Measurement and Modeling of Mean Activity Coefficients in Ternary Electrolyte System (Nicl₂/Triton X-100/H₂O) at T=298.15 ± 0.1 K

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ABSTRACT: *In this work, the results relating to the thermodynamic properties of the ternary electrolyte system of (NiCl₂ + Triton X-100 + water) using the potentiometric method were reported at T = 298.15 K. The electromotive force measurements were carried out on the galvanic cell without a liquid junction of the type: Ni²⁺-ISE | NiCl₂ (m), Triton X-100 (%wt.), H₂O (100-%wt.) | AgCl/Ag over total ionic strengths from 0.0010 to 6.0000 mol/kg for different percentage mass fraction of Triton X-100 (%wt. = 0.0, 1.0, 2.5, 5.0, 7.5, and 10.0). The mean activity coefficients of NiCl₂ were determined by using potentiometric data. Then, the mean activity coefficients of NiCl₂ were correlated with the Pitzer ion interaction model and TCPC model. The Pitzer ion-interaction parameters (β^o, β^l and $C^{\emptyset}$) and the adjustable parameters (b and S) of TCPC model were determined by correlating data for the series under-investigated system. The Pitzer ion interaction parameters were used to calculate thermodynamic properties such as the osmotic coefficients and the excess Gibbs energy of the solution. The result showed that the Pitzer ion interaction model could be used to investigate the system, successfully.*

KEYWORDS: *Mean activity coefficients; Pitzer ion interaction model; NiCl₂; Triton X-100; Potentiometric measurements; Thermodynamic properties.*

INTRODUCTION

Thermodynamic modeling of electrolyte solutions plays an important role in the design, optimization, and control of various chemical processes such as crystallization, seawater desalination, extractive distillation, gas treatment, and oilfield processing [1]. Accurate models for the thermodynamic properties of electrolyte solutions such as activity and osmotic coefficients are essential for the design and control of these processes. In an electrolyte solution such as 2-1 type, the electrolyte will dissociate into anions and cations. Thus there exists complicated interactions between ion and ion, ion and molecule, and molecule and molecule. Ion-ion interactions are governed by electrostatic forces between ions that have a much longer range than other intermolecular forces. Thus, in modeling an aqueous electrolyte solution, it is necessary to account for the long-range contribution of interactions among ions in the mixture [2]. One of the most important thermodynamic properties of an electrolyte solution is the mean ionic activity coefficient of the electrolyte. The mean ionic activity coefficient gives a measure of the deviation

of real solutions from ideality and includes all effects that lead to these deviations [2].

One ion-interaction model for the electrolyte solution has been proposed to predict the activity coefficient of each solute and osmotic coefficient of the aqueous systems by *Pitzer* [3-4]. To measure the thermodynamic properties of electrolytes in a mixed solvent, the most common methods were the isopiestic vapor pressure [5] and potentiometric techniques [6]. The electromotive force (emf) methods had the characteristics of simplicity and convenience in comparison with the other mentioned techniques.

In recent years, a number of researchers have focused on the measurement and modeling of activity coefficients of electrolytes in the mixed solvent. *Ghalami et al.* measured the mean activity coefficients of KCl in (glucose + water), (proline + water), and (diethanolamine + water) as mixed solvents by the potentiometric method [7-9]. They also investigated the thermodynamic properties of $(CaCl_2+Ca(NO_3)_2)$ in (L-alanine + water) and ionic liquid in (ethylene carbonate + water) [10-11]. *Hu et al.* studied about phase equilibrium and activity coefficients of CsF in (urea + H_2O), CsF in (N-methylformamide + H_2O), RbCl and CsCl in (ethylen carbonate + water) by potentiometric measurements [12-13]. *Rafiee et al.* obtained water activity and osmotic coefficient data of ionic liquid in lithium chloride aqueous and lithium nitrate aqueous solutions by isopiestic apparatus [14-15]. *Morales et al.* determined the mean ionic activity coefficient values for $NaClO_4$ in (PEG 4000 + H_2O) mixtures from the cell potential measurements [16]. *Dehghani et al.* used the potentiometric method to measure the mean ionic activity coefficient of sodium nitrate in aqueous solutions of PEG (1500) + sodium nitrate + water at 308.15 K [17].

We have reported in our previous works the results of mean activity coefficients and thermodynamics analysis KCl in (lactose + water), $MgCl_2$ in (glucose + water), and $CoCl_2$ in (C_2H_5OH + H_2O) by a potentiometric method using ion-selective electrodes [6, 18-19].

