and Kukatpally nalah of Hyderabad are collected and estimation of activity coefficients of these electrolytic aqueous samples was carried out using ion-selective electrodes. Aqueous electrolyte fluids thermodynamic properties i.e., activity coefficients, TDS, SAR and SAR(td) play an important role in understanding the behaviour of water from different sources which are useful in several fields such as Petroleum drilling, Oceanography, Geo-chemistry, Natural water such as sea and lake water Pollution, Biological and Industrial fluids. Water samples collected from Kukatpally nalah has more SAR and SAR (td) values showing the water quality found to be less compare to the water samples collected from Hussain sagar lake of Hyderabad.

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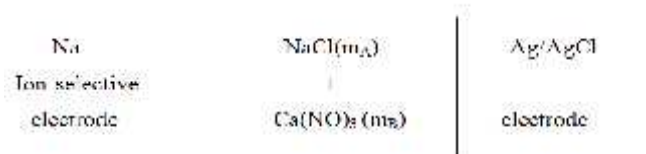
INTRODUCTION

Aqueous electrolyte solutions and their thermodynamic properties play an important role in understanding the behaviour of natural water such as sea and lake water, biological fluids, environmental pollution waters, industrial solutions and petroleum drilling fluids¹⁻³. The widely studied thermodynamic properties of these single and multicomponent electrolyte solutions activities and activity coefficients⁴⁻⁶.

The environmental water such as lake waters, river waters⁷ etc., are found to be multicomponent 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. Therefore, the efforts are being made to find the composition of the environmental waters in order to know the chemical nature and thermodynamic properties of the dissolved substances, ions and pollutants. With this view, data has been obtained on the composition and properties of environmental waters from 2 (two) different places i.e. Hussain Sagar lake at Buddha Statue and Kukatpally nalah near Moosapet of Hyderabad.

Experimental

The cell consisted of Na-ion selective electrode (Elico, ENA) and an Ag/AgCl electrode⁸⁻⁹ immersed in a mixture of aqueous NaCl and $\text{Ca}(\text{NO}_3)_2$ solution placed in a double-walled glass vessel whose temperature was maintained within $\pm 0.01^\circ\text{C}$. The cell arrangement was



Deionised, double-distilled water was used for preparation of all stock solutions. Analytical grade sodium chloride (Merck) and $\text{Ca}(\text{NO}_3)_2$ calcium nitrate (s.d.chem.) were used without further purification and drying. The stock solutions of NaCl were standardized volumetrically. AgNO_3 and $\text{Ca}(\text{NO}_3)_2$ solutions were standardized volumetrically using EDTA. All solutions were prepared by weight. Also all titrations and dilutions were made using weight burettes. The electrodes were connected to a high-impedance (10^{12}) unit gain amplifier. The output of this amplifier was measured by a Keithley DMM 191 electrometer/multimeter. The accuracy of the emf measurements was 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. In the first set, NaCl solution was taken in a double-walled glass cell and conductance water was added in successive aliquots. 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 $\text{Ca}(\text{NO}_3)_2$ solution was added in successive aliquots.

The third set was made by starting with $\text{Ca}(\text{NO}_3)_2$ solution and adding NaCl solution in aliquots. The overlapping portion

between the second and third sets was used to test the reproducibility and accuracy of the measurements.

In the fourth set, Ca(NO₃)₂ solution was taken in the cell and the emfs were noted after adding conductance water in aliquots. This set of results was used to calculate the selectivity coefficient of Na-Ion-selective electrode toward Ca²⁺ ion in Ca(NO₃)₂ solution. The solubility of Ca(NO₃)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

The emfs of sodium ion-selective electrode vs Ag/AgCl electrode in NaCl-Ca(NO₃)₂-H₂O system are given by the equation

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

Where, $k = (RT/F) \ln 10$ which is the Nernst slope and E_o is the emf due to the sodium chloride 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 $K a_{Ca}^{1/2} a_{Cl}$ term in eqn. (1) could be neglected. As $a_{Na} = (m_A + 2m_B) \gamma_{Na}$ and $a_{Cl} = m_A \gamma_{Cl}$, eqn. (1) could be rearranged as

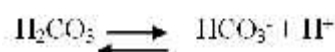
$$\gamma_{Na} = [1/(m_{Na} m_{Cl})] 10^{(E-E_o)/k} \quad (2)$$

Hence, the mean activity coefficients (γ_{\pm}) of NaCl could be determined by substituting the emfs of the cell with NaCl + Ca(NO₃)₂ mixture, i.e. E in eqn. (2). The experimental mean ionic activity coefficients of NaCl in aqueous NaCl + Ca(NO₃)₂ system were determined at different values of the ionic strength fractions (y_B) of Ca(NO₃)₂, where $y_B = 3m_B/(m_A + 3m_B)$.

The data given in table-1 one Lake and one Nalah around Hyderabad. This data shows that all these waters are slightly basic because their 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 1700 mg/litre the conductance in the range of 1100 to 2800 μ mho, indicating the presence of considerable amounts of dissolved ionic substances or electrolytes in these waters.

water is a good solvent for ionic substances and is a poor solvent for organic matter. Therefore, the environmental waters are generally considered as multicomponent electrolyte solutions. These dissolved ions play a vital role and cause major effects (health hazards) when used as (i) drinking water for cattle and village labourers, and (ii) irrigation water for crops.

