CHAPTER 3

MEASUREMENT OF SINGLE ION ACTIVITY COEFFICIENT OF ELECTROLYTES IN BINARY SYSTEMS
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3.1 INTRODUCTION

In Chapter 2 potentiometric methods were reviewed and the application of ion-selective electrodes to perform electromotive force (EMF) measurement of electrochemical cells was discussed. In this Chapter, the different techniques for EMF measurements and the calculation of single ion activity coefficient of electrolytes in binary systems will be briefly discussed.

Activity of a species in a solution is referred to as its effective concentration in that solution. In a very dilute solution, as interactions are insignificant, concentration and effective concentration are the same. But as the concentration increases, the electrostatic interaction increases and deviations from ideality are accommodated by modifying the concentration with activity coefficient. The non-ideality in aqueous solution can be attributed to ionic activity coefficient and it corresponds to interaction between different species in solution, both ionic and molecular. When the solute undergoes ionic dissociation in solution, the activities of cations and anions \((a_+, a_-)\) can be defined; so also activity coefficients \((\gamma_+, \gamma_-)\). The knowledge of individual ionic activity coefficient is important for the design of equilibrium processes involving electrolyte solutions as well as for processes involving ion-exchange and pollution
control [1]. Activity coefficients can also be used for the prediction of rate constant, equilibrium constant, chemical potential values, solubility product and for the separation of a species from a mixture of substances on the basis of the magnitude of activity coefficient.

Single ion activity coefficients are traditionally termed as not measurable by simple thermodynamic methods due to space charge interactions. Information regarding mean ionic activity coefficient is available in literature [2-7], but the absence of reliable methods for the measurement of individual ion activity coefficients is a major barrier for the study of the systems which are really complex in nature. Attempts were made to measure single ion activity coefficient of non volatile electrolytes in solution by two methods: (1) solvent activity method involving vapour pressure and Gibbs-Duhem equation; (2) electrochemical cell technique involving direct calculation of the activity of an electrolyte by measuring the EMF of the electrochemical cell. Vera and co-workers [8-12] and other researchers [13-16] demonstrated the application of ISE (Ion Selective Electrode) technique for the measurement of single ion activity coefficients. The same approach has been utilized to determine the single ion activity coefficient in this work. Measurement of the activity coefficients of both anion and cation in aqueous solutions of single electrolytes using ISE method has been demonstrated. The activity coefficients are used to find out mean ionic activity coefficient for different salts. The calculated mean ionic activity coefficients are in good agreement with the values reported by Hamer and Wu [3].

3.2 OVERVIEW OF EARLIER WORK

The problem of measurement of the activity coefficient of individual ions has been a topic of discussion for over 85 years. Lewis and Randall [17] in their classical text book
‘Thermodynamics’ stated that: “This is a problem of difficulty, and indeed we are far from any complete solution”. Some standard text books have declared that such measurements are impossible to make [18, 19]. In spite of all the discrepancies, there has been continuous effort from various research groups through the years to measure individual ionic activity coefficients by diverse techniques [10, 11, 20-29].

Bates et al. [13, 20] extended the Robinson and Stokes [4] hydration model for the mean activity coefficient of salts and proposed a model for the calculation of activity coefficients of individual ions in unassociated chlorides. Assuming that chloride ion is not hydrated, Bates et al. prepared tables for the activities of different ions in non-associating chlorides by using hydration numbers reported in the literature for cations and considering the experimental data for $\gamma_{\pm}$. The results obtained with this model, predicted that the activity coefficients of monovalent cations in non-associating chlorides are either equal or higher than those of the chloride anion. For CsCl, the model predicted the same values for the activity coefficients of cation and anion, but for all other chlorides it predicted higher value for monovalent cations. Komar and Kaftanov [21] estimated the activity coefficients of the chloride ion in a potassium chloride solution at high (11-12) and low (2-2.7) pH.

Shatkay and Lerman [22] obtained activity coefficients of sodium and chloride ions in a sodium chloride solution using Ion selective electrode (ISE) and AgCl/Ag electrode, each against a calomel reference electrode and used a modified Henderson equation to calculate the liquid junction potential. Although they used a Nernstian slope for the electrode potential, they determined the conditions under which this assumption was valid. The values of the standard potential were chosen arbitrarily. Their direct
measurements of the mean ionic activity coefficients of sodium chloride agreed well with literature data.

