Activity Coefficients of NaClO₄ in (PEG 4000 + H₂O) Mixtures at 288.15, 298.15 and 308.15 K

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ABSTRACT: *The cell potential of the cell containing two ion-selective electrodes (ISE), Na-ISE | NaClO₄ (m), PEG 4000 (Y), H2O (100-Y) | ClO₄-ISE has been measured at temperatures of (288.15, 298.15, and 308.15) K as a function of the weight percentage Y of PEG 4000 in a mixed solvent at a 1 Mpa and the standard state for measured activity coefficients will be a solution of the salt in pure water. Y was varied between (0 and 25) wt.% in five-unit steps and the molality of the electrolyte (m) was between 0.05 mol kg⁻¹ and almost saturation. The values of the standard cell potential were calculated using routine methods of extrapolation together with extended Debye-Hückel and Pitzer equations. The results obtained produced good internal consistency for all the temperatures studied. Once the standard electromotive force was determined, the mean ionic activity coefficients for NaClO₄, the Gibbs energy of transfer from the water to the PEG 4000-water mixture, and the primary NaCl hydration number were calculated.*

KEYWORDS: *NaClO₄; PEG 4000; Cell potential; Ion-selective electrode; Activity coefficient.*

INTRODUCTION

Experimental values of activity coefficients of electrolytes in salt + water + polymer systems are important in studies oriented to the prediction of liquid-liquid equilibrium of Aqueous Two-Phase Systems (ATPSs). As well, they are a relevant property for the development of thermodynamic models and for the design, operation, and optimization of separation processes through ATPSs. Additionally, this thermodynamic property, together with others, such as solvent activity, osmotic coefficient, Gibbs energy of mixture or transfer, are important for obtaining useful information about the structures and interactions that occur in these types of systems. There have few studies in recent years on the properties of systems containing electrolytes in PEG + H₂O mixtures [1-20].

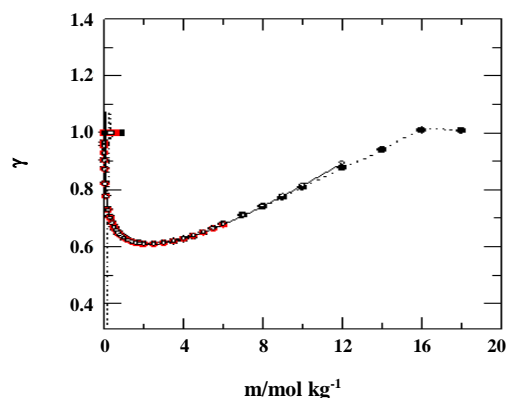Owing to the lack of bibliographic information

Fig. 1: Comparison of γ versus m for aqueous NaClO$_4$ at 298.15 K (●) Hamer and Wu (●) Pitzer (○) This study.

on mean ionic activity coefficients of electrolytes in PEG + H$_2$O, in five previous works [21-25] we studied the (LiCl, NaCl, KCl, NaNO$_3$ and NaBF$_4$) + PEG 4000 + H$_2$O systems at temperatures of (288.15, 298.15, and 308.15) K, besides the binary system NaClO$_4$ [26]. Using an experimental methodology (measurement of the cell potential, of electrochemical cells without transport containing two ion-selective electrodes) similar to previous works done by our group [27-33]. The data was compared NaClO$_4$ water at 298.15 K with the literature *Hamer* and *Wu* [34] and to the Pitzer model (using the parameters obtained in this study and also those proposed directly by Pitzer) [35] with a deviation of 0.02 units, such as in Fig. 1.

NaClO$_4$ is a highly soluble salt (almost 18 mol/kg in water at 298.15 K). For many years, NaClO$_4$ has been widely used as an electrolyte support for adjusting the ionic strength of a medium, as in polarographics studies (metal-ligand systems) [36], studies of double-layers and electrode kinetics [37, 38] and potentiometric studies (adjusting the ionic strength to work with selective electrodes) [39]. This extensive use is due not only to the high solubility of NaClO$_4$, but also to its weak tendency to form complexes with metals that may be present, which makes it a good inert electrolyte.

In the present work, experimental values were determined for the activity coefficient of NaClO$_4$ in the PEG 4000 + H$_2$O mixture at temperatures of (288.15, 298.15, and 308.15) K.

EXPERIMENTAL SECTION

According to Table 1 Sodium perchlorate monohydrate, Merck pro analysis (w = 0.99), was stored on silica gel in a desiccators and used without further purification. The solutions were continually agitated by a magnetic stirrer during the measurements. Analytical grade (Fluka) poly(ethylene glycol), with an average molar mass of 4000 and a minimum purity of 99 %, was also used without further purification.

For each set of experiments (corresponding to a wt.% of PEG 4000), working solutions were obtained by adding successive known masses of solid NaClO$_4$ to a solution previously prepared of PEG 4000 and bidistilled water ($\kappa < 10^{-6}$ S/cm). The standard uncertainty in the electrolyte molality and %wt of PEG is $\pm$0.0001 mol/kg (0.68 level of confidence)

Na-ISE (mod. 8411) and ClO4-ISE (mod. 9300) were obtained from Orion Corp. A double-wall vessel Metrohm cell was used to hold the electrodes and the solution. The temperature in the cell was kept constant at 0.05 ºC using a Hetofrig model 04 PT thermoregulator and a platinum resistance thermometer (Guildline model 9540) was used to record the temperature. The relative temperature standard uncertainty was estimated to be 0.02 % (0.68 level of confidence).

