

Measurement and Modeling of Mean Ionic Activity Coefficient in Aqueous Solution Containing NaNO₃ and Poly Ethylene Glycol

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ABSTRACT: Potentiometric investigation on {H₂O+NaNO₃+PEG1500} mixtures were made at T=308.15K, using electrochemical cells with two ion-selective electrodes, (Na⁺ glass) as the cation ion-selective electrode against (NO₃⁻ solvent-polymer PVC) as the anion ion-selective electrode. The mean ionic activity coefficients of NaNO₃ were measured at different concentrations of NaNO₃ and PEG. Maximum concentration of electrolyte and PEG were 1 mol/kg and 0.12 mol/kg, respectively. The experimental data was modeled by utilizing the modified Pitzer equation and the activity coefficient ratio of PEG was evaluated by using Maxwell's cross differential relation.

KEY WORDS: Activity coefficient; Polymer; Electrolyte solution; Ion-selective electrode.

INTRODUCTION

Water soluble and non-toxic polymers are very applicable and have been extensively utilized in different industries [1]. Their properties enable them to be used for commercial and technological applications such as purification of biological materials, pharmaceutical drugs, edible films for food coating and water treatment [2,3]. This type of polymers has been also used for liquid-liquid extraction in Aqueous Two-Phase Systems (ATPSs) which is a powerful, non-chromatographic, unit operation for the separation of biomolecules, and has been successfully applied in the purification of different biological materials, such as cells, virus, organelles, nucleic acids, proteins and enzymes [4,5].

Aqueous polymer-salt systems have several advantages over the traditional systems due to the lower viscosity, higher density and lower cost of the salt phase [6].

Since Poly Ethylene Glycol (PEG) is a water soluble and non-toxic polymer it has found several industrial applications and, hence, a number of researches have worked on determination of thermodynamic properties of aqueous solutions containing PEG [7-10].

Knowledge of activity coefficients of the constituent components in aqueous solutions is essential in calculation of phase equilibrium. A number of elaborate researches have focused on measurement and modeling of activity coefficients during recent years [11-13].

So far different direct and indirect methods for measurement of activity coefficients of species in aqueous solutions containing electrolytes are introduced. Among which, isopiestic and potentiometric techniques have been widely used [14-17]. Lin *et al.* [18] measured activity of water in solutions containing PEG and

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1021-9986/13/2/31

9/\$/2.90

different salts, by using an improved isopiestic method. The results were correlated utilizing an empirical equation which combines the long-range electrostatic contribution from Guggenheim and Fowler with the short-range virial equation. *Ninni et al.* [19] reported the water activity of binary and ternary solutions of PEGs at 298 K. They used the UNIFAC group contribution model for correlation and prediction of experimental data. *Sadeghi* [20] combined the electrolyte Wilson model together with the polymer Wilson model to represent the excess Gibbs free energy of aqueous polymer + electrolyte solutions. *Morales et al.* measured the activity coefficient of KCl, NaCl and LiCl in different mixtures containing water, salt and PEG by potentiometric method [21-23].

In the present research, potentiometric method has been used to measure mean ionic activity coefficient of sodium nitrate in aqueous solutions of PEG (1500) + sodium nitrate + water at 308.15 K. We have made advantage of the modified Pitzer equation to model the experimental data. Finally, activity coefficient ratio of PEG has been evaluated based on the Maxwell's cross differential relation.

EXPERIMENTAL SECTION

Sodium nitrate with more than 99% purity and PEG (MW~1500) were obtained from Merck Ltd. The salts were oven-dried at 120°C for 24 hours prior to use. All the solutions were prepared by de-ionized water with a conductivity of less than 0.8 $\mu\text{s}/\text{cm}$. A potentiometer (Model PP-50) with a resolution of ± 0.1 mV, Na^+ ion selective electrode (Model PY-I03) and NO_3^- ion selective electrode (Model PY-I05) were obtained from Sartorius. The electrodes were calibrated exactly according to the manufacturer instructions. A water bath with accuracy of $\pm 0.01^\circ\text{C}$ has been used in order to fix the temperature of the solution. The apparatus was equipped with a magnetic stirrer to prevent temperature and concentration gradients throughout the solution. The experiments were carried out in a jacketed glass beaker under the conditions mentioned above.