Milazzo [23, 24] suggested a procedure for determining the activity coefficient of individual ions from the variation of the EMF of electrodes with temperature. Further studies [25, 26] made by him indicated some shortcomings of this method. As the method proposed was unsuccessful, Millazo et al. [27] discussed the conditions that would be required to obtain reliable data. The values of activity coefficients of sodium and chloride ions in sodium chloride solution at different temperatures reported by Mokhov et al. [28] gave a poor reproduction of $\gamma_\pm$ for sodium chloride.

### 3.2.1 USE OF ION SELECTIVE ELECTRODES TO MEASURE THE IONIC ACTIVITY

The major breakthrough towards the measurement of the activity of individual ions was achieved with the use of ion selective electrodes. One of the advantages of ISEs is their “ability to measure the activity of ions” [30]. The ISEs have also been used for the measurement of $\gamma_\pm$ of an electrolyte in mixed electrolyte solutions [31, 32] and to measure the activities of amino acids in aqueous electrolyte solutions [10, 33-38]

An important step toward the measurement of the activity of ions was based on the finding of Kakabadse [39] that for a single electrolyte in an aqueous solution, the resultant EMF value was obtained from the direct measurement of the EMF of the ISE for the cation against the ISE for the anion, as the difference of the two EMF values of the individual ISEs with respect to a common reference electrode. Haghtalab [40] verified this finding and used the difference of the EMF readings to measure $\gamma_\pm$ for electrolytes up to high molalities [31, 32]. These experimental results made it evident that the EMF measured with a single ISE against a reference electrode contained the information on the activity of the individual ion.
Haghtalab [32] determined the mean ionic activity coefficients of NaBr in aqueous mixtures of NaBr and Ca(NO$_3$)$_2$ at 298 K at a total ionic strength of 3, 4.5 and 6 mole. The measurements were made using an electrochemical cell with the ion selective electrodes, Na-ISE against Br-ISE as a reference electrode. The mean activity coefficients of Ca(NO$_3$)$_2$ were calculated using the cross differentiation of the mean activity coefficients. He also investigated the thermodynamics of aqueous solutions of strong electrolytes for both binary and multi-component systems. Electrochemical data generated from electrochemical cells using ion-selective electrodes were used to derive activity coefficient values.

In 1996, Khoshkbarchi and Vera [10, 11] measured the activity of ions using two ISEs against a single junction reference electrode (SJRE). They used ISEs to measure the activity coefficients of individual ions in aqueous solutions of NaCl and NaBr at 298.2 K, up to of 5 mole and of KCl up to 4 mole. The mean ionic activity coefficients of NaCl, NaBr and KCl obtained from the values of the activity coefficients of the individual ions showed good agreement with values reported in the literature. The experimental results revealed that the activity coefficients are different for the anion and the cation in an aqueous solution of a single electrolyte and that, as expected from the ion-ion and ion-solvent interactions, the activity coefficient of an ion depends on the nature of its counter ion. A modified form of Pitzer's model, which distinguishes between the activity coefficients of the anion and the cation, was used to correlate the experimental results. A novel method was developed for the measurement of the activity coefficients of an amino acid and the mean ionic activity coefficient of an electrolyte in water-electrolyte-amino acid systems using electrochemical cell.

From 1996 till today, Vera and Co-workers [8, 12, 41-43] generated lot of results on single ion activity coefficient, both in single and mixed solvents. They observed that the
change of filling solution of reference electrode did not have much effect on the ionic activity coefficient and the individual activities of the ions were measured by them using ISEs. The available commercial electrodes could be used in a wide range of concentrations of the respective ion. In the systems chosen for measurements, there was no interference to the response of an ISE due to the presence of other ions in the solution because of the precautions taken during the measurement.

3.3 EXPERIMENTAL

Electrochemical cells with ion-selective electrodes and an AgCl/Ag double junction reference electrode (DJ), have been used to measure the activity coefficients of sodium, potassium, chloride and nitrate ions in aqueous solutions of sodium nitrate, potassium nitrate, sodium chloride and potassium chloride. The values of potential difference of the following cell configuration were measured and were then converted to the ionic activity coefficients.

\[
\text{ISE} | \text{electrolyte (s)} | \text{KCl, AgCl/ Ag (DJ)}
\]  

AR grade NaNO₃, NaCl, KNO₃ and KCl of 99.9 and 99.5 % purity were obtained from M/s. Loba Chemie (Mumbai) and M/s. Merck (Mumbai) respectively. The salts were oven dried for 48 h and cooled in vacuum desiccator for 24 h prior to use. A sodium ion selective electrode glass body, a potassium ion selective electrode polymer body, a nitrate ion selective electrode polymer body, a chloride ISE, solid state and a double junction reference electrode were obtained from M/s. Orion, USA. An Orion pH / ISE meter (EA 920A⁺) with a resolution of ± 0.1 mV was used to monitor the electrochemical potentials. The ISE meter had two BNC connectors for ISEs and two pin-tip connectors for the reference electrode. During the experiments, the solutions
were stirred continuously and the temperature was kept constant at 298.15 ± 2 K using a thermostatic bath.