The potentiometric measurements reported in this work were carried out on a galvanic cell containing a polymeric solvent (PVC) Ni^{2+} -ISE and Ag–AgCl electrodes, using various series of mass fractions of Triton X-100 (wt. = 0.000, 0.010, 0.025, 0.050, 0.075, 0.100) in mixture solvent (Triton X-100 + H_2O), over the ionic strength ranging from (0.0010 to 6.0000) mol/kg. The stock solution of electrolyte was prepared by adding weighted

amounts of $NiCl_2$ into the proportion volume of the (Triton X-100 + water) as a mixed solvent. The modeling of this ternary system was made based on the Pitzer ion-interaction model and the modified Three-characteristic-Parameter Correlation (TCPC) model. Then, the Pitzer ion-interaction parameters (β^o, β^1 and C^ϕ) and TCPC parameters (b, S) for the series under the investigated system were estimated by fitting experimental results with the models. Finally, the excess Gibbs energy and osmotic coefficient of water were calculated using the Pitzer ion-interaction parameters.

The main goal of this work was to give scientific literature and precise thermodynamic data about the ternary system ($NiCl_2$ + Triton X-100 + H_2O), which may allow modeling its behavior. Triton X-100 could be found in several types of cleaning compounds, ranging from heavy-duty industrial products to gentle detergents. It was also a popular ingredient in homemade vinyl record cleaning fluids together with distilled water and isopropyl alcohol. It was a good micellar catalyst [20]. And nickel chloride hexahydrate was an important material in nickel electroplating and an intermediate in the manufacture of certain nickel catalysts. It was also used to absorb ammonia in industrial gas masks [21]. It could be useful determination the mean ionic activity coefficients $NiCl_2$ in aqueous solutions containing Triton X-100 in an attempt to provide fundamental knowledge on ionic interactions in ($NiCl_2$ + Triton X-100 + water) solutions.

EXPERIMENTAL SECTION
Apparatus and reagents

All of the potentiometric measurements were made by using a digital multimeter (Eutech 2100) with a resolution of 0.1 mV. The solutions were continuously stirred 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 298.15 K ± 0.1. The conductivity measurements were carried out with a Metrohm 660 conductivity meter. An analytical balance (Sartorius GMBH 2842) with an accuracy of 0.1 mg was used throughout all experiments.

Dibutyl phthalate (DBP), potassium tetrakis (*p*-chlorophenyl) borate (KT_PClPB), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF), nickel chloride hexahydrate ($NiCl_2·6H_2O$), Triton

Table 1: The source and purity of the materials in this work.

IUPAC compound names	Abbreviations	Company	Mass fraction purity
Dibutyl phthalate	DBP	Fluka	≥0.99
Potassium tetrakis(p-chlorophenyl) borate	KT$_P$ClPB	Fluka	≥0.99
Poly(vinyl chloride)	PVC	Fluka	High molar
Tetrahydrofuran	THF	Fluka	≥0.99.5
Nickel chloride hexahydrate	NiCl$_2$·6H$_2$O	Merck	≥0.99
Triton X-100	C$_{14}$H$_{22}$O(C$_2$H$_4$O)n (n=9-10)	Merck	≥0.99

X-100 and all other reagents used were purchased from Merck and Fluka and all of them were of analytical reagent grade (Table 1). All aqueous solutions were prepared by using doubly distilled water whose specific conductance was less than 2.0×10^{-4} S/m. The stock solution of nickel chloride was prepared using NiCl$_2$ in a mixed solvent.

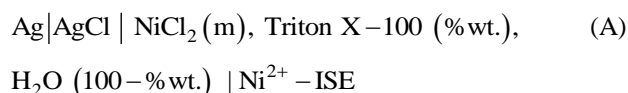### Preparation of nickel ion selective electrode and Ag-AgCl electrode

The nickel ion selective electrode was prepared in accordance with the general procedure of PVC membrane construction [6]. For this aim, an optimized mixture containing 30 mg of powdered PVC, 60 mg plasticizer DBP, 5 mg additive KT$_P$ClPB, and 2 ml of dry freshly distilled THF were added into a glass dish of 2 cm diameter. To this solution for the fabrication of the Ni^{2+}-selective 5 mg of 1, 4- bis (2-(5- methyl-4- phenylthiazol-2-yl) hydrazinyl) benzene (BMPHB) as an ionophore was added and mixed very well. The solvent was evaporated at room temperature. After 2 hours the polymer membrane could be easily removed from the plate. Then the transparent PVC membrane was taken up from the plate and attached to the end of a glass tube with a diameter of 1 cm and height of 5 cm by means of PVC-THF viscose solution. The Ni^{2+}-selective electrodes were each time backfilled with a NiCl$_2$ internal filling solution of 0.01 mol/dm^3. The electrodes were conditioned in 0.01 mol/dm^3 solution of NiCl$_2$ for 48 h respectively. The Ni^{2+}-selective electrode was calibrated versus a saturated calomel reference electrode in the 1-10^{-4} mol/dm^3 concentration range of a solution of NiCl$_2$ before using each series of measurements. The Ni^{2+}-ISE was then conditioned overnight in the appropriate mixed solvent solution before each series of measurements.