The cell potential measurements were carried out with a 614 Keithley Electrometer, with inner impedance greater than $5 \cdot 10^{13}$ Ω with a resolution of $\pm$ 0.10 mV.

Depending on the concentration of the NaClO$_4$ studied, it was observed that after approximately (30-45) minutes, the variation of the potential with time was very small [around 0.10 mV per (15-20) min]. The reading at this point in time was considered to represent the cell in equilibrium. Depending on the temperature, the cell potential standard uncertainty can be estimated between (0.01 – 0.03) mV (0.68 level of confidence).

RESULTS AND DISSCUSSION

Mean ionic activity coefficient values for NaClO$_4$ in PEG 4000 + H$_2$O mixtures were determined from the cell potential measurements of the following *bi*-ISE cells without transference:

$$\text{Na}-\text{ISE}\big|\text{NaClO}_4(m), \text{PEG 4000 (Y)}, \qquad (1)$$

$$\text{H}_2\text{O}(100-\text{Y})\big|\text{ClO}_4-\text{ISE}$$
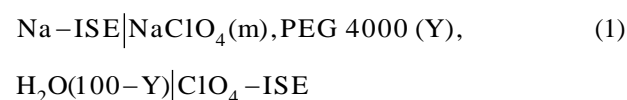
In these cells, m is the molality of NaClO$_4$ anhydrous (mol NaClO$_4$ / kg mixed-solvent), considered for this study NaClO4 monohydrate is used and therefore a correction to the use of anhydrous NaClO$_4$ is performed

Table 1: Chemical substances employed in this work.

Component	Source	Purity (mass fraction %)
NaClO$_4$ H$_2$O	MERCK	>99
PEG 4000	FLUKA	>99

using a relationship between the molecular weights of both compounds, in the working solution in the mixed solvent and *Y* the wt.% of PEG 4000 in the mixture.

Applying the Nernst-Nikolsky equation, the following expression is obtained:

$$E = E^{0*} - 2k \log m\gamma \qquad (2)$$

Where *E* is the cell potential of the cell, $k = (\ln 10)RT/F$, is the Nernst theoretical slope and *m* and γ are the molality and mean ionic coefficients of NaClO$_4$. E^{o*} is the apparent cell potential (molal scale) of the cell and contains the potential of asymmetry of both selective electrodes. In general, we have verified [21-33] that these asymmetric potentials are small, independent of the solvent composition and remain practically constant during the period of time that this type of study lasts.

Table 2 shows *E* values for different temperatures and different mixtures of PEG 4000 + H$_2$O as a function of NaClO$_4$ molality. Since the activity coefficients of NaClO$_4$ and parameters Pitzer in pure water are well known for each temperature [35], the values of *E* that appear in Table 2 for 0 of PEG 4000, allow for carrying out a calibration of the electrode system using Eq. (2). The uncertainty of the activity coefficients of 0.0001 units shows the correct use of the equation and a good relationship between the activity coefficients and temperature at different wt.% of PEG 4000.

A very good linear relationship is obtained when *E* vs. -2log*m* γ is plotted at each temperature studied. The *k* values obtained, when applying a least-squares regression analysis to the previous plots, were (56.96 γ0.02, 58.21 γ 0.02, and 59.07 γ0.03) mV at (288.15, 298.15, and 308.15) K in comparison with the theoretical values 57.17 at 288.15 K, 59.16 at 298.15 K and 61.14 at 308.15 K, respectively, with correlation coefficients greater than 0.9999 in all cases. The standard deviations were (0.10, 0.11, and 0.15) mV at (288.15, 298.15, and 308.15) K, respectively.

Once the electrodes were calibrated and found to be functioning correctly, the next very important step was the determination of E^{0*} for each wt.% PEG 4000 and temperature studied. The determination of E^{0*} was carried out following a method similar to that proposed by Hitchcock [40] and using the equations of extended Debye-Hückel and Pitzer, to represent the dependency of log γ on molality. For 1:1 electrolytes, these equations may be written as:

- Extended Debye-Hückel equation [40]

$$\log \gamma = -\frac{A\sqrt{m}}{1 + Ba\sqrt{m}} + cm + dm^2 - \qquad (3)$$

$$\log(1 + 0.002mM) + Ext$$

$$A = 1.8247 \times 10^6 \, \rho^{1/2} / (\varepsilon_r T)^{3/2} \quad kg^{1/2} mol^{-1/2} \qquad (3a)$$

$$B = 50.2901 \, \rho^{1/2} / (\varepsilon_r T)^{1/2} \quad kg^{1/2} mol^{-1/2} \, \overset{\circ}{A}^{-1} \qquad (3b)$$

- Pitzer equation [41]

$$\ln g = f^g + B^g m + C^g m^2 \qquad (4)$$

$$f^g = -A_j \left[\frac{\sqrt{m}}{1 + b\sqrt{m}} + \frac{2}{b} \ln(1 + b\sqrt{m}) \right] \qquad (4a)$$

$$B^\gamma = 2\beta^0 + \frac{2\beta^1}{\alpha^2 m} \left[1 - (1 + \alpha\sqrt{m} - \alpha^2 m/2) \exp(\alpha\sqrt{m}) \right] \qquad (4b)$$

All symbols have their usual meaning. The values of the physical properties and the values of the different constants are shown in Table 3. By combining Equations (2) and (3) or (2) and (4), the values of E^{0*}, according to the different models used, can be optimized, as well as the characteristic ionic interaction parameters of each model. These values are presented in Table 4, as well as the corresponding standard deviation of the fit.

