

Research Article

New Data on Activity Coefficients of Potassium, Nitrate, and Chloride Ions in Aqueous Solutions of KNO_3 and KCl by Ion Selective Electrodes

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Ion selective electrodes (ISEs) are used to measure the single-ion activity coefficients in aqueous solutions of KNO_3 and KCl at 298.15 K against a double-junction reference electrode. The EMF responses of ISEs up to 0.01 m are plotted to obtain the slope and intercept values. The obtained slopes and intercepts are used in Nernst equation for higher concentrated solutions for calculation of individual ion activity coefficient. The mean ionic activity coefficients are estimated from single ion activity coefficient, and the obtained results are compared with the literature values.

1. Introduction

Activity of a species in a solution is referred to as its effective concentration in that solution. In 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. When the solute undergoes ionic dissociation in solution, then we can define activities of cations and anions (a_+ , a_-), so also activity coefficients (γ_+ , γ_-). The knowledge of individual ionic activity coefficients 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 value, and solubility product and for the separation of a species from a mixture of substances on the basis of their high or low activity coefficient. Single-ion activity coefficients are traditionally termed as not measurable by simple thermodynamic methods due to space charge interactions. But people have tried to measure single-ion

activity coefficient of nonvolatile electrolytes in solution by two methods: (1) solvent activity method involving vapour pressure and Gibbs-Duhem equation and (2) electrochemical cell technique involving direct calculation of the activity of an electrolyte by measurement of EMF of ions in an electrochemical cell. In recent past, Vera and coworkers [2–5] and few other researchers [6–9] demonstrated the application of ion selective electrode (ISE) technique for measurement of single-ion activity coefficients. The same approach has been utilized to find out the single-ion activity coefficient in this work. The coefficients are used to find out mean ionic activity coefficient for different salts. Most of the groups working on electrolyte solutions have given information on activity and osmotic pressure of the solvent. Individual activity coefficient of salts is rarely reported.

In this paper, ion selective electrodes (ISEs) have been used to measure the activity coefficients of individual ions of KNO_3 from ~ 0.001 m to ~ 3.5 m and KCl from ~ 0.001 m to ~ 5 m at 298 K and atmospheric pressure. The calculated mean activity coefficients from single-ion activity coefficients are compared with the literature value [9, 10].

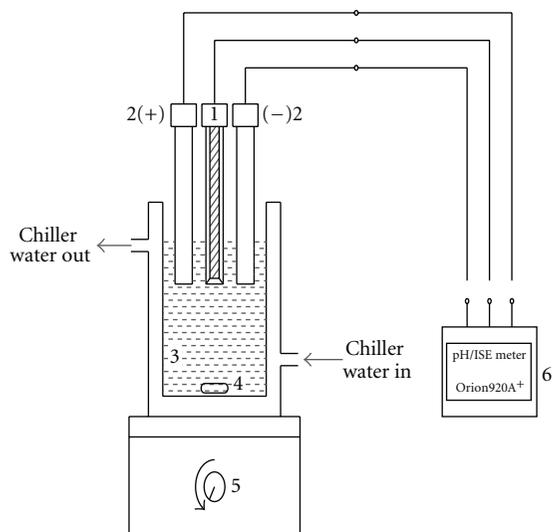


FIGURE 1: Schematic diagram of the experimental system. (1) reference electrode, (2) ISE,(+) cation,(-) anion, (3) thermostated cell, (4) stirring bar, (5) magnetic stirrer, (6) pH/ISE meter.

2. Experimental Work

KNO_3 and KCl of 99.9% and 99.5% purity were obtained from LOBA CHEMIE (Mumbai) and MERCK (Bombay), respectively. The salts were oven dried for 48 h and then cooled in vacuum desiccator for 24 h prior to use. The main features of the apparatus that was designed to conduct the experiment include a double-wall jacketed vessel, ion selective electrode, a double-junction reference electrode, a thermostatic bath, a mV meter, a temperature probe, and a magnetic stirrer. Figure 1 shows the schematic diagram of the experimental system. The temperature in the double-wall jacketed vessel is controlled by water from a thermostatic bath. The temperature of water in the thermostatic bath is stabilized by using an additional cooling bath. The temperature of the sample solution is maintained at 298.15 ± 0.1 K. A pH/ISE meter Orion920A⁺ with a resolution of ± 0.1 mV was used to monitor the electromotive force (EMF) values with two BNC connectors for ISEs and two pin-tip connectors for the reference electrode.