For fabrication of the Ag–AgCl electrode an Ag wire was electrolyzed in 0.1 mol/dm^3 HCl solution, as described in the literature [22]. The Ag–AgCl electrode prepared was used as both an internal reference and chloride-selective electrode. The Ag–AgCl electrode was calibrated versus a saturated calomel reference electrode in the 1–10^{-4} mol/dm^3 concentration range of a solution of pure NiCl$_2$ before using each series of measurements. The Ag–AgCl electrode was conditioned overnight in the appropriate mixed electrolyte system before each series of measurements, too.

Potentiometric measurements

The cell arrangements in this work were as follows:

$$\text{Ag}\left|\text{AgCl}\right| \text{NiCl}_2\left(m\right), \text{ Triton X}-100 \left(\%\text{wt.}\right), \qquad (A)$$
$$\text{H}_2\text{O}\left(100-\%\text{wt.}\right) \mid \text{Ni}^{2+}-\text{ISE}$$

where *wt.* was the mass fraction of Triton X-100 in the mixed solvent (Triton X-100 + H$_2$O). The emf measurements of the galvanic cell A were made by using the standard addition procedure. For this purpose, the concentrated electrolyte solutions were added into the cell containing a specified volume of the Triton X-100–water as a mixed solvent. The standard edition steps were carried out using a proper burette and suitable Hamilton syringes (CH-7402 Bonaduz). In each series and for each standard addition step, data collection was performed for 20 min by using a multimeter. As usual, all measurements were performed under stirring conditions, and the temperature was kept constant at 298.15 K (±0.1 K), employing a double-wall container enabling the circulation of thermostat water from a Model GFL circulation.

Table 2: The values Debye–Huckel parameters for the osmotic coefficient ($A_\emptyset$), the solvent relative permittivity (ε_r)
and density (ρ) in different mass fractions (wt.) of Triton X-100–water mixed solvent systems at 298.15 K and 101.325 kPa.

Triton X-100 (%wt.)	$A_\emptyset$ (kg.mol$^{-1/2}$)	ε	ρ (kg/dm^3)
0[a]	0.3915	78.6	0.9972
0.0	0.3915	78.6	0.9972
1.0	0.4104	76.2	0.1007
2.5	0.4203	75.1	0.1011
5.0	0.4368	73.3	0.1015
7.5	0.4531	71.6	0.1018
10.0	0.4719	69.8	0.1023

THERMODYNAMIC MODELS

Pitzer ion interaction model

According to the Pitzer ion interaction model, the mean molal activity coefficient ($\gamma\pm$) for NiCl$_2$ in the mixed solvent was inscribed as [3]:

$$\ln\gamma_{\pm NiCl_2} = 2f^\gamma + \frac{4}{9}B^\gamma_{NiCl_2}I + \frac{2\sqrt{2}}{9}C^\varphi_{NiCl_2}I^2 \tag{1}$$

$$f^\gamma = -A_\varphi\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I})\right] \tag{2}$$

$$B^\gamma_{MX} = 2\beta^o_{MX} + \frac{2\beta^1_{MX}}{\alpha_1^2 I}\left[1-(1+\alpha_1\sqrt{I}-\frac{\alpha_1^2}{2}I)e^{-\alpha_1\sqrt{I}}\right] \tag{3}$$

In these equations α and b were assumed to be constant with the values of 2.0 and 1.2 kg$^{1/2}$ mol$^{-1/2}$ respectively, both in water and in Triton X-100–water mixtures; I indicated the total ionic strength on a molality scale. β^o, β^1, and $C^\emptyset$ showed solute-specific interaction Pitzer parameters for a single salt electrolyte solution that their values should be determined for NiCl$_2$ in Triton X-100–water mixtures. $A_\emptyset$ denoted the Debye–Huckel parameter for the osmotic coefficients defined by:

$$A_\varphi = \frac{1.4006\times10^6\rho^{\frac{1}{2}}}{(\varepsilon_r T)^{\frac{3}{2}}} \text{ kg}^{\frac{1}{2}}.\text{mol}^{-\frac{1}{2}} \tag{4}$$

where ρ was the solvent density (kg/m^3); ε_r was the solvent relative permittivity, and T was the kelvin temperature. The Debye–Huckel parameter for the osmotic coefficients ($A_\emptyset$) of water and the mixed solvent (Triton X-100 + water) were calculated by using Ed. (4). For this purpose, the values of the physical properties (ρ and ε_r) of solvents were taken from the literature [20]. The Debye–Huckel parameter for the osmotic coefficients ($A_\emptyset$) and the values of the physical properties (ρ and ε_r) for different solvents are shown in Table 2.