In Table 4, except for higher wt.% PEG 4000, the values of E^{0*} obtained with both models are in good agreement (standard errors inferiors to 1 mV). The extended Debye-Hückel equation, offers excellent standard deviations for the fits, comparable to those obtained with the Pitzer model.

Table 2: Experimental cell potential E and mean ionic activity coefficients γ at different NaClO₄ molality and weight percentage of PEG 4000-H₂O mixtures at (288.15, 298.15 and 308.15) K at 0.1 Mpaᵃ.

288.15 K								
0 wt. %			5 wt. %			10 wt. %		
m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ
0.0469	161.28	0.8139	0.0207	125.50	0.9487	0.0258	136.04	0.8472
0.0873	189.62	0.7755	0.0565	165.42	0.7789	0.0711	181.07	0.7652
0.1616	217.07	0.7295	0.1249	201.56	0.7318	0.1053	198.75	0.7386
0.2526	236.97	0.6979	0.1720	216.69	0.7213	0.1897	224.48	0.6893
0.4103	258.35	0.6619	0.3126	242.15	0.6639	0.2920	243.77	0.6613
0.6057	275.46	0.6336	0.4681	260.96	0.6485	0.4185	259.74	0.6372
0.8878	292.31	0.6076	0.7710	283.71	0.6236	0.5687	273.44	0.6186
1.1986	305.68	0.5897	1.1142	300.51	0.6060	0.7523	285.96	0.6023
1.5855	318.39	0.5764	1.5271	315.11	0.5939	1.0705	301.75	0.5824
2.0210	329.65	0.5677	1.9939	327.58	0.5852	1.4000	313.98	0.5702
2.6401	342.46	0.5630	2.5584	339.61	0.5816	1.8542	327.15	0.5618
3.7032	359.56	0.5671	3.3304	352.88	0.5843	2.4567	340.08	0.5507
4.9760	375.68	0.5846	4.4089	367.76	0.5962	3.2258	353.35	0.5484
6.8544	393.97	0.6143	4.9963	374.65	0.6047	4.2285	367.34	0.5551
8.6445	408.76	0.6568						
10.1995	419.69	0.6942						
10.8894	424.07	0.7105						
15 wt. %			20 wt. %			25 wt. %		
m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ
0.0317	140.80	0.8061	0.0160	108.10	0.8626	0.0451	150.72	0.7625
0.0863	185.98	0.7383	0.0700	173.41	0.7378	0.0924	182.80	0.7112
0.1466	209.77	0.7032	0.1451	206.15	0.6898	0.1526	205.36	0.6795
0.2674	236.61	0.6634	0.2413	229.00	0.6585	0.2349	224.81	0.6540
0.4368	258.57	0.6329	0.3930	250.86	0.6289	0.3586	243.92	0.6304
0.6912	279.06	0.6052	0.5407	265.20	0.6108	0.5449	262.87	0.6086
0.9906	295.31	0.5865	0.7559	280.35	0.5934	0.7220	275.71	0.5954
1.4122	311.22	0.5674	1.0458	295.16	0.5786	1.0201	291.62	0.5813
1.7307	320.56	0.5592	1.4602	310.60	0.5661	1.4593	308.39	0.5703
2.0972	329.58	0.5538	1.9009	323.12	0.5601	1.7822	317.96	0.5666
2.6701	341.27	0.5509	2.4327	335.20	0.5587	2.1966	328.27	0.5662
3.1796	349.98	0.5517	2.9860	345.67	0.5625	2.6691	338.04	0.5677
3.8296	359.61	0.5565	3.5473	354.68	0.5681	3.2808	348.75	0.5735
4.4021	367.07		4.2038	363.86	0.5771	4.0676	360.34	0.5847

***Table 2: Experimental cell potential E and mean ionic activity coefficients γ at different NaClO₄ molality and
weight percentage of PEG 4000-H₂O mixtures at (288.15, 298.15 and 308.15) K at 0.1 Mpaᵃ. (Continued)***

298.15 K

0 wt. %			5 wt. %			10 wt. %		
m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ
0.0283	137.18	0.8710	0.0255	130.25	0.8508	0.0320	139.17	0.8248
0.0740	180.72	0.7878	0.0651	173.77	0.7897	0.0702	175.23	0.7674
0.1255	204.94	0.7501	0.1185	201.45	0.7497	0.1135	197.52	0.7374
0.2086	227.84	0.7097	0.2115	228.19	0.7130	0.1862	220.15	0.7033
0.3529	251.72	0.6727	0.4368	261.84	0.6718	0.2807	239.04	0.6779
0.4325	261.09	0.6605	0.7450	286.85	0.6459	0.3639	251.20	0.6651
0.6357	278.67	0.6363	1.1649	308.12	0.6291	0.4889	264.86	0.6486
0.8761	293.58	0.6201	1.6707	325.71	0.6211	0.6191	276.07	0.6393
1.1272	305.53	0.6104	2.3267	342.43	0.6208	0.8000	288.23	0.6293
1.4430	317.25	0.6013	2.9172	354.33	0.6265	1.0809	302.63	0.6192
1.7981	327.95	0.5962	3.5687	365.39	0.6374	1.4209	315.92	0.6127
2.2518	339.26	0.5955	4.3292	376.26	0.6514	1.9234	330.98	0.6096
2.8849	352.28	0.6013	4.6197	379.88	0.6558	2.4632	343.70	0.6122
3.6706	365.28	0.6111				3.1889	357.45	0.6207
4.8085	380.72	0.6331				3.8058	367.25	0.6313
6.0261	394.57	0.6644						
9.7621	426.34	0.7688						

