# Thermodynamic study of the quaternary electrolyte (NaCl + NaNO$_3$ + HCONH$_2$ + H$_2$O) system using potentiometric measurements at $T$ = (298.2 and 303.2) K

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## ABSTRACT

In this work, the thermodynamic properties of the quaternary electrolyte (NaCl + NaNO$_3$ + HCONH$_2$ + H$_2$O) system, using the potentiometric method, are reported. The potentiometric measurements were carried out on the galvanic cells without liquid junction of the types:

Ag–AgCl|NaCl ($m_A$), (100-w%) H$_2$O + w% HCONH$_2$|Na–ISE,
Ag–AgCl|NaCl ($m_1$), NaNO$_3$ ($m_2$), (100-w%) H$_2$O + w% HCONH$_2$|Na–ISE and
NO$_3$–ISE|NaNO$_3$ ($m_B$), (100-w%) H$_2$O + w% HCONH$_2$|Na–ISE

over total ionic strengths from 0.001 to 4.000 mol · kg$^{-1}$. Different series of the salt molal ratios $r$ ($r = m_{NaCl}/m_{NaNO_3}$ = 0.1, 1, 2.5, 5.0, 10.0) and pure NaCl in mixed solvent system containing 10% mass fraction of formamide were used for the measurements at $T$ = (298.2 and 303.2) K. The modeling of this quaternary system was made based on the Pitzer ion-interaction model. In according to Pitzer graphical method, the mixed ionic interaction parameters ($\theta_{ClNO_3}$, $\psi_{NaClNO_3}$) were evaluated for each series of the studied system. Then, the obtained parameters were used to calculate the values of the mean activity coefficients of NaNO$_3$, the osmotic coefficients, solvent activity and the excess Gibbs free energies for the whole series of the studied mixed electrolyte system at $T$ = (298.2 and 303.2) K.

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## 1. Introduction

Recently, there has been an increasing amount of work concerning the investigation of the thermodynamic properties of mixed aqueous electrolyte solutions because of their importance in areas such as chemistry, chemical engineering, biology, geology, atmospheric science, and food processing [1–4]. To make easy the use of mixed electrolytes in these processes, it is desirable to know accurately the thermodynamic properties of aqueous multicomponent systems. To measure the thermodynamic properties in mixed electrolyte solutions, the potentiometric method presents advantages such as rapidity and relative simplicity to produce experimental data, in comparison with the other techniques [5,6].

During the last decades, the series of ion-interaction models for electrolyte solution have been proposed to predict the activity coefficient of each solute and osmotic coefficient of aqueous systems. Among them, the Pitzer ion-interaction model is one of the most famous and useful models. Pitzer equations, with much accuracy, correlate the thermodynamic properties of mixed aqueous

electrolyte systems. The Pitzer model extended the Debye–Hückel method with a virial expansion to account for the ionic strength dependence of the binary repulsive short-range forces, and higher order interactions [7,8].
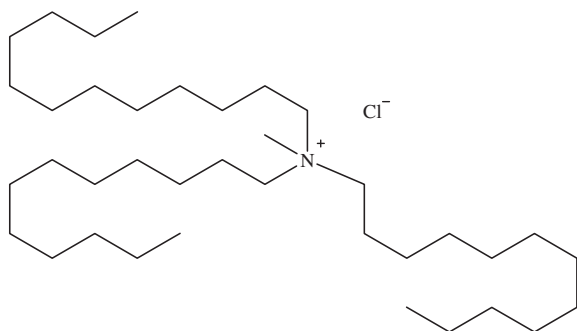
Thermodynamic properties of mixed electrolytes in aqueous solution have been investigated by the emf method, but rarely in mixed solvents of water with organic solvent [9,10]. In addition, formamide is a widely used as a solvent and reagent in organic synthesis and chemical analysis. So, knowledge of the thermodynamic properties of systems containing formamide is required for understanding the nature of various ionic interactions in electrolyte mixtures and separation technique in many chemical industries. In this work, the results relating to the thermodynamic properties of the quaternary electrolyte (NaCl + NaNO$_3$ + HCONH$_2$ + H$_2$O) system using the potentiometric method are reported. The system of present study is one of the systems which thermodynamic data have not been reported in the literatures. However, the mean activity coefficients of NaCl in the (NaCl + NaNO$_3$ + HCONH$_2$ + H$_2$O) system were determined on a galvanic cell containing a solvent polymeric (PVC) Na–ISE Ag/AgCl electrodes at $T$ = (298.2 and 303.2) K. We have reported in our previous papers the ability of the solvent polymeric membrane electrode for determination of activity coefficients for