TCPC model

The Three-Characteristic-Parameter Correlation (TCPC) model was a simple and easy-to-use semi-empirical model which was first proposed by *Lin et al.* [23]. It was a combination of the Pitzer long-range interaction and short-range solvation effect.

$$\ln\gamma = \ln\gamma^{PDH} + \ln\gamma^{SV} \tag{5}$$

Ge et al. [24] modified this model and obtained the TCPC parameters for a larger number of single salts aqueous solutions. This model was also extended for a number of electrolytes dissolved in methanol, ethanol, 2-propanol, and so on [24]. Temperature-dependent parameters for a number of common single salts were also compiled, available at [25]. The performance of the TCPC model in correlation with the measured activity coefficient or osmotic coefficients was found to be comparable with Pitzer-like models.

According to this model, the mean activity coefficient was combined with the Pitzer–Debye–Huckel (PDH) term in consideration of the long-range interaction between ions and the solvation effect term to represent the short-range

ion–molecule interaction. Thus, the mean activity

$$\ln\gamma_{\pm NiCl_2} = -A_\varnothing \left[\frac{\sqrt{m}}{1+b\sqrt{m}} + \left(\frac{2}{b}\right)\ln\left(1+b\sqrt{m}\right) \right] + \qquad (6)$$

$$\left(\frac{S}{2T}\right)m^{2n}$$

In this model, (*b* and *S*) were the adjustable parameters. *b* was the distance of the closest approach parameter, which represented the closest distance between ions; *S* was the solvation parameter, which could have described the interactions between ions and solvent molecules including the solvation effect or some kind of association effect of ions; and *n* was assumed as a constant, 0.645, in the case of a concentration range that was not very high (generally <6 mol/kg).

RESULT AND DISCUSSION

The efficiency of Ni²⁺-ISE and Ag-AgCl electrode pairs

For this purpose, the molalities of NiCl$_2$ in solutions (*m*) were selected from 0.0003 to 2.000 mol/kg to determine the corresponding potential (E_A) using cell (A). The Nernst equation for cell (A) was:

$$E_A = E^\circ + s\log I \cdot \gamma_{\pm NiCl_2} \qquad (7)$$

The $\gamma_{\pm NiCl_2}$ was the mean activity coefficient of NiCl$_2$ in solution. The E^0 and *s* referred to the experimental standard potential and the Nernst slope, respectively, and *I* was the whole ionic strength of the solution. Also, the phrase I.$\gamma_{\pm NiCl_2}$ was the equivalent of the activity of NiCl$_2$ (a_{NiCl_2}) in solution.

The mean activity coefficients of pure NiCl$_2$ ($\gamma_{\pm NiCl_2}$) in water were calculated based on the Pitzer equation using the Pitzer parameters are taken from the literature [26]. Then the potentials measured were plotted against $\log a_{NiCl_2}$ to check the efficiency of the respective electrode pair to determine the mean activity coefficients of NiCl$_2$. The amount of linear correlation coefficient ($R^2 = 0.9999$) in Fig. 1 showed that the results obtained agreed with the literature [26] and the electrode pair used was well-suitable for our measurements.

Determination of the mean activity coefficients and Pitzer parameters

The emf values of cell (A) were measured at different series of electrolyte molalities in pure water and in Triton X-100–water mixed solvents through changing of electrolyte concentration by standard addition method [6, 8,16]. The emf

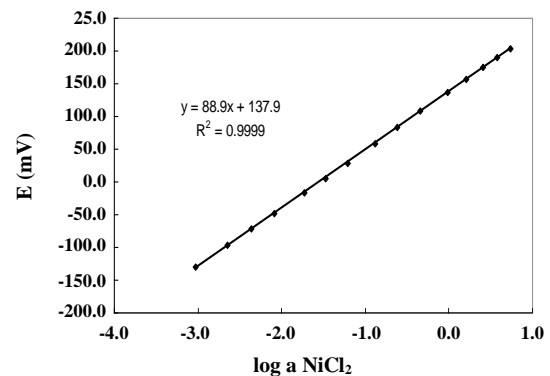coefficient for NiCl$_2$ could be calculated as: data was illustrated in Table 3.

Fig. 1: The plot of emf versus $\log a_{NiCl_2}$ for calibration of Ni²⁺-ISE and Ag-AgCl electrode pair at 298.15K.

In order to determine the accuracy of the mean activity coefficient values, the pair electrodes were each time-calibrated in standard NiCl$_2$ solutions with a concentration range 1-10⁻⁴ mol/kg before performing each series of measurements in systems. The corresponding slope (*s*) and the experimental standard potential (Eᵒ) were presented in Table 4.

Then the mean activity coefficients for NiCl$_2$ in the solvents were determined from the emf measurements using the galvanic cell (A) according to Eq. (7). Fig. 2 presented the variation of the NiCl$_2$ mean activity coefficients versus the ionic strength in water, and different mass fractions of Triton X-100 in mixed solvents at T = 298.15 K.