The electrodes were conditioned according to the manufacturer’s procedure prior to the experiment. The main features of the apparatus, designed to conduct the experiment include a double wall jacketed vessel, ion selective electrode, a double junction reference electrode, a thermostatic bath, a high impedance millivolt meter, a temperature probe, and a magnetic stirrer. Fig. 3.1 shows the schematic diagram of the experimental setup. The temperature in the double wall jacketed vessel was controlled by water from a thermostatic bath. The temperature of water in the thermostatic bath was stabilized by using an additional cooling bath.

Fig. 3.1: Schematic diagram of the experimental system

ASTM Grade-1 water as per ASTM D-1193 [44] with a resistivity of 18.2 MΩ·cm at 298.15 K and TOC < 15 ppb from a MILLIPORE Simplicity system was used in the experiments for reagent/solution preparation and as water standard. All the solutions were prepared based on molality and the water was also weighed. Solutes were accurately weighed in a precision Shimadzu AUW220D balance (220 g, 0.01 mg resolution). When not in use, the solutions were kept in air-tight closed condition in a JULABO SW-22 Shaker Bath at 298.15 ± 0.1 K. JULABO SW-22 Shaker Bath was coupled with JULABO FP-40 chiller for cooling. To ensure ripple-free power supply to all the equipment, AC supply was regulated with an uninterrupted power supply (APC), set at high sensitivity. The ambient conditions were monitored with a Cole-Parmer hygrometer (0.1%) comprising a thermometer (0.1 K) and pressure sensor (0.1 kPa).

The experiments were initiated with the lowest concentration of electrolyte and the concentration was increased by addition of electrolyte. The EMF of both the cation and anion ISE were measured against a double junction reference electrode. The readings of the potentiometer were recorded only when the drift was less than 0.1 mV. To avoid the bias potential between different reference electrodes, in each experiment, the response of both cation and anion ISEs were measured simultaneously against the same reference electrode. In order to minimize the risk of concentration gradient in the beaker, the solutions were stirred continuously during the experiment with a magnetic stirrer and the temperature was kept constant using thermostatic bath.

**3.4 CALIBRATION OF ION SELECTIVE ELECTRODES**

For the electrodes to exhibit Nernstian behaviour, they were calibrated using the standard solutions supplied along with the electrodes. Three buffer solutions were prepared from the standard solutions differing 10 times each in concentration.
For a 1:1 electrolyte, the EMF (E) values of the cells obtained from these solutions could be represented by an equation given by Butler and Roy [45]

\[ E = E^0 + S \ln a = E^0 + 2S \ln (m\gamma_{\pm}) \]  

(3.1)

where, E is the potential of the cell, \( E^0 \) is the standard EMF of the cell, S is the slope of the electrode’s response to the ionic activities, \( \gamma_{\pm} \) is the mean activity coefficient and m is the molality.

When ISEs were used for determining the activity coefficients of electrolytes in binary systems, it was reported that the use of the theoretical value of the reversible Nernstian slope as S in Eq. (3.1) could not be justified [13]. In the present study, both \( E^0 \) and S were treated as adjustable parameters and could be obtained by optimization method. The variation of \( \ln m \) with E (mV) for the calibration of different ISEs with their respective salts is shown in Figs. 3.2 to 3.5 respectively. The slope and intercept of Eq. (3.1) were calculated from these plots in very dilute region.

![Graph](image)

Fig. 3.2: Variation of the potential of NaNO₃ (E) with concentration
Fig. 3.3: Variation of the potential of NaCl (E) with concentration

Fig. 3.4: Variation of the potential of KNO₃ (E) with concentration
Chapter 3

3.5 RESULTS AND DISCUSSION

The ISEs used in this work were calibrated prior to the experiment. The cell arrangement for the experiments were

Na glass body ISE | NaNO₃ (m₁) | NO₃ polymer body ISE  (3.II)

Na glass body ISE | NaCl (m₂) | Cl solid-state ISE  (3.III)

K polymer body ISE | KNO₃ (m₁) | NO₃ polymer body ISE and  (3.IV)

K polymer body ISE | KCl (m₂) | Cl solid-state ISE  (3.V)

