Activity Coefficients of $NaNO_3$ in Poly(ethylene glycol) 4000 + Water Mixtures at (288.15, 298.15, and 308.15) K

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The potential difference of the cell containing two ion-selective electrodes (ISE), Na-ISE|$NaNO_3(m)$, PEG 4000(w), $H_2O(1 - w)$|NO_3-ISE, has been measured at temperatures of (288.15, 298.15, and 308.15) K as a function of the mass fraction w of poly(ethylene glycol) 4000 (PEG 4000) in a mixed solvent. w was varied between 0 and 0.25 in 0.05-unit steps, and the molality of the electrolyte (m) was between (0.004 and 5.800) $mol \cdot kg^{-1}$, approximately. The values of the standard potential difference, E^0, were determined 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 E^0 was determined, the mean ionic activity coefficients for $NaNO_3$ were calculated.

Introduction

Experimental values of mean ionic 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).[1−5] 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.[2,3,6,7] Additionally, this thermodynamic property together with others, such as solvent activity, osmotic coefficient, and 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 are no experimental studies to measure the mean ionic activity coefficient of electrolyte in salt + water + polymer systems, except for the NaCl + H_2O + poly(ethylene glycol) 4000 (PEG 4000) system.[8] However, there are several articles reporting water activity, and the majority of these were carried out at 298.15 K,[9−14] except those conducted by Sadeghi et al., who measured water activity at different temperatures.[7,15]

In the present work, experimental values were determined for the mean ionic activity coefficient of $NaNO_3$ in the PEG 4000 + H_2O mixture at temperatures of (288.15, 298.15, and 308.15) K, using an experimental methodology similar to earlier work carried out by our group.[8,16] We are interested in studying this system given that in the process of $NaNO_3$ crystallization from aqueous solutions derived from the lixiviation of natural nitrate (caliche) perchlorate ions are present as impurities. With of the objective of developing a method for eliminating these impurities prior to crystallization, our group has carried out studies of the partition of $NaClO_4$ and $KClO_4$ at (288.15, 298.15, and 308.15) K with good results, using the aqueous two-phase system generated by the addition of PEG 4000 to the aqueous dissolution of sodium nitrate. Other electrolytes, such as NaCl, KCl, and LiCl, have also been partitioned using the ATPS formed by $NaNO_3$ + H_2O + PEG 4000. Given that it is relevant to know the thermodynamic properties of the electrolytes involved to model the partition of these salts, we have programmed a series of experimental studies to determine mean ionic activity coefficient of electrolytes in water + PEG medium. The present work has the objective of obtaining experimental information associated with the $NaNO_3$ + H_2O + PEG 4000 system.

Experimental Section

Sodium nitrate (Merck pro analysi, 99.5 %) was vacuum-dried at 373 K for 2 days before use. Afterward, it was stored over silica gel in desiccators and used without further purification. Analytical grade (Fluka) poly(ethylene glycol), with an average molar mass of 4000 (PEG 4000) and a minimum purity of 99 %, was also used without further purification.

For each set of experiments (corresponding to a mass fraction of PEG 4000), working solutions were obtained by adding successive known masses of solid $NaNO_3$ to a solution previously prepared of PEG 4000 and bidistilled water ($\kappa < 10^{-6}$ $S \cdot cm^{-1}$). The uncertainties in the electrolyte molality and mass fraction of PEG are evaluated to be about 0.2 %. The solutions were continually stirred with a magnetic stirrer, and the temperature was controlled at ± 0.03 K. The potential difference measurements were carried out with a 614 Keithley electrometer having inner impedance greater than $5 \cdot 10^{13}$ Ω with a resolution of ± 0.1 mV. Depending on the mass fraction of PEG in the mixture, the potential difference uncertainty can be estimated between (0.1 and 0.4) mV, approximately.