Then, the Pitzer ion interaction parameters (β^o, β^1 and $C^\varnothing$) were determined by correlating the mean activity coefficients of NiCl$_2$ with the Pitzer model (eq. 1) by an iteration minimization procedure employing the Microsoft MATLAB program. Table 5 showed the results of Pitzer ion-interaction parameters obtained from the iteration minimization procedure for the investigated systems at T = 298.15 K.

The values of β^o and β^1 obtained in the fit using the Pitzer model were plotted in Fig. 3 against the reciprocal value of the relative permittivity of the Triton X-100–water mixture solvent. As observed, both β^o, which could be identified with the total binary ionic interactions, and β^1, which could be identified with the interactions between unlike-charged ions, changed linearly with $1/\varepsilon$. The linear dependence observed in this study was reasonable,

following behavior similar to other electrolytes in different   aqueous mixtures of organic solvents [8].

Table 3: The values of measured emf in different mass fractions of Triton X-100 (wt.) at 298.15 K and 101.325 kPa.

m(mol. Kg^1)	E (mV)	E (mV)	E (mV)	E (mV)	E (mV)	E (mV)
	%wt. = 0.0	%wt. = 1.0	%wt. = 2.5	%wt. = 5.0	%wt. = 7.5	%wt. =10.0
0.0003	-130.0	-72.0	-97.9	-79.5	-71.7	-83.3
0.0008	-96.4	-52.2	-73.7	-50.8	-44.8	-54.6
0.0017	-72.2	-26.3	-58.1	-34.3	-39.2	-30.9
0.0033	-48.5	-1.5	-23.7	-21.4	-19.3	-16.6
0.0083	-17.1	13.5	-10.9	4.5	7.4	8.6
0.0167	5.7	28.8	7.4	18.9	25.3	29.9
0.0333	28.9	46.2	25.1	39.5	44.8	50.2
0.0833	58.8	68.0	50.3	65.8	72.6	76.9
0.1667	82.9	85.1	69.1	85.8	91.3	96.1
0.3333	108.3	103.0	88.8	106.6	110.4	114.3
0.6667	136.6	124.0	111.5	130.7	134.6	137.1
1.0000	157.1	140.0	129.0	148.5	153.5	156.1
1.3333	174.6	153.0	144.0	164.3	171.2	175.3
1.6667	189.4	164.0	156.0	178.1	186.1	193.4
2.0000	203.6	174.0	167.0	191.0	199.5	208.0

Table 4: The slope electrodes (s) and the experimental standard potential (E°) for different mass fractions of Triton X-100 (wt.) at 298.15 K and 101.325 kPa.

%wt.	0.0	1.0	2.5	5.0	7.5	10.0
E°/mV	138.3	129.0	126.2	154.5	166.2	189.1
u(E°) /mV[a]	0.11	0.09	0.12	0.16	0.17	0.14
s /mV.decade^{-1}	89	64	73.5	77.8	79.1	90.5
u(s) /mV.decade[a]	0.04	0.06	0.01	0.07	0.03	0.08
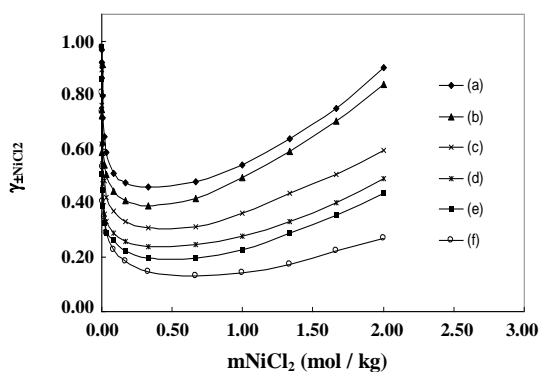
Fig. 2: The Plot of the mean activity coefficients of NiCl$_2$ versus the molality of NiCl$_2$ at different mass fractions of Triton X-100 (wt.) at 298.15 K, (a) wt. = 0.000, (b) wt. = 0.010, (c) wt. = 0.025, (d) wt. = 0.050, (e) wt. = 0.075, (f) wt. = 0.100.

Calculation of thermodynamic properties by the Pitzer model

The Pitzer parameters obtained were used to predict the thermodynamic properties of the under investigation system by the Pitzer model. The osmotic coefficients (ϕ) and the excess Gibbs energy (G^E) for all of the under investigation series could be calculated by utilizing the following equations

$$\varphi - 1 = 2f^\varphi + \frac{4}{9}IB^\varphi_{NiCl_2} + \frac{4\sqrt{2}}{27}I^2C^\varphi_{NiCl_2} \quad (8)$$

$$f^{\varphi} = -\frac{A_{\varphi}\sqrt{I}}{1+b\sqrt{I}} \tag{9}$$

Table 5: Values obtained for Pitzer parameters (β^o, β^1 and $C^{\emptyset}$) and standard deviation (σ) of the fits for NiCl₂ electrolyte in different mass fractions of Triton X-100 (wt.) at 298.15 K and 101.325 kPa[a].