The potential of the respective ISE was measured against a double junction reference electrode and is related to the ionic activity coefficient of the corresponding ion by Nernst equation. For a solution containing an electrolyte of molality m₁, the Nernst
equations for the potentials of a cation and an anion ISE, \( E_+ \) and \( E_- \) in the electrochemical cell of type 3.II, ISE\( | \) NaNO\(_3\)\( | \) reference electrode, can be written as

\[
E_+ = E_+^0 + \frac{RT}{z_+F} \ln(m_+\gamma_+)
\]  
\( (3.2) \)

\[
E_- = E_-^0 + \frac{RT}{z_-F} \ln(m_-\gamma_-)
\]  
\( (3.3) \)

where \( \gamma \) is the activity coefficient, \( R \) is the universal gas constant, \( T \) is absolute temperature, \( F \) is Faraday’s constant, \( z \) is the charge number, and subscripts plus and minus sign denote the cation and the anion respectively. The terms \( E_+^0 \) and \( E_-^0 \) in Eqs. (3.2) and (3.3) are linear combinations of the junction potential, reference electrode potential and ISE potentials:

\[
E_+^0 = E^{\text{ref}}_+ + E^J + E_+^{\text{ISE}}
\]  
\( (3.4) \)

\[
E_-^0 = E^{\text{ref}}_- + E^J + E_-^{\text{ISE}}
\]  
\( (3.5) \)

where, superscripts ‘ref’ and ‘J’ denote the potential of the reference electrode and junction potential and the terms \( E_+^{\text{ISE}} \) and \( E_-^{\text{ISE}} \) include all asymmetry, internal solution and reference potential of the cation and anion ISE respectively. Subtracting Eq. (3.3) from Eq. (3.2) and substituting Eqs. (3.4) and (3.5), a relation between the difference in the potential of a cation and an anion ISE is obtained with the mean ionic activity coefficient of the electrolyte, \( \gamma^{(1)}_{z\pm} \), in cell type (1) as

\[
E_+ - E_- = (E_+^{\text{ISE}} - E_-^{\text{ISE}}) + \frac{RT}{F} \left( \frac{z_+ z_-}{z_+ + z_-} \right) \ln \frac{\gamma^{(1)}_{z_+ u_+ u_-}}{\gamma^{(1)}_{z_+ u_+ u_-}} m_y^{(l)}
\]  
\( (3.6) \)
For a 1:1 electrolyte, equation (3.6) simplifies to

$$E_s - E = (E_s^{ISE} - E_s^{ISE}) + \frac{2RT}{F} \ln(n_i \gamma_i^{(3)})$$  \hspace{1cm} (3.7)

Equation (3.7) is valid only when the reference electrode is same both for cation and anion ISEs. The more general form of Eq. (3.7) for NaNO₃, NaCl, KNO₃ and KCl solutions is

$$\Delta E_{NaNO_3} = E_0^{NaNO_3} + 2S \ln(m_i \gamma_i^{(1)})$$  \hspace{1cm} (3.8)

$$\Delta E_{NaCl} = E_0^{NaCl} + 2S \ln(m_i \gamma_i^{(2)})$$  \hspace{1cm} (3.9)

$$\Delta E_{KNO_3} = E_0^{KNO_3} + 2S \ln(m_i \gamma_i^{(3)})$$  \hspace{1cm} (3.10)

$$\Delta E_{KCl} = E_0^{KCl} + 2S \ln(m_i \gamma_i^{(4)})$$  \hspace{1cm} (3.11)

Determination of activity coefficients of electrolytes by ISEs is a rapid method. However, some interference from other ions will be there at high concentrations. To avoid the interferences, the experiments were performed with dilute solutions, by measuring the EMF of both the cation and the anion ISEs against a double junction reference electrode. The sample and the standard solutions were maintained at the same ionic strength. Figs 3.6 and 3.7 depict the ion activity coefficients of sodium, chloride and nitrate ions at various molalities in aqueous solutions of NaNO₃ and NaCl.
Fig. 3.6: Variation of activity coefficient values of NaCl with concentration

Fig. 3.7: Variation of activity coefficient values of KNO₃ with concentration

The numerical data for the ionic activity coefficients in the aqueous solutions of KCl and NaNO₃ are presented in Tables 3.1 and 3.2 respectively along with the literature value for the sake of comparison.
Table 3.1: Single ion activity coefficient and mean activity coefficient values for aqueous solution of KCl