ASTM Grade-1 water as per ASTM D-1193 [11] with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$ 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 are weighed in a precision Shimadzu AUW220D balance (220 g, 0.01 mg resolution). When not in use, the solutions are kept in airtight closed condition in a JULABO SW-22 Shaker Bath at 298.15 ± 0.1 K. JULABO SW-22 Shaker Bath is coupled to JULABO FP-40 chiller for cooling. To ensure the ripple-free power supply to all the equipments, AC supply is regulated with an uninterrupted power supply (APC), set at high sensitivity. The ambient conditions are monitored with a Cole-Parmer hygrometer (0.1%) consisting of thermometer (0.1°C) and pressure sensor (0.1 kPa).

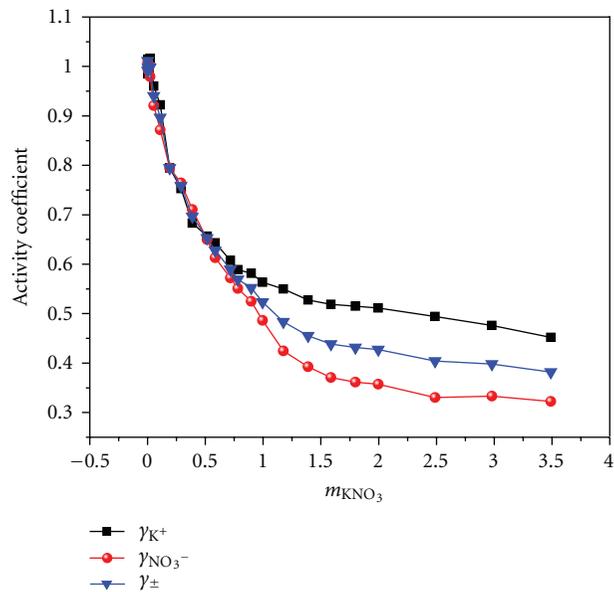


FIGURE 2: Variation of activity coefficient values of KNO_3 with concentration.

The experiments were performed by measuring the EMF of both the cation and the anion ISE against a double-junction reference electrode. To avoid the bias potential between different reference electrodes, in each experiment, the responses of both cation and anion ISE were measured at the same time versus 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 the thermostatic bath.

3. Results and Discussion

The ISEs used in this work were calibrated with the standard solution supplied along with the respective ISEs. The cell arrangements were

K polymer body ISE | $\text{KNO}_3 (m_1)$ | NO_3 polymer body ISE,

K polymer body ISE | $\text{KCl} (m_2)$ | Cl solid-state ISE.

The potential of an ISE versus a reference electrode is related to the ionic activity coefficient of the corresponding ion by the Nernst equation. For a system containing an electrolyte at molality m_1 , the Nernst equations for the potentials of a cation and an anion ISE, E_+ , and E_- , in the electrochemical cell of type 1, ISE | KNO_3 | reference electrode, can be written as

$$E_+ = E_+^0 + \frac{RT}{z_+F} \ln(m_+ \gamma_+), \quad (1)$$

$$E_- = E_-^0 + \frac{RT}{z_-F} \ln(m_- \gamma_-), \quad (2)$$

TABLE 1: Individual activity coefficient and mean activity coefficient values of KNO₃ solution.

m (mol/kg)	γ_{K^+}	$\gamma_{NO_3^-}$	γ_{\pm} (Expt.)	γ_{\pm} (Hamer and Wu) [10]
0.0012	0.985	0.998	0.991	0.964
0.0021	1.015	1.008	1.011	0.95
0.005	1.003	0.992	0.997	0.924
0.014	0.996	1.003	0.999	0.896
0.021	1.017	0.98	0.998	0.86
0.053	0.96	0.921	0.94	0.797
0.109	0.922	0.871	0.896	0.735
0.191	0.795	0.795	0.795	0.662
0.289	0.753	0.764	0.759	0.614
0.387	0.683	0.71	0.697	0.577
0.516	0.656	0.65	0.653	0.546
0.585	0.643	0.613	0.628	0.521
0.717	0.607	0.572	0.59	0.498
0.781	0.589	0.551	0.57	0.478
0.897	0.581	0.525	0.552	0.46
0.995	0.563	0.486	0.523	0.444
1.175	0.55	0.425	0.483	0.415
1.389	0.528	0.393	0.455	0.39
1.587	0.519	0.371	0.439	0.369
1.798	0.515	0.361	0.431	0.35
1.996	0.512	0.357	0.427	0.332
2.488	0.494	0.33	0.404	0.297
2.98	0.476	0.333	0.398	0.269
3.49	0.452	0.323	0.382	0.246