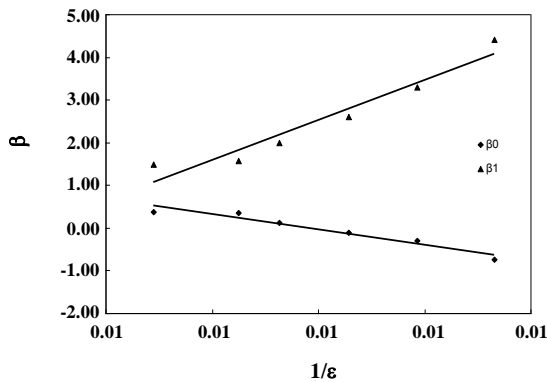| Triton X-100 (%wt.)	β^o (kg.mol^{-1})	β^1 (kg.mol^{-1})	$C^{\emptyset}$ (Kg^2.mol^{-2})	σ
0[a]	0.3753	1.4133	-0.0133	
0.0	0.3688	1.4945	-0.0124	0.0000
1.0	0.3493	1.5817	-0.0012	0.0006
2.5	0.1315	1.9856	0.0708	0.0048
5.0	-0.1147	2.6074	0.1680	0.0093
7.5	-0.3014	3.2946	0.2436	0.0156
10.0	-0.7461	4.4043	0.4058	0.0239

Fig. 3. Variation of β^o and β^1 versus the reciprocal value of the relative permittivity of the Triton X-100 –water mixture in different mass fractions of Triton X-100.

Fig. 4: The Plot of the osmotic coefficients (ϕ) of water against the molality of NiCl₂ at different mass fractions of Triton X-100 (wt.) at 298.15 K, (a) wt. = 0.000, (b) wt. = 0.010, (c) wt. = 0.025, (d) wt. = 0.050, (e) wt. = 0.075, (f) wt. = 0.100.

$$B_{MX}^{\varphi} = \beta_{MX}^{o} + \beta_{MX}^{1}e^{-\alpha_1\sqrt{I}} \tag{10}$$

$$\frac{G^E}{RT} = I(1 - \varphi + \ln\gamma_{\pm NiCl_2}) \tag{11}$$

Figs. 4 and 5 showed the plot of osmotic coefficients (ϕ), the excess Gibbs energy (G^E) versus the whole ionic strength of the solution, respectively. It could be seen that the excess Gibbs energy was decreased by increasing the mass fraction of Triton X-100 in the mixed solvent. On the other hand, the non-ideal behavior of these electrolytic systems increased by increasing the mass fraction of Triton X-100.
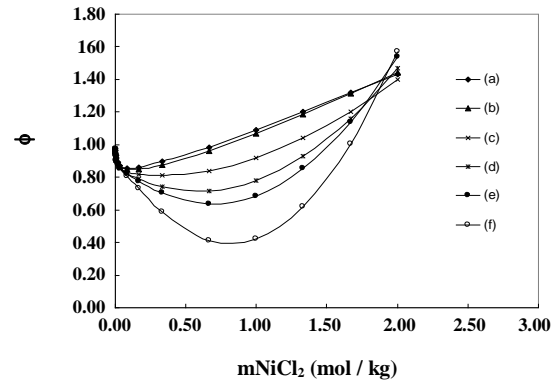
Estimation of TCPC parameters

The modified TCPC model was applied to correlate the experimental activity coefficient data for the under-investigation electrolyte system at 298.15 K. The adjustable parameters of TCPC model were obtained by an iteration minimization procedure employing the Microsoft Excel (solver) program. The parameters found for NiCl₂ in various Triton X-100-water mixed solvent systems containing 0.0, 1.0, 2.5, 5.0, 7.5, and 10 percent mass fractions of Triton X-100 in a solvent were illustrated in Table 6.

CONCLUSIONS

The mean activity coefficients of NiCl₂ in the (NiCl₂ +

Triton X-100 + water) system were determined by a potentiometric method using a solvent polymeric ion-selective membrane electrode and Ag-AgCl electrodes

both of which were prepared in our laboratory. The emf measurements were made for NiCl₂ in various Triton X-100-water mixed solvent systems containing 0.0, 1.0,

TABLE 6. The adjustable parameters of the modified TCPC model (b, S) for NiCl₂ in various mass fractions of Triton X-100 (wt.) at mixed solvent systems at 298.15 K and 101.325 kPaᵃ.