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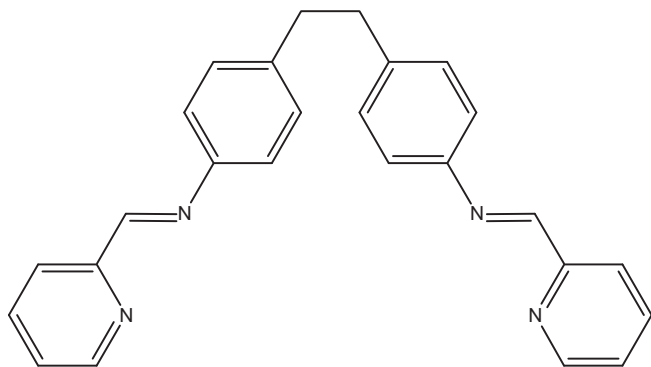
**SCHEME 1.** The structure of 14E-4-(E-4-((pyridine-2yl)methyleneamino)phen-ethyl)-N-((pyridine-2-yl)benzeneamine (EPBA).



**SCHEME 2.** The structure of tridodecyl methyl ammonium chloride.

binary and ternary electrolyte solutions [11–15]. In the present study, the ability of the solvent polymeric membrane electrode to determine of the thermodynamic properties of the quaternary electrolyte ($NaCl + NaNO_3 + HCONH_2 + H_2O$) system are reported. Different series of the salt molal ratios $r$ ($r = m_{NaCl}/m_{NaNO_3}$ = 0.1, 1, 2.5, 5.0, 10.0) and pure NaCl in mixed solvent system containing 10% mass fraction of formamide were used for the measurements over ionic strength ranging from 0.0010 to 4.000 mol · kg$^{-1}$ at $T$ = (298.2 and 303.2) K. The modeling of this quaternary system was made based on the Pitzer ion-interaction model. In according to Pitzer graphical method, the mixed ionic interaction parameters ($\theta_{ClNO_3}, \psi_{NaClNO_3}$) were evaluated for the studied system. The resulting values of the mean activity coefficients, the osmotic coefficients, the solvent activity and the excess Gibbs free energy together with Pitzer ion-interaction parameters for the series under investigated system are reported.

## 2. Experimental

### 2.1. Apparatus and reagents

All of the potentiometric measurements were made using a digital multimeter (Martini instruments Mi180) whose resolution was 0.1 mV. The output of the multimeter was connected to a personal computer (AMD) by the RS232 connector for data acquisition. The Mi 5200 software together with Microsoft Excel (Office 2007) software were used for data acquisition and calculations. The solutions were stirred continuously using a magnetic stirrer (Delta Model HM-101) at a slow constant rate to avoid concentration gradients in the test solutions. A Model GFL circulation water bath was used to control the temperature of the test solution at $T$ = (298.2 ± 0.1 and 303 ± 0.1) K.