15 wt. %			20 wt. %			25 wt. %		
m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ
0.0256	125.75	0.8139	0.0246	121.01	0.7959	0.0337	134.55	0.7641
0.0616	166.21	0.7530	0.0685	168.57	0.7303	0.0677	166.50	0.7169
0.0996	188.62	0.7255	0.1278	197.67	0.6962	0.1274	195.72	0.6788
0.1491	207.47	0.7036	0.1842	214.76	0.6775	0.1872	213.73	0.6595
0.2461	230.78	0.6762	0.2608	231.07	0.6607	0.2799	232.55	0.6400
0.3497	247.21	0.6585	0.3506	244.98	0.6470	0.4505	254.99	0.6198
0.5386	267.45	0.6380	0.5381	265.20	0.6289	0.7542	279.63	0.6027
0.8469	288.91	0.6203	0.7651	282.00	0.6167	1.1251	299.17	0.5946
1.1916	305.37	0.6105	1.1328	300.97	0.6061	1.6293	317.77	0.5931
1.5895	319.59	0.6063	1.6046	318.23	0.6020	2.1473	332.16	0.5982
2.1367	334.55	0.6063	2.0570	330.88	0.6031	2.7830	346.16	0.6088
2.7933	348.42	0.6102	2.6828	344.88	0.6099	3.5040	359.09	0.6245
3.6174	362.44	0.6218	3.3144	356.38	0.6198	4.3878	372.01	0.6439
4.3170	372.45	0.6351	4.4850	373.55	0.6432	4.7925	377.16	0.6527

Table 2: Experimental cell potential E and mean ionic activity coefficients γ at different NaClO₄ molality and weight percentage of PEG 4000-H₂O mixtures at (288.15, 298.15 and 308.15) K at 0.1 Mpaᵃ. (Continued)

308.15 K								
0 wt. %			5 wt. %			10 wt. %		
m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ
0.0175	109.71	0.9029	0.0291	128.65	0.8176	0.0297	128.94	0.7840
0.0642	170.93	0.8140	0.0779	176.75	0.7805	0.0745	173.61	0.7467
0.1228	201.69	0.7745	0.1279	200.97	0.7624	0.1137	194.18	0.7308
0.1939	223.50	0.7506	0.2025	223.15	0.7417	0.1628	211.70	0.7182
0.2821	241.55	0.7334	0.2828	239.76	0.7342	0.2365	229.87	0.7045
0.4440	263.46	0.7143	0.3723	252.93	0.7209	0.3536	249.35	0.6889
0.6367	280.91	0.6998	0.5500	271.69	0.7034	0.5555	271.53	0.6757
0.8679	295.88	0.6873	0.7968	289.79	0.6909	0.7661	287.11	0.6638
1.0774	306.76	0.6844	1.2257	311.26	0.6825	1.0034	300.63	0.6596
1.3615	318.81	0.6850	1.6608	326.78	0.6816	1.3438	315.33	0.6559
1.7155	330.94	0.6886	2.2235	342.22	0.6879	1.7752	329.87	0.6592
2.3486	347.10	0.6892	2.7907	354.78	0.7001	2.2972	343.66	0.6665
3.0499	361.36	0.7008	3.4524	366.99	0.7180	2.9539	357.60	0.6801
3.9694	376.47	0.7229	4.1813	378.45	0.7412	3.9197	374.11	0.7071
5.2720	393.73	0.7619						
7.4417	416.16	0.8357						
11.1683	443.91	0.9564						
15 wt. %			20 wt. %			25 wt. %		
m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ	m (mol kg⁻¹)	-E (mV)	γ
0.0265	-121.7000	0.7753	0.0329	129.52	0.7189	0.0417	140.40	0.7321
0.0732	-170.7200	0.7298	0.0768	170.64	0.6873	0.1010	182.98	0.6935
0.1341	-200.2200	0.7077	0.1173	191.31	0.6730	0.1648	205.30	0.6569
0.1998	-219.7000	0.6945	0.1888	214.51	0.6576	0.2280	221.38	0.6494
0.2931	-238.2500	0.6796	0.2865	234.93	0.6450	0.3122	237.12	0.6447
0.4738	-261.9100	0.6667	0.3732	248.00	0.6388	0.4343	253.73	0.6404
0.7545	-284.8800	0.6551	0.5629	268.05	0.6260	0.6102	270.83	0.6362
1.1041	-304.2500	0.6530	0.7729	283.00	0.6102	0.8389	287.11	0.6356
1.5923	-323.3600	0.6571	1.1175	302.19	0.6134	1.2449	307.79	0.6409
2.0032	-335.1800	0.6576	1.5477	319.56	0.6214	1.8270	328.60	0.6551
2.4938	-347.1900	0.6676	2.0682	335.45	0.6338	2.3636	342.95	0.6698
3.0561	-358.5600	0.6799	2.7218	350.95	0.6515	3.1825	360.50	0.7003
3.7725	-370.8600	0.7000	3.5059	365.67	0.6738	3.8626	372.10	0.7234
4.3864	-380.0000	0.7194	4.5776	381.77	0.7063	4.5768	382.97	0.7546