All the solutions were prepared on molality base with a resolution of $\pm 10^{-4}$ gr and all the experiments were carried out at 308.15 ± 0.1 K. Seven sets of experiments were performed at 0, 0.02, 0.04, 0.06, 0.08, 0.1 and 0.12 molalities of PEG. During each set of experiments, the concentration of NaNO_3 was increased in 10 steps from

0.1 to 1 molal by addition of salt, while the concentration of PEG was kept constant. The data was recorded only when the potentiometer reported the voltage with a deviation less than 0.1 mV per minute. All the experiments were repeated three times and the averaged values were reported.

THEORITICAL SECTION

Electrical potential difference is obtained by subtracting the electrical potential of anion ion selective electrode from the electrical potential of cation ion selective electrode [13].

$$\Delta E = E_{\text{cation}} - E_{\text{anion}} \quad (1)$$

In the case of a 1:1 single electrolyte system;
Cation ISE | Electrolyte (m_s) | Anion ISE (I)

Potential difference between the two cation and anion ion selective electrodes can be expressed as follows:

$$\Delta E^{(I)} = E^0 + 2S \ln(m_s \gamma_{\pm}^{(I)}) \quad (2)$$

Where $\Delta E^{(I)} = E_{\text{cation}} - E_{\text{anion}}$ and $\gamma_{\pm}^{(I)}$ is the mean ionic activity coefficient of the electrolyte in the cell of type (I). S is the Nernstian slope of electrodes and equal to RT/F , in which R is the universal gas constant, T is the absolute temperature, and F is the Faraday number. The term E^0 is the standard electro motive force (e.m.f.) of the cell which includes all the asymmetry, internal solution, and reference potentials of the cation and the anion ion-selective electrodes [24]. It is evident from equation (2) that the value of S can be obtained from a linear regression of the values of $\Delta E^{(I)}$ plotted against $\ln(m_s \gamma_{\pm}^{(I)})$. The values of $\gamma_{\pm}^{(I)}$ can be obtained from literature at each molality of m_s [25]. In the presence of the solute, the electrochemical cell of type (I) changes to the following form of cell (II) and the mean ionic activity coefficient of NaNO_3 is changed, correspondingly.

Cation ISE | Electrolyte (m_s) + Solute (m_p) | Anion ISE (II)

Nernst equation for cell (II) is then as follows:

$$\Delta E^{(II)} = E^0 + 2 \ln(m_s \gamma_{\pm}^{(II)}) \quad (3)$$

In the above equation, S and E^0 have the same values as those in Eq. (2).

Table 1: Coefficients of Eq. (6)

$\chi^{(0)}$	$\chi^{(1,0)}$	$\chi^{(1,1)}$	ξ	ω	α_0	rmsd ^a
1.62935	0.00195	-0.01677	0.42162	-6.43548	0.07359	0.00971

^a root mean square deviation

Subtracting Eq. (3) from Eq. (2) and rearranging gives:

$$\ln\left(\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}\right) = (\Delta E^{(II)} - \Delta E^{(I)})/2S \quad (4)$$

Having the values of $\Delta E^{(I)}$ and $\Delta E^{(II)}$ and evaluating S , the ratio of the mean ionic activity coefficients of the electrolyte ($\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}$) in the presence of polymer, to the corresponding value in the absence of polymer, at the same electrolyte molality, can be calculated. Maxwell cross-differential relation can be utilized for determination of activity coefficient ratio of the polymer in the presence and absence of the electrolyte

$$\left(\frac{\gamma_p^{(II)}}{\gamma_p^{(I)}}\right) : \left(\frac{\partial^2 G^E}{\partial m_S \partial m_P}\right) = \left(\frac{\partial^2 G^E}{\partial m_P \partial m_S}\right) \Rightarrow v \left(\frac{\partial \ln \gamma_+}{\partial m_P}\right)_{m_S, T, P} = \left(\frac{\partial \ln \gamma_P}{\partial m_S}\right)_{m_P, T, P} \quad (5)$$

In the above equation, G^E is the excess Gibbs free energy of the mixture and v is the sum of the stoichiometric coefficients of the electrolyte ions ($v = v_+ + v_-$).