Triton X-100 (wt%)	n	b	S	σ
0.0	0.645	-0.2856	535.8171	0.2159
1.0	0.645	-0.2818	535.6620	0.3553
2.5	0.645	-0.2694	429.7258	0.4539
5.0	0.645	-0.2648	369.6452	0.6200
7.5	0.645	-0.2626	344.7542	0.7504
10.0	0.645	-0.2563	206.8570	0.7354
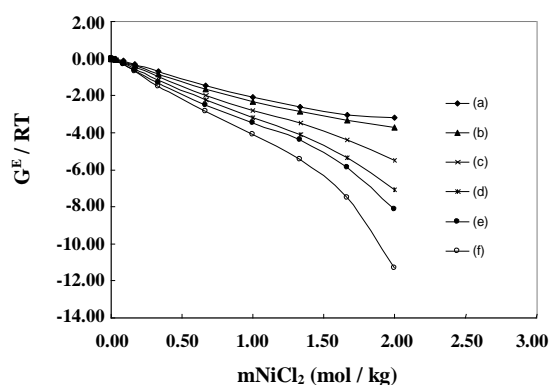
Fig. 5: The Plot of the excess Gibbs energy for the solution against the molality of NiCl₂ at different mass fractions of Triton X-100 (wt.) at 298.15 K, (a) wt. = 0.000, (b) wt. = 0.010, (c) wt. = 0.025, (d) wt. = 0.050, (e) wt. = 0.075, (f) wt. = 0.100.

2.5, 5.0, 7.5, and 10.0 percentage mass fractions of Triton X-100 over the entire range of total ionic strengths at a temperature of 298.15 K and 101325 Pa. The experimental data were correlated with Pitzer and TCPC models. The adjustable parameters for each of them were determined. It could be concluded that based on the Pitzer ion-interaction model satisfactory modeling of the investigated system was observed. The obtained Pitzer parameters were used for the evaluation of the other thermodynamic properties such as osmotic coefficients (ϕ) and excess Gibbs energy (G^E). The results showed that a clear relationship existed between the adjustable parameters of TCPC model and the physical properties of the system, too.

Nomenclatures

Symbols

m	Molality of Nicl₂ in solution
wt.	Mass fraction of Triton X-100 in the mixture (Triton X-100 + H₂O)
I	Ionic strength on molality scale
y	Ionic strength fraction
G^E	Excess Gibbs energy
E_A	Potential of cell A
r	Salt molal ratio
R	Gas constant
R^2	Linear coefficient of determination
k	(ln10)RT/ZF
s	External Nernst slope
T	Kelvin scale temperature, K

Greek letters

α	Constant
β^0, β^1, and C^φ	Pitzer empirical parameters for pure salt
$\gamma_{\pm NiCl_2}$	Mean activity coefficients of NiCl₂ on molality scale
ϕ	Osmotic coefficient
$A_\emptyset$	Debye–Hückel coefficient for the osmotic coefficient
S	Solvation parameter
b	Distance of the closest approach parameter
n	A constant equal 0.645

Research Article

REFERENCES

[1] Ghanadzadeh H., Daghbandan A., Akbarizadeh M., Applying Pareto Design of GMDH-Type Neural

[2] Boukhalfa N., Meniai A.H., Thermodynamic Modeling of Aqueous Electrolytes Type 2-1, *Procedia Eng.*, **148**: 1121–1129 (2016).

[3] Pitzer K.S., Mayorga G., Thermodynamics of Electrolytes. I I. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent, *J. Phys. Chem.*, **77**: 2300-2308 (1973).

[4] Pitzer K.S., Kim J.J., Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes, *J. Am. Chem. Soc.,* **96**: 5701-5707 (1974).

[5] Ivanovic T., Popovic D.Z., Miladinovic J., Rard J.A., Miladinovic Z.P., Pastor F.T., Isopiestic Determination of the Osmotic and Activity Coefficients of $\{yK_2HPO_4+(1- y)KH_2PO_4\}(aq)$ at T = 298.15 K, *J. Chem. Thermodyn*., **142**: 1-15 (2020).

[6] Norouzi N.Z., Bagherinia M.A., Mean Activity Coefficients Measurements and Thermodynamic Modeling of the Ternary Mixed Electrolyte KCl + Lactose + Water System at T = 298.15 K, *Phys. Chem. Res.*, **5**: 783-794 (2017).

[7] Ghalami-Choobar B., Mohammadian M., Thermodynamic modeling of the KCl+Glucose+Water System Based on Potentiometric Measurements at 298.15 K, *J. of Mol. Liq.*, **154**: 26–30 (2010).

[8] Ghalami-Choobar B., Mirzaie S., Thermodynamic Study of (KCl+proline+water) System Based on Potentiometric Measurements at T=(298.2 and 303.2) K, *J. Mol. Liq.*, **169**: 124–129 (2012).

[9] Nasiri-Lohehsara T., Ghalami-Choobar B., Thermodynamic Study and Modeling of the (KCl + diethanolamine + water) Ternary System Based on Potentiometric Measurements at T = (298.2 and 308.2) K, *J. Mol. Liq.*, **232**: 440–448 (2017).