ᵃ *Standard uncertainties u are u(T) = 0.02 K, u(m) = 0.0001 mol/kg , u(E) = 0.10 mV, u(γ) = 0.0001 (0.68 level of confidence)*

Table 3: Values of mole fraction ($X_{PEG4000}$), average molecular mass (M), density (ρ), relative permittivity ($ε_r$),
Bjerrum interionic (q), Debye-Hückel (A, B) and Pitzer ($A_ϕ$) constants as a function of the weight percentage
of PEG4000 in PEG4000–H₂O mixtures at (288.15, 298.15 and 308.15) K, at 0.1Mpaᵃ.

wt. %	$10^4\,X_{PEG4000}$	M (g/mol)	ρ (g/cm³)	$ε_r$	q	A (kg/mol)$^{1/2}$	B (kg/mol)$^{1/2}$ Å^{-1})	$A_ϕ$(kg/mol)$^{1/2}$
				288.15 K				
0	0.000	18.015	0.9991	82.06	3.53	0.5016	0.3269	0.3850
5	2.370	18.959	1.0077	76.10	3.81	0.5641	0.3409	0.4330
10	5.002	20.007	1.0169	71.80	4.04	0.6183	0.3526	0.4746
15	7.942	21.177	1.0260	66.10	4.38	0.7031	0.3691	0.5397
20	11.247	22.494	1.0352	62.90	4.61	0.7608	0.3801	0.5840
25	14.990	23.984	1.0443	60.00	4.83	0.8202	0.3909	0.6296
				298.15 K				
0	0.000	18.015	0.9970	78.38	3.57	0.5100	0.3285	0.3915
5	2.370	18.959	1.0053	72.40	3.87	0.5768	0.3432	0.4428
10	5.002	20.007	1.0140	67.10	4.17	0.6493	0.3580	0.4984
15	7.942	21.177	1.0227	60.80	4.61	0.7560	0.3777	0.5803
20	11.247	22.494	1.0315	56.10	4.99	0.8566	0.3949	0.6576
25	14.990	23.984	1.0402	52.60	5.33	0.9475	0.4096	0.7273
				308.15 K				
0	0.000	18.015	0.9940	74.86	3.62	0.5192	0.3301	0.3986
5	2.370	18.959	1.0020	68.40	3.96	0.5969	0.3467	0.4582
10	5.002	20.007	1.0103	60.30	4.49	0.7241	0.3708	0.5558
15	7.942	21.177	1.0186	52.70	5.14	0.8898	0.3983	0.6831
20	11.247	22.494	1.0269	45.60	5.94	1.1101	0.4299	0.8521
25	14.990	23.984	1.0353	41.50	6.53	1.2837	0.4525	0.9854

ᵃ *Standard uncertainties u are u(T) = 0.02 K, u(M) = 0.005 g/mol , u(ρ) = 0.0002 g/cm³, u($ε_r$) = 0.03, u(A) = 0.0002 (kg/mol) $^{1/2}$,*
u(B) = 0.0002 (kg/mol)$^{1/2}$ Å^{-1}, u($A_ϕ$) = 0.0002 (kg/mol)$^{1/2}$ (0.68 level of confidence).

The values of $β^0$ (which can be identified with interaction of like and unlike charged ions), $β^1$ (which can be identified with the interactions between unlike charged ions) and $C^γ$ (which represents triple ionic interactions) obtained in the fit using the Pitzer model are plotted in Fig. 2 against of the reciprocal value of the relative permittivity of the PEG 4000 + H₂O mixture, for the three temperatures studied. It is interesting to note that these parameters (at least $β^0$ and $β^1$) present a linear tendency with $1/ε_r$, following behaviour similar to other electrolytes 1:1 in different aqueous mixtures of organic solvents. In relation to the parameter $Cγ$ it is not a simple matter to reach a conclusion concerning the variation

with $1/ε_r$ given its low value and the major uncertainty in its determination.

The average values for E^{0*}, which appear in the last column of Table 4, were used to calculate the mean ionic coefficients γ from Equation 2 that are listed in Table 1 for different molalities of NaClO₄ and wt.% of PEG 4000 at studied temperature. Fig. 3 shows log γ vs. $m^{1/2}$ for the three temperatures and for the six wt.% of PEG 4000 studied. All the curves show a typical profile of the variation of log γ with molality, which, as is well known, is governed by two types of short-range interactions including those of ion-ion and ion-solvent. In accordance with the preceding behavior, it can be assumed that

Table 4: Summary of both standard cell potential and the parameter values obtained for the Debye-Hückel and Pitzer equations, in different PEG4000 – H₂O mixtures at (288.15, 298.15 and 303.15) K, at 0.1 Mpaᵃ.