MODELING

In this work, among the various applicable thermodynamic models, the modified Pitzer equation has been utilized to correlate the activity coefficients of NaNO_3 . This model was first proposed by Merida *et al.* [26] and has later been successfully applied by different researchers [13,27]. In an aqueous mixture containing an electrolyte and a polymer, different binary interaction parameters must be taken into account. However, the most important and the most effective ones are the ion-polymer and polymer-polymer binary interaction parameters. Taking into account the dependence of ion-polymer binary interaction parameters on both the

ionic strength of the solution and the polymer molality, the following equation for mixture of one electrolyte plus polymer is proposed:

$$\ln\left(\frac{\gamma_{\pm}^{(II)}}{\gamma_{\pm}^{(I)}}\right) = \chi m_P + \chi' m_P m_S + \xi m_P m_S + \omega m_P^2 \quad (6)$$

Where χ accounts for ion-polymer interaction, and $\chi' = \partial \chi / \partial I$ represents the influence of ionic strength on ion-polymer binary interactions. ξ and ω refer to ternary interactions of polymer-ion-ion and polymer-polymer-ion, respectively. Both ξ and ω are assumed to be independent of the ionic strength of the solution, due to their small values. Parameters χ and χ' in Eq. (6) are defined by Eqs. (7) and (8).

$$\chi = \chi^{(0)} + (\chi^{(1,0)} + \chi^{(1,1)} m_P) \cdot (2/\alpha_0^2 I) \quad (7)$$

$$\left[1 - (1 + I^{1/2}) \exp(-\alpha_0 I^{1/2})\right] \chi' = \partial \chi / \partial I = \quad (8)$$

$$\left(\chi^{(1,0)} + \chi^{(1,1)} m_P\right) \cdot (2/\alpha^2 I^2) \left[-1 + \left(1 + \left(1 + \frac{1}{2} I^{1/2} + \frac{1}{2} \alpha_0 (1 + I^{1/2})\right) \exp(-\alpha_0 I^{1/2})\right)\right]$$

In the above equations, I is the ionic strength of the solution, $\chi^{(1,0)}$ and $\chi^{(1,1)}$ are adjustable parameters and α_0 is a constant.

The non-linear optimization procedure of Davidon-Fletcher-Powell (DFP) [28–30] has been used to fit the experimental data. The Root Mean Square Deviation (RMSD) is used as the objective function and is defined by Eq. (9):

$$\text{rmsd} = \left\{ \frac{1}{n} \sum_{i=1}^n \left[\left(\frac{\gamma_{\pm}^{(II)}}{\gamma_{\pm}^{(I)}} \right)_i^{\text{exp}} - \left(\frac{\gamma_{\pm}^{(II)}}{\gamma_{\pm}^{(I)}} \right)_i^{\text{calc}} \right]^2 \right\}^{1/2} \quad (9)$$

Where, n is the number of data points. The experimental data points have been correlated to obtain the coefficients of Eq. (6). The results are presented in Table 1.