When the environment water or an aqueous solution is exposed to atmosphere, the carbon dioxide (gas) from the atmospheric air is dissolved in the water, resulting in the formation of bicarbonate (HCO₃⁻) and (CO₃²⁻) ions in water. Then, an equilibrium is established between the dissolved CO₂, HCO₃⁻ ion and CO₃²⁻ ion in solution.



The acid dissociation constant and pK^a values of carbonic acid are given below.

$$\text{Carbonic acid: } K_{a1} = 4.3 \times 10^{-7}; pK_{a1} = 6.37$$

$$K_{a2} = 5.6 \times 10^{-11}; pK_{a2} = 10.25$$

From these dissociation constants it could be calculated that at a P^H less than 4.4 only free CO₂ is present. Between a pH of 4.3 and 6.3, CO₂ is replaced by HCO₃⁻ ion until at a pH of 8.3 essentially no free CO₂ remains. Between pH of 8.3 and 12 certain fraction of HCO₃⁻ is gradually converted into CO₃²⁻. 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 ion¹⁰.

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 Fortran/Basic has been developed for calculating the activity coefficients of the 2 cations and 2 anions in these multielectrolyte environmental fluid,

Table -1

Composition of Environmental Fluids

S.No	Place of Waters	Bulk properties			Ionic Composition (moles/litre)			
		pH	Conduc tivity	TDS	Cations		Anions	
					Na ⁺	Ca ²⁺	NO ₃ ⁻	Cl ⁻
1.	Hussain Sagar lake near Budha Statue	8.4	1128	704	0.00626	0.00205 (82)	0.00018 (11)	0.00725 (257)
2.	Kukatpally Nalah near Moosapet	7.9	2800	1695	0.01392	0.00259 (104)	0.00092 (57)	0.01368 (485)

Further analysis has revealed that the ionic species predominantly present in these waters are Na⁺, Ca²⁺ as cations and NO₃⁻, 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, 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

These ionic activity coefficients (γ_{+} and γ_{-} values) have been used to estimate the mean ionic activity coefficient (γ_{\pm}) values of the 4 electrolytes that are possible (2 x 2 = 4) for these cations and anions¹¹. These activity coefficient values are listed in Tables (2) and (3), Table-2 the γ_{\pm} values in the water of Hussain Sagar lake at Buddha Statue, Table-3 The γ_{\pm} values in the water of Kukatpally Nalah near Moosapet.

However, the United States Public Health Drinking Water Standards¹² (USPHS) are shown in table-4. Comparing Table-

1 and Table-4 we find that all the waters (untreated) in lakes and nalah in and around Hyderabad are NOT suitable as drinking waters because many parameters such as (1) total dissolved solids (TDS), (2) specific conductances, (3) chloride ion concentration, (4) nitrate ion concentration and (5) Ca²⁺ 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 2-3 are quite useful in designing and optimizing the treatment processes.

Table -2 Activity coefficients of ions and electrolytes in water of Hussain Sagar Lake, Near Budha Statue (I=0.01742)

Cations →	Na ⁺	Ca ²⁺
Anions ↓	Na=0.8715	Ca = 0.5651
NO ₃ ⁻	NaNO ₃	Ca(NO ₃) ₂
NO ₃ = 0.8813	= 0.8764	=0.7600
Cl ⁻	NaCl	CaCl ₂
Cl = 0.8829	= 0.8772	=0.7609

Table – 3 Activity Coefficients of Ions and Electrolytes in Water of Kukatpally Nalah Near Moosapet (I=0.02859)

Cations →	Na ⁺	Ca ²⁺
Anions ↓	Na=0.8470	Ca = 0.4897
NO ₃ ⁻	NaNO ₃	Ca(NO ₃) ₂
NO ₃ = 0.8543	= 0.8506	=0.7097
Cl ⁻	NaCl	CaCl ₂
Cl = 0.8577	= 0.8523	=0.7115

Table-4 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
pH	6.0 to 8.5
Conductance	300 µmho cm ⁻¹

The usefulness of the lake and nalah waters for agricultural purposes is determined by the relative concentration of sodium ions as compared to the total concentration of calcium ions (cf. Table -1). This sodium hazard could be estimated using the parameter ‘sodium absorption ratio (SAR)’ which is defined as

$$SAR = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}}$$

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

$$SAR(td) = \frac{[Na^+] \gamma_{Na^+}}{\sqrt{([Ca^{2+}] \gamma_{Ca^{2+}} + [Mg^{2+}] \gamma_{Mg^{2+}})^{1/2}}}$$

The activity coefficient values estimated in the present work and listed in Tables 2-3 are used to calculate the simple SAR values and SAR (td) values for 2 different waters studied. The values are listed in Table-5

Table -5 The SAR and SAR (td) values

Sl. No.	Water	Concentrations of Ions and Activity Coefficients ()	SAR	SAR (td)
1.	Hussain Sagar lake near Budha Statue	Na = 0.00626 : = 0.8715 Ca = 0.00410 : = 0.5651	0.109	0.126
2.	Kukatpally Nalah near Moosapet	Na = 0.01392 : = 0.8470 Ca = 0.00518 : = 0.4897	0.220	0.265

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. The activity coefficients of the dissolved ions/electrolytes are quite useful in understanding and treatment of drinking waters and agricultural waters.

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.

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