w	E^{0*} (mV)	a (Å)	c (kg/mol)	d (kg/mol)^2	σ(mV)	E^{0*} (mV)	$\beta^{(0)}$ (kg/mol)	$\beta^{(1)}$ (kg/mol)	C^{γ} (kg/mol)^2	σ(mV)	$<E^{0*}>$ (mV)
					288.15 K						
0	-323.12	3.43	0.0284	0.00036	0.10	-322.57	0.0471	0.1935	-0.00148	0.11	-322.85 ± 0.39
0.05	-320.09	4.30	0.0302	-0.00096	0.11	-319.80	0.0597	0.3658	-0.00346	0.13	-319.94 ± 0.20
0.10	-325.16	4.47	0.0263	-0.00118	0.13	-325.10	0.0631	0.4250	-0.00460	0.15	-325.13 ± 0.04
0.15	-322.04	5.50	0.0221	-0.00442	0.07	-322.32	0.0609	0.6830	-0.00100	0.08	-322.18 ± 0.20
0.20	-319.54	5.76	0.0312	-0.00723	0.05	-320.49	0.0802	0.7486	-0.00414	0.08	-320.02 ± 0.67
0.25	-317.04	6.15	0.0385	-0.01203	0.07	-317.92	0.0875	0.9137	-0.00464	0.10	-317.48 ± 0.62
					298.15 K						
0	-324.63	3.46	0.0416	-0.00051	0.08	-324.23	0.0638	0.1945	-0.00382	0.12	-324.43 ± 0.28
0.05	-323.86	4.80	0.0386	-0.00264	0.08	-323.81	0.0710	0.4404	-0.00473	0.06	-323.84 ± 0.03
0.10	-322.84	5.19	0.0425	-0.00477	0.07	-323.02	0.0826	0.5657	-0.00663	0.07	-322.93 ± 0.13
0.15	-321.18	6.17	0.0464	-0.01246	0.09	-321.73	0.0858	0.8588	-0.00522	0.11	-321.46 ± 0.39
0.20	-319.33	6.93	0.0553	-0.02436	0.05	-320.63	0.0970	1.0864	-0.00577	0.21	-319.98 ± 0.92
0.25	-318.26	7.46	0.0625	-0.03757	0.11	-320.76	0.1177	1.2081	-0.00923	0.21	-319.50 ± 1.75
					308.15 K						
0	-322.65	5.02	0.0484	-0.00384	0.16	-322.12	0.0662	0.4778	-0.00338	0.16	-322.39 ± 0.37
0.05	-320.22	6.45	0.0458	-0.00851	0.15	-320.61	0.0719	0.6675	-0.00217	0.10	-320.42 ± 0.20
0.10	-321.33	6.87	0.0586	-0.01799	0.16	-322.28	0.0880	0.8957	-0.00420	0.15	-321.81 ± 0.67
0.15	-320.81	7.74	0.0812	-0.04250	0.12	-321.26	0.1056	1.3263	-0.00629	0.11	-321-04 ± 0.32
20	-319.41	9.03	0.1114	-0.10708	0.17	-323.72	0.1381	1.6834	-0.01060	0.21	-321.56 ± 3.05
25	-316.55	9.21	0.1341	-0.11938	0.14	-322.21	0.1489	1.6588	-0.01227	0.14	-319.38 ± 4.01

ᵃ Standard uncertainties u are u(T) = 0.02 K, u(E^{0*}) = 0.10 mV , u(a) = 0.02 Å, u(c) = 0.0003 kg/mol , u(d) = 0.00002(kg/mol)^2 , u($\beta^{(0)}$) = 0.0002 kg/mol, u($\beta^{(1)}$) = 0.0002 kg/mol, u(C^{γ}) = 0.00003 (kg/mol)^2 (0.68 level of confidence).

the ion-ion interactions are much more significant than the ion-solvent interactions when the PEG 4000 concentration increases.

In Table 5 shows that, for temperature studied <a> values are greater than the sum of the ionic radii Krestov [42], wich indicates an ion solvation in the system.

In effect, according to Bjerrum's theory [43], ion-pairs formation requires an inter-ionic distance that is less than a critical distance, q, defined as:

$$q = \left|z_+ z_-\right| e^2 / 2\varepsilon_r kT \tag{5}$$

Where all the symbols have their usal meaning. In Table 6 it can be verified that the system under study

at three temperatures there is a tendency to $a > q$, so there is solvation of ions in the system.

The standard Gibbs energy of transfer, ΔG_t^0 defined as the difference between the standard Gibbs energy per mole of electrolyte in a pure solvent, usually water, and that in another pure or mixed solvent, is a measure of the change in the total energy of the solute when it is transferred from one solvent to another at infinite dilution and can be easily calculated from the values of E^{0*} according to the expression:

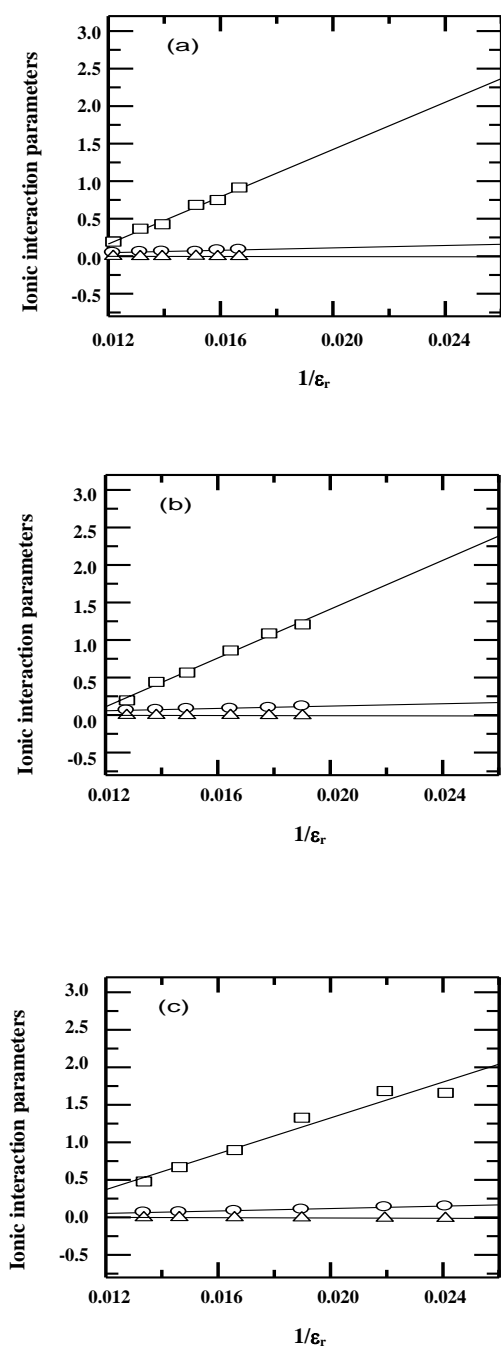$$\mathrm{D}G_t^0 = -zF(E_s^0 - E_w^0) = -zF\left[(E_s^{0*} - E_w^{0*}) - (E_s^{asym} - E_w^{asym})\right] \tag{6}$$