Table 2. Experimental data for the mean ionic activity coefficient of NaNO_3 ($\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}$) at different molalities of NaNO_3 and PEG at $T = 308.15 \text{ K}$

$\gamma_{\pm}^{m(2)}/\gamma_{\pm}^{m(1)}$										
m (NaNO_3) mol Kg^{-1}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
m (PEG) mol Kg^{-1}										
0.02	1.002	1.006	1.008	1.010	1.015	1.020	1.022	1.024	1.027	1.030
0.04	1.013	1.020	1.023	1.027	1.037	1.040	1.047	1.052	1.057	1.060
0.06	1.068	1.074	1.077	1.079	1.088	1.093	1.099	1.103	1.105	1.108
0.08	1.082	1.090	1.092	1.094	1.103	1.108	1.116	1.118	1.122	1.125
0.1	1.100	1.111	1.115	1.121	1.126	1.129	1.135	1.142	1.144	1.147
0.12	1.104	1.117	1.123	1.127	1.137	1.142	1.147	1.151	1.153	1.156

Using the adjusted parameters the activity coefficient of polymer can be calculated based on Maxwell equation. Activity coefficient ratio of polymer in the presence and absence of electrolyte $\left(\frac{\gamma_p^{(II)}}{\gamma_p^{(I)}}\right)$ has been determined by differentiation of Eq. (6) with respect to m_p following by integration with respect to m_s .

$$\ln \left(\frac{\gamma_p^{(II)}}{\gamma_p^{(I)}} \right) = \nu \int \left(\frac{\partial \ln \left(\frac{\gamma_{\pm}^{(II)}}{\gamma_{\pm}^{(I)}} \right)}{\partial m_p} \right)_{m_s, T, P} . dm_s \quad (10)$$

RESULTS AND DISCUSSION

In this work, the potential differences of sodium and nitrate ion selective electrodes have been measured at different concentrations of NaNO_3 ($m_s = 0.1$ - 1 mol/kg with 0.1 interval) and PEG ($m_p = 0.02$ - 0.12 mol/kg with 0.02 interval) at constant temperature equals to 308.15 K . The accuracy of the measured data has been investigated using available experimental activity coefficient data on aqueous solution of NaNO_3 . In Table 2 mean ionic activity coefficient ratio of NaNO_3 at different molalities of salt and polymer is presented. In Fig. 1, the mean ionic activity coefficient of sodium nitrate is depicted against the molality of PEG at fixed molality of sodium nitrate. The results show that at different molalities of sodium nitrate the presence of PEG has the same effect on the activity coefficient of salt. Meanwhile, it can be seen that the presence of PEG increases the activity coefficient of electrolyte. It means that in the presence of PEG the solubility of NaNO_3 can decrease. This result is observed

at different molalities of NaNO_3 . In Fig. 2 the activity coefficient ratios of NaNO_3 at different molalities is depicted as a function of molalities of PEG. It can be seen that the molality of electrolyte has a positive effect on augmentation of activity coefficient ratio. In our point of view, this phenomenon can be referred to ion-dipole interaction between PEG and the present ions. Meanwhile, the slope of figures show that the effect of PEG on activity of electrolyte decreases at higher molalities. In Fig. 3, the results of our modeling are presented. As it is observed, the model is able to correlate the experimental data fairly good. In Fig. 4, activity coefficient ratios of PEG in the presence and absence of electrolyte versus electrolyte molality is illustrated at different molalities of PEG. It is also evident that the presence of electrolyte has caused an increase in the activity coefficient of PEG. It is worth mentioning that in this case the effects of electrolyte on the activity coefficient of PEG increases at higher molalities.

CONCLUSIONS

In this work new potentiometric measurement experiments have been performed on $\{\text{H}_2\text{O} + \text{NaNO}_3 + \text{PEG1500}\}$ mixtures at $T = 308.15 \text{ K}$. Using two ion selective electrodes, the mean ionic activity coefficients of NaNO_3 have been measured at different concentrations of NaNO_3 and PEG. All the produced experimental data have been correlated using a modified version of Pitzer equation. Maxwell's cross differential relation has been utilized for calculation of activity coefficient ratio of PEG.