Results

Mean ionic activity coefficient values for $NaNO_3$ in PEG 4000 + water mixtures were determined from the potential difference measurements of the following bi-ISE cells without transference

$$\text{Na-ISE}|NaNO_3(m),\ \text{PEG 4000}(w),\ H_2O(1 - w)|NO_3\text{-ISE} \qquad (1)$$

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Table 1. Experimental Potential Difference (E) and Mean Ionic Activity Coefficients (γ) at Different $NaNO_3$ Molality (m) and Mass Fraction of PEG 4000 (w) in the PEG 4000 + Water Mixture at (288.15, 298.15, and 308.15) K

T = 288.15 K								
w = 0			w = 0.05			w = 0.10		
m / mol·kg^{-1}	$-E$ / mV	γ	m / mol·kg^{-1}	$-E$ / mV	γ	m / mol·kg^{-1}	$-E$ / mV	γ
0.0436	132.5	0.8186	0.0212	101.7	0.8337	0.0162	95.7	0.8556
0.0856	162.4	0.7683	0.0488	140.3	0.7970	0.0456	142.1	0.7870
0.1446	185.2	0.7254	0.0871	166.3	0.7600	0.0783	166.0	0.7478
0.2517	208.9	0.6766	0.1817	198.2	0.6997	0.1421	191.9	0.6998
0.4333	231.9	0.6292	0.3052	220.4	0.6559	0.2660	218.3	0.6417
0.6881	250.5	0.5798	0.5321	243.3	0.6010	0.4849	243.3	0.5870
1.2038	272.7	0.5219	0.8907	264.1	0.5495	0.8982	267.5	0.5199
1.8822	289.5	0.4707	1.4779	283.3	0.4905	1.4453	285.2	0.4641
2.9177	305.4	0.4204	2.2526	298.6	0.4401	2.2179	301.4	0.4213
4.3539	319.3	0.3744	3.3150	312.3	0.3958	3.2601	314.9	0.3778
6.0667	330.6	0.3386	4.5696	323.2	0.3589	4.5135	325.8	0.3411
			6.1187	333.0	0.3276			

w = 0.15			w = 0.20			w = 0.25		
m / mol·kg^{-1}	$-E$ / mV	γ	m / mol·kg^{-1}	$-E$ / mV	γ	m / mol·kg^{-1}	$-E$ / mV	γ
0.0144	93.2	0.8462	0.0206	109.5	0.8172	0.0224	122.3	0.8028
0.0382	136.6	0.7741	0.0540	152.8	0.7568	0.0627	166.3	0.7065
0.0792	168.2	0.7127	0.1000	177.9	0.6824	0.1135	191.5	0.6537
0.1292	189.3	0.6724	0.1808	205.5	0.6640	0.2034	215.9	0.6009
0.2469	216.2	0.6103	0.2990	227.0	0.6231	0.3509	238.4	0.5519
0.4402	239.7	0.5536	0.5324	251.2	0.5743	0.5563	256.9	0.5083
0.8606	266.3	0.4880	0.9173	272.9	0.5196	0.8920	275.4	0.4629
1.3957	284.7	0.4384	1.4209	289.6	0.4721	1.4699	294.4	0.4144
2.0631	299.8	0.4040	2.1360	304.5	0.4260	2.1774	308.4	0.3725
2.8091	310.8	0.3716	3.1232	317.8	0.3824	2.9949	319.3	0.3385
3.8248	321.2	0.3376	4.4594	329.4	0.3396	4.2287	330.4	0.3008
4.9746	329.7	0.3089						

T = 298.15 K								
w = 0			w = 0.05			w = 0.10		
m / mol·kg^{-1}	$-E$ / mV	γ	m / mol·kg^{-1}	$-E$ / mV	γ	m / mol·kg^{-1}	$-E$ / mV	γ
0.0037	17.8	0.9540	0.0100	63.0	0.8525	0.011	78.0	0.8784
0.0253	108.2	0.8415	0.0321	120.1	0.8240	0.034	128.4	0.8036
0.0623	150.2	0.7875	0.0709	157.3	0.7826	0.0704	161.4	0.7550
0.1284	183.1	0.7355	0.1434	189.7	0.7373	0.1771	203.0	0.6873
0.2381	210.7	0.6869	0.2665	217.5	0.6897	0.3421	232.2	0.6363
0.4169	235.2	0.6389	0.4604	241.5	0.6439	0.5657	253.8	0.5915
0.7903	262.4	0.5792	0.8642	268.2	0.5837	0.9912	277.4	0.5401
1.3150	283.4	0.5288	1.4204	288.6	0.5330	1.5666	295.7	0.4919
2.2084	304.0	0.4745	2.0439	303.1	0.4944	2.3880	312.0	0.4464
3.3411	319.7	0.4287	2.8232	315.1	0.4545	3.4812	326.0	0.4047
4.9953	334.3	0.3835	4.4308	331.8	0.4038	5.2076	340.0	0.3575
7.3231	347.8	0.3422	6.4394	344.6	0.3585			