where γ is the activity coefficient, R is the universal gas constant, T is absolute temperature, F is the Faraday number, z is the charge number, and subscripts plus and minus signs denote the cation and the anion, respectively. The terms E_+^0 and E_-^0 in (1) and (2) are a linear combination of the junction potential, reference electrode potential, and ISE potential:

$$E_+^0 = E^{\text{ref}} + E^J + E_+^{\text{ISE}}, \quad (3)$$

$$E_-^0 = E^{\text{ref}} + E^J + E_-^{\text{ISE}}, \quad (4)$$

where superscripts ref and J denote the potential of the reference electrode and junction potential and the terms E_+^{ISE} and E_-^{ISE} include all asymmetry, internal solution, and reference potential of the cation and anion ISE, respectively. By subtracting (1) from (2) and considering (3) and (4), we obtain a relation between the difference of the potential of a cation and an anion ISE with the mean ionic activity coefficient of the electrolyte, $\gamma_{\pm}^{(1)}$, in cell type (1) as

$$E_+ - E_- = \left(E_+^{\text{ISE}} - E_-^{\text{ISE}} \right) + \frac{RT}{F} \left(\frac{z_+ + z_-}{z_+ z_-} \right) \times \ln (v_+^{v_+} v_-^{v_-})^{1/(v_+ + v_-)} m_1 \gamma_{\pm}^{(1)}. \quad (5)$$

For a 1 : 1 electrolyte, (5) simplifies to

$$E_+ - E_- = \left(E_+^{\text{ISE}} - E_-^{\text{ISE}} \right) + \frac{2RT}{F} \ln (m_1 \gamma_{\pm}^{(1)}). \quad (6)$$

Equation (6) is valid only when the reference electrode is same both for cation and anion ISE. The more general form of (6) for KNO₃ and KCl solution is

$$\Delta E_{\text{KNO}_3} = E_{\text{KNO}_3}^0 + 2S \ln (m_1 \gamma_{\pm}^{(1)}), \quad (7)$$

$$\Delta E_{\text{KCl}} = E_{\text{KCl}}^0 + 2S \ln (m_2 \gamma_{\pm}^{(2)}). \quad (8)$$

Direct determination of activity coefficients of electrolytes by ISEs is a rapid method. However some interference from interfering ions will be there at high concentrations. To get rid of these discrepancies, the experiments were performed by measuring the EMF of both the cation and the anion ISE against a double-junction reference electrode, and dilute solution was used. The responses of both cation and anion ISE were measured at the same time with the same reference electrode, and the solutions were stirred continuously during the experiment with a magnetic stirrer to minimize the problem of concentration gradient.

The activity coefficient values for K ISE and NO₃ ISE are given in Table 1 and that of K ISE and Cl ISE are given in Table 2. The activity coefficient plots for the two systems are shown in Figures 2 and 3, and the comparison of the experimental data with the Hamer and Wu data is shown in Figures 4 and 5, respectively.

TABLE 2: Individual activity coefficient and mean activity coefficient values of KCl solution.

m (mol/kg)	γ_{K^+}	γ_{Cl^-}	γ_{\pm} (Expt.)	γ_{\pm} (Hamer and Wu) [10]
0.001	0.998	0.962	0.98	0.965
0.002	1.006	0.957	0.981	0.951
0.005	0.998	0.926	0.961	0.927
0.01	1	0.902	0.95	0.901
0.0201	0.985	0.858	0.919	0.869
0.05	0.972	0.795	0.879	0.816
0.0982	0.97	0.747	0.851	0.768
0.1983	0.938	0.674	0.795	0.717
0.3049	0.901	0.62	0.747	0.687
0.3999	0.904	0.602	0.738	0.665
0.5001	0.896	0.582	0.722	0.649
0.6032	0.885	0.563	0.706	0.636
0.7003	0.884	0.554	0.7	0.626
0.7996	0.88	0.544	0.692	0.617
0.8968	0.879	0.537	0.687	0.61
0.9926	0.88	0.532	0.684	0.604
1.1899	0.875	0.521	0.675	0.594
1.3844	0.874	0.513	0.669	0.586
1.5817	0.871	0.506	0.664	0.58
1.7923	0.863	0.498	0.656	0.576
1.9895	0.863	0.495	0.654	0.573
2.5039	0.857	0.487	0.646	0.568
2.9837	0.865	0.492	0.653	0.568
3.4982	0.865	0.495	0.654	0.571
3.994	0.871	0.503	0.662	0.576
4.4897	0.88	0.515	0.673	0.584
4.7909	0.884	0.523	0.68	0.589
4.9908	0.888	0.528	0.685	0.593