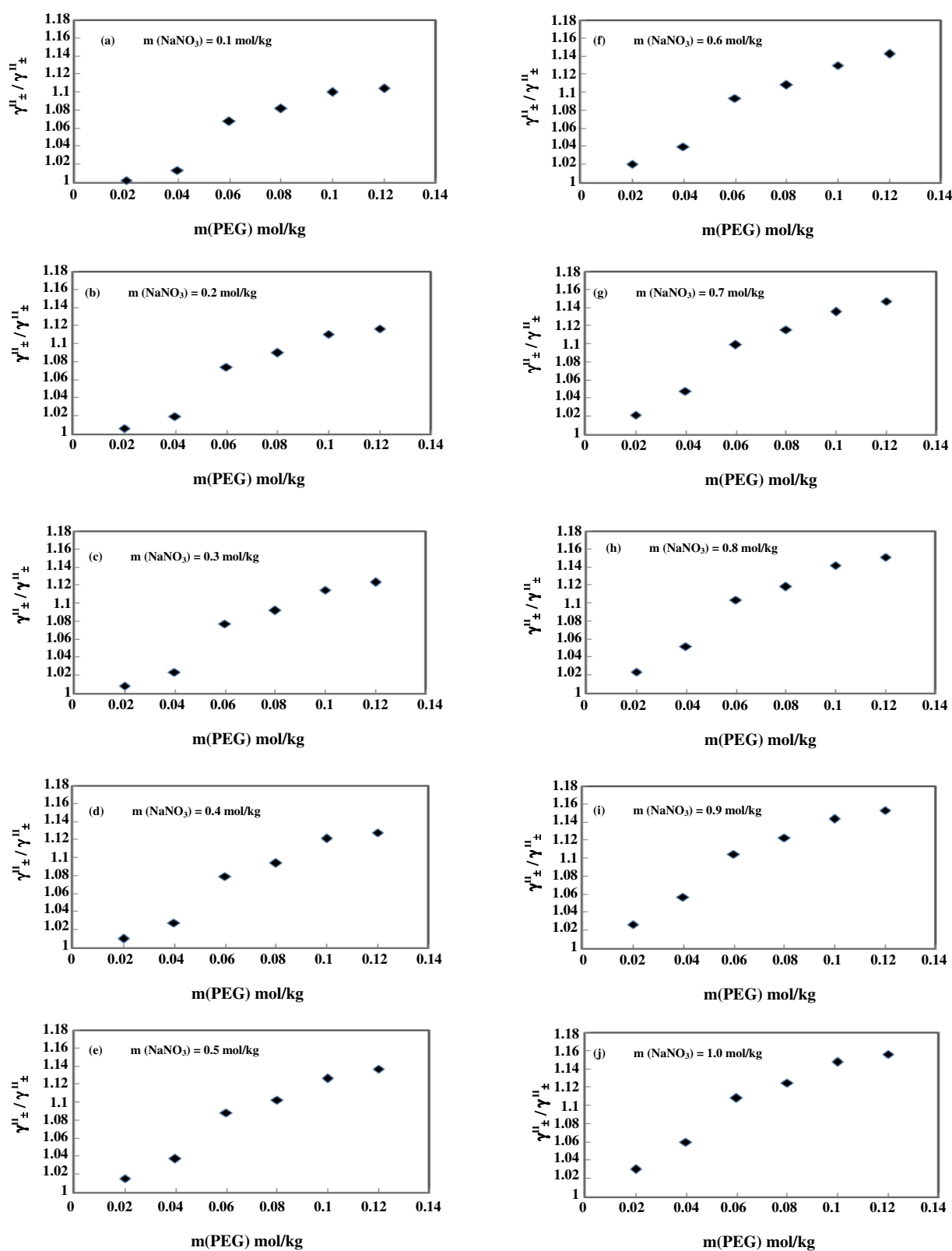


Fig. 1: Experimental data for the mean ionic activity coefficient of NaNO_3 as a function of molality of PEG at different NaNO_3 molalities: $m(\text{NaNO}_3) = 0.1$ (a); 0.2 (b); 0.3 (c); 0.4 (d); 0.5 (e); 0.6 (f); 0.7 (g); 0.8 (h); 0.9 (i); 0.1 (j). (\diamond) $\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}$, ($T=308.15$ K).