w = 0.15			w = 0.20			w = 0.25		
m / mol·kg^{-1}	$-E$ / (mV)	γ	m / mol·kg^{-1}	$-E$ / mV	γ	M / mol·kg^{-1}	$-E$ / mV	γ
0.012	88.4	0.8829	0.0056	54.8	0.9263	0.0140	105.5	0.8476
0.0412	143.8	0.7727	0.0267	124.6	0.7845	0.0376	148.3	0.7383
0.0749	170.2	0.7179	0.0694	167.8	0.7124	0.0738	177.7	0.6759
0.1451	199.4	0.6633	0.1413	199.6	0.6587	0.1451	207.2	0.6182
0.2612	225.2	0.6156	0.2573	226.0	0.6118	0.2638	233.2	0.5706
0.4826	251.3	0.5603	0.4631	251.4	0.5635	0.5157	261.7	0.5148
1.0602	284.4	0.4930	0.8480	276.8	0.5103	0.8899	284.3	0.4679
1.7817	304.9	0.4412	1.4041	297.2	0.4626	1.4021	302.6	0.4275
2.5526	318.4	0.4029	2.1445	313.7	0.4207	2.0497	317.2	0.3910
3.6355	331.1	0.3643	3.0110	326.3	0.3850	2.8478	329.1	0.3567
4.8605	340.9	0.3311	4.2970	338.5	0.3440	4.0226	341.0	0.3200

Table 1. Continued

$T = 308.15$ K

$w = 0$			$w = 0.05$			$w = 0.10$		
m	$-E$		m	$-E$		m	$-E$	
$\text{mol}\cdot\text{kg}^{-1}$	mV	γ	$\text{mol}\cdot\text{kg}^{-1}$	mV	γ	$\text{mol}\cdot\text{kg}^{-1}$	mV	γ
0.0071	43.0	0.9821	0.0083	57.0	0.9459	0.0044	33.0	0.9932
0.0172	83.6	0.8841	0.0247	108.4	0.8451	0.0208	104.6	0.8292
0.0348	117.4	0.8314	0.0501	140.3	0.7647	0.0584	153.4	0.7486
0.0773	155.9	0.7782	0.0962	172.5	0.7347	0.1396	194.0	0.6792
0.1982	201.1	0.7175	0.1945	205.5	0.6814	0.2547	221.8	0.6319
0.4250	236.5	0.6566	0.3037	226.1	0.6460	0.4604	248.9	0.5857
0.7504	261.9	0.6032	0.6189	258.2	0.5842	0.8428	275.7	0.5330
1.1624	281.4	0.5646	0.9797	278.5	0.5431	1.2598	293.0	0.4957
1.8598	301.4	0.5164	1.4597	295.5	0.5039	1.8937	310.0	0.4558
2.8747	319.1	0.4680	2.1450	311.4	0.4642	2.7527	324.9	0.4164
4.2790	334.8	0.4240	3.3274	328.8	0.4168	4.1399	340.2	0.3705
6.3630	349.5	0.3772	4.8079	342.6	0.3751			