Dibutyl phthalate (DBP), potassium tetrakis(p-chlorophenyl) borate (KT$_P$ClPB), Tridodecyl methyl ammonium Chloride(TDMAC), high molar mass poly(vinyl chloride) (PVC), tetrahydrofuran (THF), formamide (HCONH$_2$), sodium chloride (NaCl), sodium nitrate (NaNO$_3$), and all other reagents used were purchased from Merck, and Fluka chemical company and all of them were of analytical reagent grade. All primary stock solutions were prepared by mass using doubly distilled water and formamide. The stock aqueous solution of mixed electrolyte were prepared from sodium chloride and sodium nitrate by adding weighed amounts of solid using an analytical balance (Sartorius GMBH 2842) with accuracy 0.1 mg, double-distilled water whose specific conductance was less than $2.0 \cdot 10^{-4}$ S · m$^{-1}$ and formamide with mass fraction purity (>0.999). The conductivity measurements were carried out by means of a Metrohm 660 conductometer with a type cell of constant cell 1.17 cm$^{-1}$ and having an uncertainty of 1%.

### 2.2. Preparation of electrodes and Potentiometric measurements

The 14E-4-(E-4-((pyridine-2-yl)methyleneamino)phenethyl)-N-((pyridine-2-yl) benzene-amine (EPBA) was used as the ionophore, which was prepared according to the reported method in the literature [16]. The EPBA acts as neutral ion carrier in plasticized polymeric membrane for fabrication of Na-selective electrode. Also, tridodecyl methyl ammonium chloride was used as
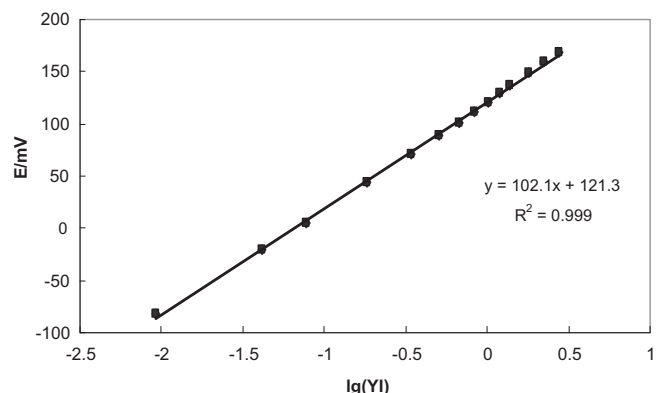


**FIGURE 1.** The plot of cell (A) emf versus lg($yl$) for calibration of Na–ISE and Ag–AgCl electrode pair at $T$ = 298.2 K.

**TABLE 1**
Pitzer parameter values $\beta^{(0)}$, $\beta^{(1)}$ and $C^\phi$ for single electrolyte of NaCl and NaNO$_3$.

| Electrolyte | $\beta^{(0)}/$ (kg · mol$^{-1}$) | $\beta^{(1)}/$ (kg · mol$^{-1}$) | $C^{(\phi)}/$ (kg$^2$ · mol$^{-2}$) | Reference |
|---|---|---|---|---|
| | | $T$ = 298.2 K | | |
| NaCl | 0.0828 | 0.1609 | 2.66 · 10$^{-4}$ | [18] |
| NaNO$_3$ | 0.0019 | 0.3785 | 0.00147 | This work |
| | | $T$ = 303.2 K | | |
| NaCl | 0.0902 | 0.1958 | 0.00016 | This work |
| NaNO$_3$ | 0.0027 | 0.5677 | 0.0012 | This work |

**TABLE 2**
Values of the slope and experimental standard potentials for each series of the mixed electrolyte systems defined by its molal salt ratio ($r = m_{NaCl}/m_{NaNO_3}$) at $T$ = 298.2 K and 303.2 K.

| $r$ | 10 | 5 | 2.5 | 1 | 0.1 |
|---|---|---|---|---|---|
| | | | $T$ = 298.2 K | | |
| $s$ | 113.1 | 112.9 | 105.9 | 114.9 | 117.1 |
| $E^0$ | 205.9 | 201.1 | 119.6 | 104.2 | 52.4 |
| | | | $T$ = 303.2 K | | |
| $s$ | 103.0 | 104.6 | 111.7 | 103.7 | 107.2 |
| $E^0$ | 126.7 | 114.8 | 109.3 | 109.4 | 62.1 |