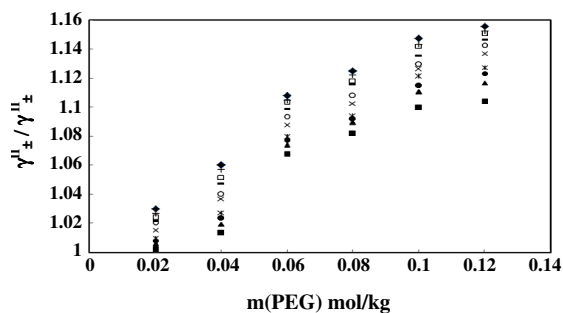


Fig. 2: Experimental data for the mean ionic activity coefficient of NaNO_3 as a function of molality of PEG at different NaNO_3 molalities: $m(\text{NaNO}_3) = 0.1$, \blacksquare ; 0.2 , \blacktriangle ; 0.3 , \bullet ; 0.4 , $*$; 0.5 , \times ; 0.6 , \circ ; 0.7 , $-$; 0.8 , \square ; 0.9 , $+$; 1.0 , \blacklozenge , ($T=308.15$ K).

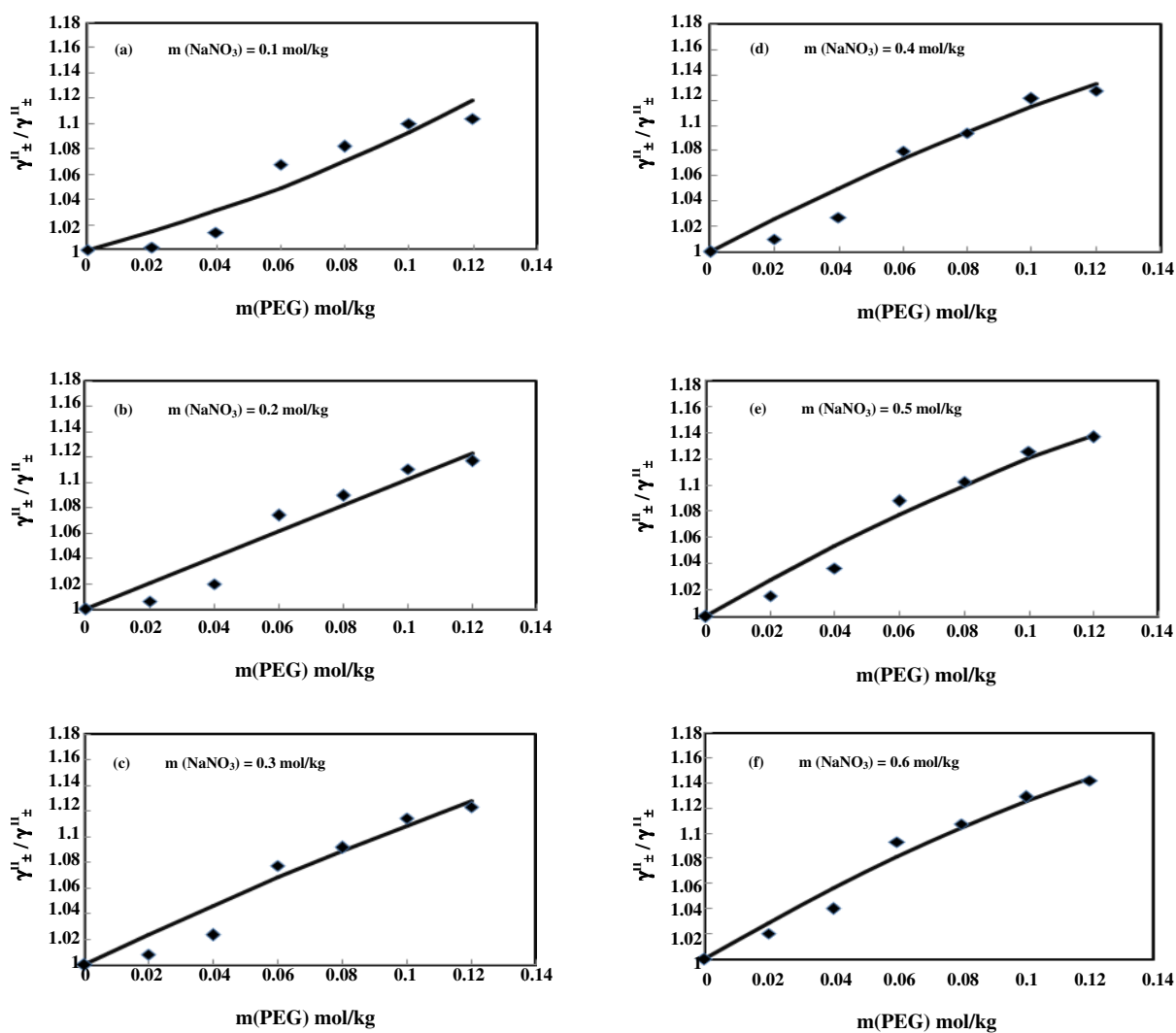


Fig. 3: The mean ionic activity coefficient of NaNO_3 as a function of molality of PEG at different NaNO_3 molalities: $m(\text{NaNO}_3) = 0.1$ (a); 0.2 (b); 0.3 (c); 0.4 (d); 0.5 (e); 0.6 (f); 0.7 (g); 0.8 (h); 0.9 (i); 0.1 (j). (\blacklozenge) $\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}$ experimental data; (—) $\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}$ calculated by equation (6), ($T=308.15$ K).