[10] Ghalami-Choobar B., Mossayyebzadeh-Shalkoohi P., Thermodynamic Modeling of Quaternary ($CaCl_2$ + $Ca(NO_3)_2$ + Lalanine + water) System Based on Potentiometric Measurements at T (298.2, 303.2 and 308.2) K: Experimental Measurements and Thermodynamic Modeling, *Fluid Phase Equilib.,* **437**: 103-117 (2017).

Network for Solid-Liquid Equilibrium of Binary Systems (Isotactic Poly 1-Butene (1)-Organic Solvents (2)), *Iran. J. Chem. Chem. Eng. (IJCCE),* **33 (1):** 67-73 (2014).

[11] Ghalami-Choobar B., Nosrati Fallahkar T., Thermophysical properties of 1-ethyl-3-Methylimidazolium Bromide Ionic Liquid in Water Ethylene Carbonate Mixtures at T (298.2, 308.2 and 318.2) K, *Fluid Phase Equilib.*, **496**: 42-60 (2019).

[12] Hao X., Li S., Zhai Q., Jiang Y., Hu M., Activity Coefficients of CsF in (Urea + H_2O) or (N-methylformamide + H_2O) Mixed Solvents at 298.2 K, *J. Mol. Liq.,* **220**: 829–835 (2016).

[13] Hao X., Li S., Zhai Q., Jiang Y., Hu M., Phase Equilibrium and Activity Coefficients in Ternary Systems at 298.15 K: RbCl/CsCl + Ethylene Carbonate + Water, *J. Chem. Thermodyn.*, **98**: 309–316 (2016).

[14] Rafiee H.R., Frouzesh F., The study of Thermodynamic Properties of the Ternary (1-ethyl-3-methylimidazolium Hydrogen Sulfate + Lithium Chloride + Water) System and Corresponding Binary Systems at Different Temperatures and Ambient Pressure, *J. Chem. Thermodyn.,* **102**: 95–104 (2016).

[15] Rafiee H.R., Frouzesh F., The Effect of Ionic Liquid 1-Ethyl-3-Methylimidazolium Hydrogen Sulfate on Thermodynamic Properties of Aqueous Lithium Nitrate Solutions at Different Temperatures and Ambient Pressure, *J. Mol. Liq.*, **237**: 120–127 (2017).

[16] Morales J.W., Héctor R.G., Hernández-Luis F., Rodríguez-Raposo R., Activity Coefficients of $NaClO_4$ in (PEG 4000 + H_2O) Mixtures at 288.15, 298.15 and 308.15 K, *Iran. J. Chem. Chem. Eng. (IJCCE),* **39(2)**: 145-157 (2020).

[17] Modarresi S., Dehghani M.R., Alimardani P., Kazemi Sabzvar S., Feyzi F., Measurement and Modeling of Mean Ionic Activity Coefficient in Aqueous Solution Containing $NaNO_3$ and Poly Ethylene Glycol, *Iran. J. Chem. Chem. Eng. (IJCCE),* **32(2)**: 31-39 (2013).

[18] Rouhi A., Bagherinia M.A., Mean Activity Coefficient Measurement and Thermodynamic Modelling of the Ternary Mixed Electrolyte ($MgCl_2$

+ Glucose + Water) System at T = 298.15 K, *J. Chem. Thermodyn.*, **91**: 286–291 (2015).

[19] Bagherinia M.A., Pournaghdi M., Determination and Modeling of Activity Coefficients of Cobalt Chloride in the (Water + Ethanol) Mixed Solvent System by

[21] Dai P, Huang H., Ding Z, He Y, Liu S, Osmotic Coefficient and Mean Ion Activity Coefficient of $NiCl_2$ Aqueous Solution at Several Temperatures, *J. Chem. Thermodyn.,* **100**: 72–78 (2016).

[22] Bates R.G., "Determination of pH, Theory and Practice", Second ed., John Wiley, New York, (1964).

[23] Lin C.L., Lee L.S., Tseng H.C., A Three-Characteristic-Parameter Correlation Model for Strong Electrolyte Solutions, *Fluid Phase Equilib*., **90**: 57-79 (1993).

[24] Ge X., Zhang M., Guo M., Wang X., Correlation and Prediction of Thermodynamic Properties of Nonaqueous Electrolytes by the Modified TCPC Model, *J. Chem. Eng. Data,* **53:** 149-159 (2008).

[25] Ge X., Wang X., A Simple Two-Parameter Correlation Model for Aqueous Electrolyte Solutions across a Wide Range of Temperatures, *J. Chem. Eng. Data,* **54**: 179-186 (2009).

[26] Kim H.T., Frederick W.J., Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 'C. 1. Single Salt Parameters, *J. Chem. Eng. Data*, **33:** 177-184 (1988).

Potentiometric Method at 298.15 K, *J. Mol. Liq.,* **199**: 339–343 (2014).

[20] Asami K., Dielectric Properties of Water in Triton X-100 (Nonionic Detergent)–Water Mixtures, *J. Phys.: Condens. Matter,* **19**: 1-10 (2007).