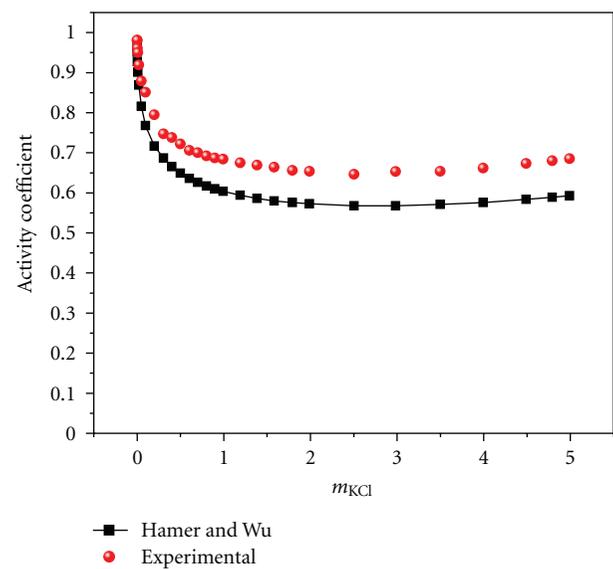
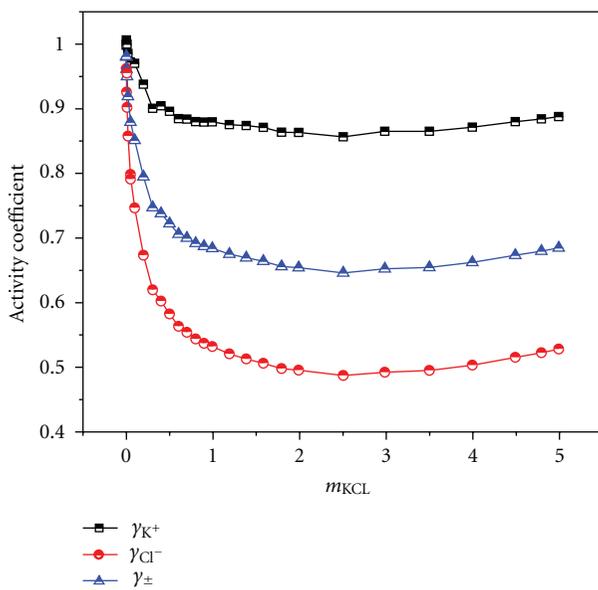


FIGURE 3: Variation of activity coefficient values of KCl with concentration.

FIGURE 4: Comparison of experimental activity coefficient values of KCl with the literature values.

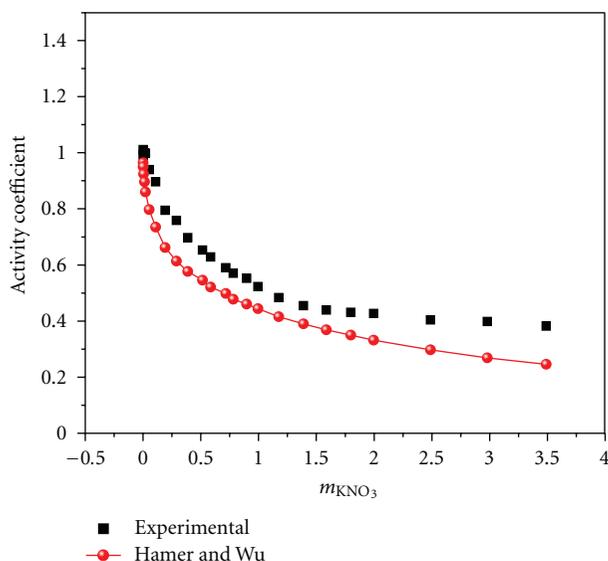


FIGURE 5: Comparison of experimental activity coefficient values of KNO_3 with the literature values.

4. Conclusion

The two cells were successfully used to calculate the Single-ion activity coefficient of K^+ , Cl^- , and NO_3^- by using a double-junction reference electrode. The experimental results confirm that the activity coefficients of cation and anion in aqueous single electrolyte solutions of KNO_3 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.

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