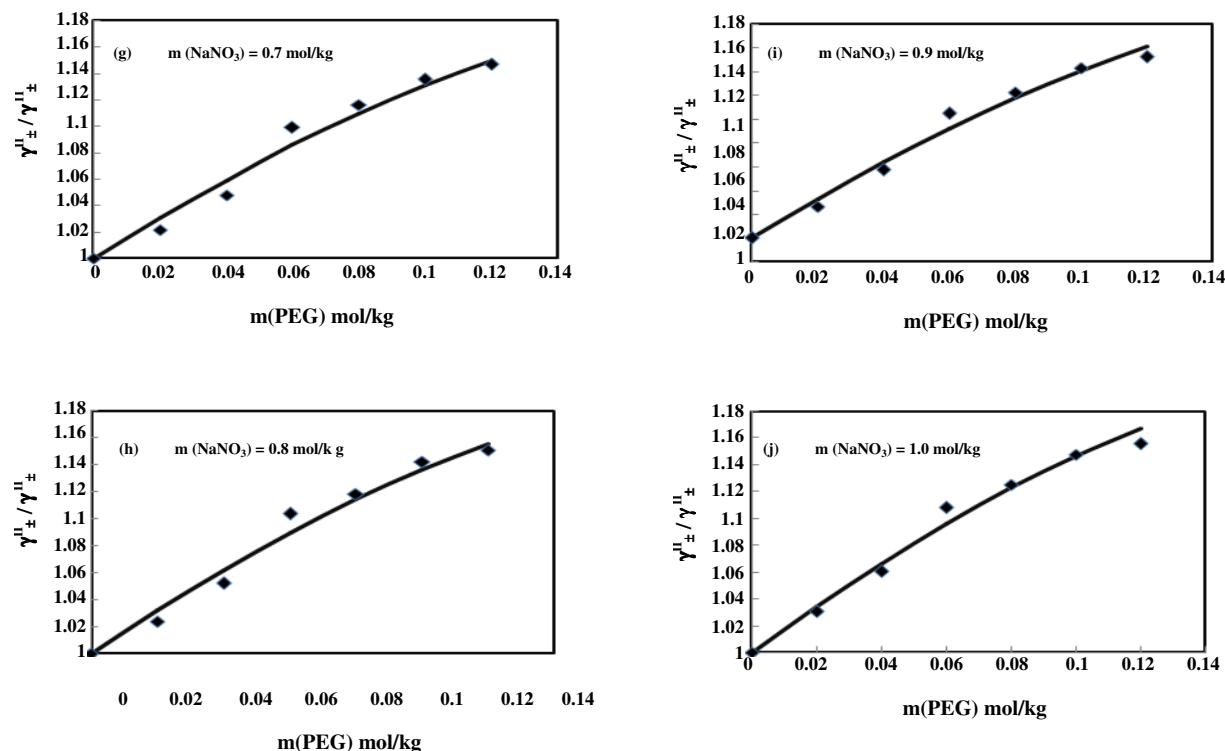


Fig. 3: The mean ionic activity coefficient of NaNO_3 as a function of molality of PEG at different NaNO_3 molalities: $m(\text{NaNO}_3) = 0.1$ (a); 0.2 (b); 0.3 (c); 0.4 (d); 0.5 (e); 0.6 (f); 0.7 (g); 0.8 (h); 0.9 (i); 1.0 (j). (\blacklozenge) $\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}$ experimental data; (—) $\gamma_{\pm}^{(II)}/\gamma_{\pm}^{(I)}$ calculated by equation (6), ($T=308.15$ K).

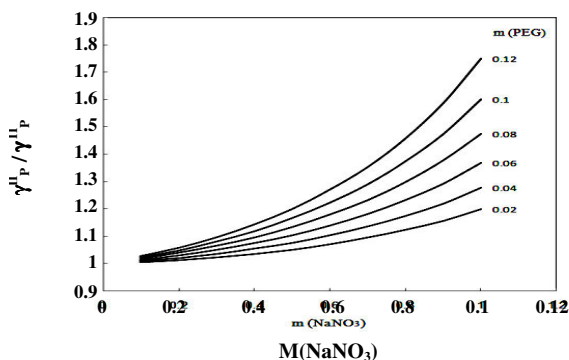


Fig. 4: The ratio of the activity coefficient of PEG ($\gamma_P^{(II)}/\gamma_P^{(I)}$) as a function of NaNO_3 molality for different PEG molalities.

The results show that sodium nitrate has a salting out effect on PEG and solubility of PEG decreases in the presence of sodium nitrate. PEG has the same effect on the solubility of electrolyte. It can be concluded that PEG has more effect at lower molalities, while, sodium nitrate is more effective at higher concentrations.

Nomenclature

$\Delta E^{(I)}$	Potential difference in electrochemical cell with NaNO_3 but without the presence of PEG
$\Delta E^{(II)}$	Potential difference in electrochemical cell with NaNO_3 and PEG
ΔE°	Standard potential difference of the cell
S	Nernstian slope

m	Concentration in molality
m_P	Molality of polymer
m_S	Molality of NaNO_3
$\gamma_{\pm}^{(I)}$	Mean ionic activity coefficient of NaNO_3 in aqueous solution without PEG
$\gamma_{\pm}^{(II)}$	Mean ionic activity coefficient of NaNO_3 in aqueous solution with PEG
γ_P	Activity coefficient of polymer
G^E	Excess Gibbs free energy
T	Temperature
P	Pressure
v	Stoichiometric coefficient
χ	Ion-polymer interaction
χ'	$\partial\chi/\partial(I)$
I	Ionic strength
ξ	Ternary interactions of polymer-ion-ion
ω	Ternary interactions of polymer-polymer-ion
α_0	Fixed value
$\chi^{(0)}$	Adjustable parameter
$\chi^{(1,0)}$	Adjustable parameter
$\chi^{(1,1)}$	Adjustable parameter

Received : Mar. 16, 2011 ; Accepted : Oct. 30, 2012

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