Fig. 2: Plot of Pitzer parameters, β^0 (○), β^1 (□), C^γ ($\triangle$), for NaClO₄ in PEG 4000 –H₂O mixtures at 288.15 K (a), 298.15 K (b) and 308.15 K (c), as a function of the inverse of the relative permittivity.
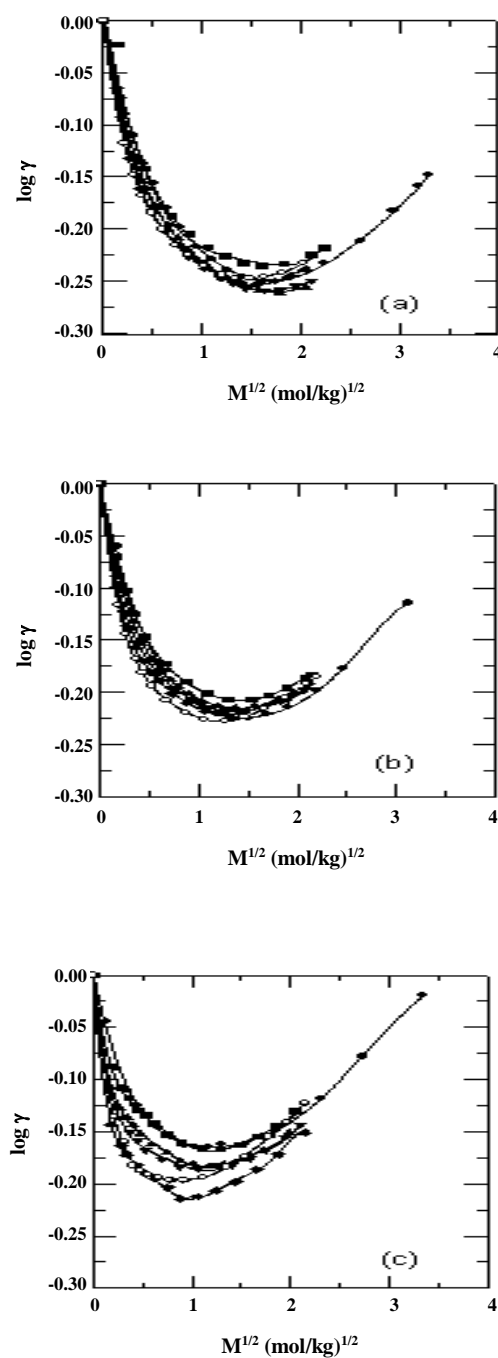
Fig. 3: Plot of log γ vs $m^{1/2}$ for NaClO₄ in PEG 4000 + H₂O at 288.15 K (a), 298.15 K (b), and 308.15 K (c) for different wt.% of PEG 4000 ○ 0 % ● 5 %, ■ 10 %, ▲15 %, ▼ 20 %, ♦ 25 %.

where E^0, E^{0*}, and E^{asym} stand for the standard potential, the apparent standard potential and the asymmetry potential ($\varepsilon_K^{asym} + \varepsilon_{Cl}^{asym}$), respectively.

Subscript s refers to mixed solvent and w to water. All the other symbols have their usual meaning. As mentioned previously, in our case, E^{asym} is a constant

Table 5: Average ion size parameter, <a>, for NaClO4 + PEG 4000 + H2O system (288.15, 298.15 and 308.15) K, and the sum of the ionic radii.

<a> (Å)			$(r_+ + r_-)$ (Å)
288.15 K	298.15 K	308.15 K	
4.94±1.04	5.67±1.48	7.39±1.61	3.31

Table 6: Values (a – q) as a function of mass fraction of PEG 4000 288.15, 298.15 and 308.15) K, for NaClO4 + PEG 4000 + H2O system at 0.1 Mpa[a].