<table>
<thead>
<tr>
<th>Conc. (mol.kg(^{-1}))</th>
<th>(\gamma_{K^+})</th>
<th>(\gamma_{Cl^-})</th>
<th>(\gamma_z) (Expt.)</th>
<th>(\gamma_z) (Ref. [3])</th>
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</thead>
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<td>0.001</td>
<td>0.998</td>
<td>0.962</td>
<td>0.980</td>
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Table 3.2: Individual activity coefficient and mean activity coefficient values for NaNO₃ solution

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<tr>
<th>Conc. (mol.kg⁻¹)</th>
<th>γ⁺Na</th>
<th>γ⁻NO₃</th>
<th>γ±(Expt.)</th>
<th>γ±(Ref. [3])</th>
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<td>2.996</td>
<td>0.487</td>
<td>0.402</td>
<td>0.442</td>
<td>0.437</td>
</tr>
</tbody>
</table>
The mean activity coefficient of each salt was obtained from the relation:

$$\gamma_\pm = \left( \gamma_+^{\nu^+} \gamma_-^{\nu^-} \right)^{1/(\nu^+ + \nu^-)}$$  \hspace{2cm} (3.12)

From the Tables 3.1 and 3.2 and Figs. 3.6 and 3.7, it is evident that the activity coefficients of the cation and anion are nearly equal in very dilute solutions, but with increase in concentration they deviate from each other i.e., their contribution to non-ideal behaviour increases. The mean ionic activity coefficient obtained from the experimental measurements is generally larger than the literature reported values [3]. The mean ionic activity coefficients derived from the present study are compared with literature data in Figs. 3.8 to 3.11.

Fig. 3.8: Comparison of experimental activity coefficient values for NaNO₃ with literature
Fig. 3.9: Plot of comparison of experimental mean ionic activity coefficients of NaCl with literature

Fig. 3.10: Comparison of experimental mean ionic activity coefficients of KNO₃ with literature
Fig. 3.11: Plot of comparison of experimental mean ionic activity coefficients of KCl with literature

As the concentration of the solution is increased, the activity coefficient of the electrolyte falls to a minimum and then rises to values which may be considerably greater than unity. The main cause for these high values is considered to be due to the hydration of ions. Hydration increases the activity coefficient of the electrolyte in aqueous solutions by two ways:

1. By weakening the electrostatic interaction between ions due to their greater separation

2. By removing water from the role of solvent to become a part of the hydrated ion

Figures 3.8 to 3.11 reveal that the agreement between the literature and the experimental values for NaNO₃ and NaCl electrolytes is good, but for potassium salts deviation from literature value is found, which could be because of the impurities present in the potassium salts.
The thermodynamic properties of electrolyte solutions depend not only on hydration but also on the ion-ion and ion-solvent interactions. Ions in solution interact with each other as well as with water molecules. At low concentrations, these interactions can be ignored, but at higher concentrations ions behave as if they are less concentrated than they really are. Therefore, the ionic activity coefficients can be interpreted in terms of the combination of Debye-Huckel equation, hydration effect and interionic interactions. In very dilute region, Debye-Huckel equation alone is applicable, but with increasing concentration the other two effects dominate and should be considered.

SUMMARY

In very dilute solutions of electrolytes, the ions are surrounded by only water molecules. Interionic and ion-solvent interactions are negligible and the solution behaves ideally. When the concentration of ions in the solution is greater than approximately 0.01 m, a shielding effect arises around the ions i.e., the cations tend to surround the nearby anions and anions tend to surround the nearby cations. These interactions make the solution non-ideal and one can define activities for cations and anions ($a_+$ and $a_-$) separately. The difference between activity and other measures of composition arises because molecules in non-ideal solutions interact with each other which give rise to activity coefficients ($\gamma_+$ and $\gamma_-$). When there is ion-ion interaction, effective concentration decreases, i.e., activity will decrease. Similarly, when ion-solvent interaction exists, some of the solvent molecules become separated from the bulk solution and effective concentration and also activity will increase. For the aqueous solutions of NaNO$_3$, NaCl, KNO$_3$ and KCl systems under investigation, electrochemical cells were assembled using suitable ISEs and EMFs were measured using a double junction reference electrode to calculate the single ion activity coefficient of $K^+$, $Na^+$, $Cl^-$ and NO$_3^-$ . The experimental results confirmed that the
activity coefficients of cation and anion in aqueous single electrolyte solutions of KNO₃, NaNO₃, NaCl and KCl were different from each other over the whole range of concentration studied which is attributed to the ion-ion and ion-solvent interactions. The activities of both ions were measured independently and the data were found to be reliable.
REFERENCES

1. G. Eisenman, Glass electrodes for hydrogen and other cations, Marcel Dekker, New York (1967)