$w = 0.15$			$w = 0.20$			$w = 0.25$		
m	$-E$		m	$-E$		m	$-E$	
$\text{mol}\cdot\text{kg}^{-1}$	mV	γ	$\text{mol}\cdot\text{kg}^{-1}$	mV	γ	$\text{mol}\cdot\text{kg}^{-1}$	mV	γ
0.0059	54.2	0.9573	0.0102	82.1	0.8526	0.0339	152.3	0.7074
0.0244	118.7	0.7846	0.0244	121.2	0.7484	0.1054	196.2	0.5249
0.0509	152.3	0.7143	0.0589	161.8	0.6717	0.1797	222.1	0.5041
0.1235	193.1	0.6395	0.1007	186.5	0.6286	0.3247	248.2	0.4586
0.2284	220.8	0.5862	0.2028	218.6	0.5753	0.6304	276.3	0.4034
0.4581	252.3	0.5325	0.3693	246.0	0.5323	0.9889	296.5	0.3778
0.8455	279.1	0.4805	0.6543	271.6	0.4893	1.3498	308.0	0.3445
1.3800	300.2	0.4400	1.0455	292.0	0.4516	1.9084	324.8	0.3355
2.0414	316.4	0.4049	1.6366	311.0	0.4142	2.6237	337.7	0.3120
2.8228	329.2	0.3737	2.4142	326.7	0.3787			
4.0476	342.3	0.3344	3.3123	338.4	0.3449			

Table 2. Pitzer Parameters β^0, β^1, and C^ϕ in Function of Temperature for the $NaNO_3 + H_2O$ System

T	β^0	β^1	$10^2\cdot C^\phi$
K	$\text{kg}\cdot\text{mol}^{-1}$	$\text{kg}\cdot\text{mol}^{-1}$	$\text{kg}^2\cdot\text{mol}^{-2}$
288.15	−0.00383	0.15888	0.04405
298.15	0.00345	0.23760	−0.00967
308.15	0.00926	0.30729	−0.04770

In these cells, m is the molality of $NaNO_3$ (moles of $NaNO_3$/kg of mixed solvent) in the working solution in the mixed solvent, and w is the mass fraction of PEG 4000 in the mixture.

Applying the Nernst−Nikolsky equation,[17,18] the following expression is obtained

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

where E, m, and γ are the potential difference of the cell, the molality, and the stoichiometric mean ionic activity coefficient of $NaNO_3$, respectively, whereas $k = (\ln 10)RT/F$ is the Nernst theoretical slope (R, T, and F stand for the gas constant, the absolute temperature, and the Faraday constant, respectively). E^{0*} is the apparent standard potential (molal scale) of the cell and contains the potential of asymmetry of both selective electrodes. In general, we have verified[19,20] 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 1 shows E values for different temperatures and different mixtures of PEG 4000 + water as a function of $NaNO_3$ molality. Since the mean ionic activity coefficients of $NaNO_3$ in pure water are well-known for each temperature,[21] the values of E that appear in Table 1 for zero mass fraction of PEG 4000 allow for carrying out a calibration of the electrode system using eq 2. The parameters of the Pitzer model used in this calibration (with $\alpha = 2\ \text{kg}^{1/2}\cdot\text{mol}^{-1/2}$) are shown in Table 2. These parameters were obtained by correlating the values of β^0, β^1, and C^ϕ as reported by Wijesinghe and Rard[21] between (273.15 and 423.15) K for the $NaNO_3 + H_2O$ system.

A very good linear relationship is obtained when E vs $-2 \log m\gamma$ is plotted at each temperature studied. The k values obtained, when applying a least-squares regression analysis to the previous plots, were (56.27 ± 0.08, 57.83 ± 0.10, and 60.46 ± 0.10) mV at (288.15, 298.15, and 308.15) K, respectively, with correlation coefficients greater than 0.9999 in all cases. The standard deviations were (0.3, 0.4, and 0.4) mV at (288.15, 298.15, and 308.15) K, respectively. These values are more than acceptable levels for a system containing two ion-selective electrodes. In these calculations, it has been assumed that $k_{Na} \cong k_{NO_3} \cong k \cong (k_{Na} + k_{NO_3})/2$.