(a – q) (Å)			
w	288.15 K	298.15 K	308.15 K
0	- 0.10	-0.11	1.40
0.05	0.49	0.93	2.49
0.10	0.43	1.02	2.38
0.15	1.12	1.56	2.60
0.20	1.15	1.94	3.09
0.25	1.32	2.13	2.68

[a] *Standard uncertainties u are u(T) = 0.02 K, (0.68 level of confidence).*

Table 7: Standard Gibbs energy of transference, ΔG_t^0 , for the NaClO₄ + PEG 4000 + H₂O system at (288.15, 298.15 and 308.15) K, at 0.1 Mpa[a].

wt.% PEG 4000	ΔG_t^0 (kJ/mol)		
	288.15/K	298.15/K	308.15/K
0	0.00	0.00	0.00
5	-0.28	-0.06	-0.19
10	-0.22	-0.15	-0.06
15	-0.06	-0.29	-0.13
20	-0.27	-0.43	-0.08
25	-0.52	-0.48	-0.29

[a] *Standard uncertainties u are u(T) = 0.02 K, u(ΔG_t^0) = 0.05 kJ/mo¹ (0.68 level of confidence).*

value, small and independent of the composition of the solvent, which allows us to affirm, that $\left(E_s^{asym} - E_w^{asym} \right)$ is negligible compared to $\left(E_s^{0*} - E_w^{0*} \right)$, and thus Equation (5) may be used without any problems, although the studied cell is not exactly thermodynamic owing to the presence of the aforementioned asymmetry potential (any extra-thermodynamic assumption has been explicitly made).

Table 7 shows the values calculated for each temperature. All values of the standard Gibbs energy transfer with respect to temperature have a negative value, indicating that the transfer process is spontaneous and may promote an increase in hydration of the electrolyte in the mixture. Furthermore, in all cases, an increase in the standard Gibbs energy transfer is observed with decreasing PEG 4000 in the mixture, which may indicate an increase in hydration of electrolyte in the mixture. This relation between standard Gibbs energy and the temperature seems to be related to increased moisture PEG 4000, although there may be other causes of this behavior [34]. You may also notice that the values for a weight.% PEG Constantly, decrease with an increase in temperature. This indicates that a higher hydration electrolyte temperature increases.

To estimate the number of hydration of NaClO₄ in each case in Fig. 4 shows the ratio ΔE^o versus –k log w,
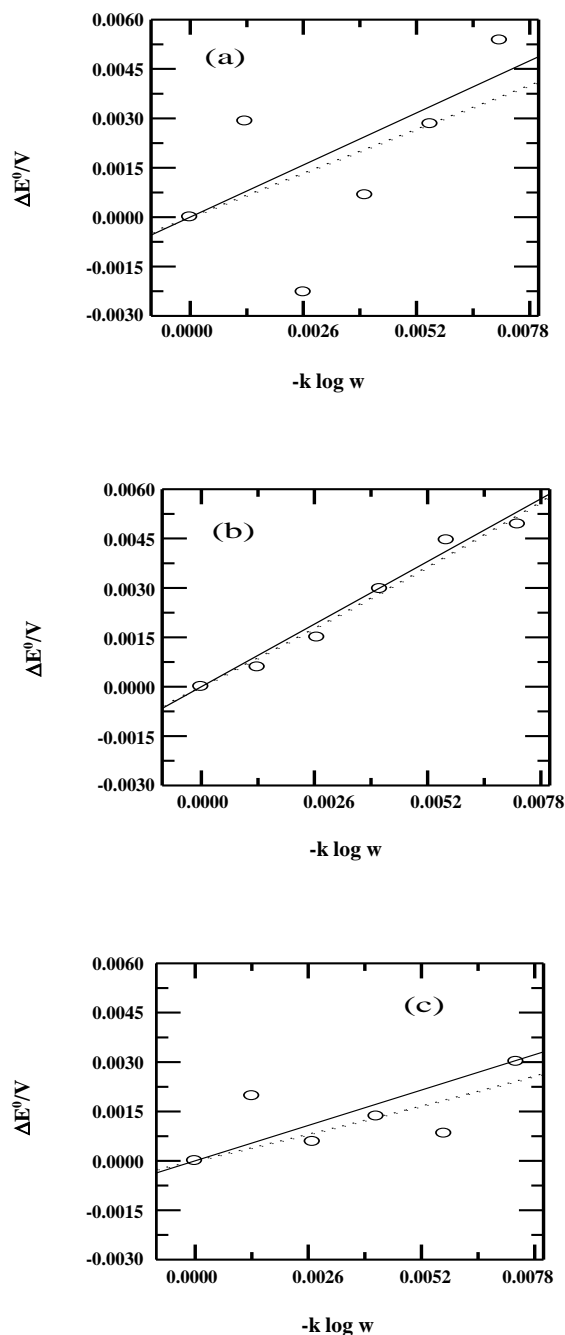
Fig. 4: Variation of ΔE⁰ with mass fraction of H₂O (w) in PEG 4000 + H₂O mixture. (a) 288.15 K; (b) 298.15 K; (c) 308.15 K.

where one can observe excellent linear correlations for all cases shown. The values found for n_{hidr} were: 0.61 ($r^2 = 0.969$) for the temperature of 288.15 K, 0.98 ($r^2 = 0.973$) for the temperature of 298.15 K and 0.41 ($r^2 = 0.934$) for the temperature of 308.15 K.

CONCLUSIONS

Using the bi-ISE cell Na-ISE | NaClO₄ (m), PEG 4000 (Y), H₂O (100 − Y) | ClO₄-ISE, we have determined the mean ionic activity coefficients of NaClO₄ in water at (288.15, 298.15, and 308.15) K from cell potential measurements. A good fit of the experimental data was obtained with the used of Pitzer and Debye−Hückel.

The activity coefficients obtained in this study at 298.15 K were contrasted with the literature and they made a good agreement, which allows affirming the correct experimental method developed in this work.

An excellent behaviour of the electrodes used, in spite of the broad range of concentrations employed in the study, is observed.

The variability of the hydration number with temperature may be due to effect of the values of ΔG_t^0 calculated for each temperature.

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