Once the electrodes have been calibrated and found to be operating correctly, the next very important step is the determination of E^{0*} for each temperature studied. The determination of E^{0*} was carried out following a method similar to that proposed by Hitchcock[22] and using the extended Debye−Hückel and Pitzer equations to represent the dependency of $\log \gamma$ on concentration. For 1:1 electrolytes, these equations may be written as:

- Extended Debye−Hückel equation[23]

$$\log \gamma = -\frac{A\sqrt{m}}{1 + Ba\sqrt{m}} + cm + dm^2 - \log(1 + 0.002mM) + \text{Ext} \qquad (3)$$

Table 3. Summary of Both Standard Potential Difference and the Parameter Values Obtained for the Extended Debye−Hückel and Pitzer Equations, in Different *w*PEG 4000 + (1 − *w*)Water Mixtures at (288.15, 298.15, and 303.15) K

	E^{0*}	a	c	d	σ^a	E^{0*}	$\beta^{(0)}$	$\beta^{(1)}$	C^γ	σ	$<E^{0*}>$
w	mV	Å	$kg\cdot mol^{-1}$	$kg^2\cdot mol^{-2}$	mV	mV	$kg\cdot mol^{-1}$	$kg\cdot mol^{-1}$	$kg^2\cdot mol^{-2}$	mV	mV
						288.15 K					
0	−295.4	3.58	−0.01988	0.00129	0.1	−295.5	−0.00383	0.15888	0.00066	0.2	−295.4 ± 0.1
0.05	−299.1	4.34	−0.02826	0.00101	0.2	−299.0	−0.00805	0.36631	0.00156	0.1	−299.0 ± 0.1
0.10	−304.8	4.24	−0.02824	0.00154	0.1	−304.7	0.00082	0.38438	0.00009	0.1	−304.7 ± 0.1
0.15	−308.8	3.86	−0.01906	0.00266	0.2	−308.7	0.02871	0.36156	−0.00615	0.2	−308.7 ± 0.1
0.20	−308.9	5.80	−0.02881	−0.00594	0.1	−309.3	0.00543	0.80616	0.00112	0.2	−309.1 ± 0.3
0.25	−318.5	4.53	−0.03428	0.00505	0.4	−318.7	0.03461	0.58663	−0.00718	0.2	−318.7 ± 0.1
						298.15 K					
0	−301.7	3.72	−0.01416	0.00029	0.5	−301.6	0.00345	0.23760	−0.00014	0.5	−301.7 ± 0.0
0.05	−302.6	5.25	−0.01810	−0.00257	0.3	−302.6	0.00141	0.51135	0.00001	0.3	−302.6 ± 0.0
0.10	−308.8	5.02	−0.01747	−0.00222	0.2	−308.8	0.01283	0.55232	−0.00195	0.2	−308.8 ± 0.0
0.15	−316.9	4.93	−0.02110	−0.00053	0.3	−317.1	0.03171	0.61524	−0.00589	0.2	−317.0 ± 0.2
0.20	−318.5	5.97	−0.02393	−0.00728	0.1	−319.3	0.03258	0.91355	−0.00408	0.2	−318.9 ± 0.6
0.25	−328.0	5.35	−0.02263	0.00035	0.3	−328.6	0.05033	0.94229	−0.00826	0.1	−328.3 ± 0.4
						308.15 K					
0	−303.4	4.59	−0.01639	0.00107	0.3	−303.6	0.00926	0.30729	−0.00072	0.5	−303.5 ± 0.1
0.5	−311.6	4.24	−0.01077	0.00035	0.3	−311.6	0.02062	0.36168	−0.00471	0.3	−311.6 ± 0.0
0.10	−317.6	4.97	−0.01463	0.00040	0.2	−317.9	0.03238	0.60723	−0.00644	0.2	−317.7 ± 0.2
0.15	−326.2	4.72	−0.00155	−0.00154	0.3	−326.6	0.06269	0.76353	−0.01275	0.2	−326.4 ± 0.2
0.20	−330.8	6.18	−0.01300	−0.00070	0.2	−332.0	0.06410	1.37033	−0.00809	0.2	−331.4 ± 0.9
0.25	−347.5	4.52	0.02932	−0.00629	0.4	−349.0	0.14799	1.12768	−0.03284	0.4	−348.2 ± 1.1

[a] $\sigma = [\sum(E^{\mathrm{exptl}} - E^{\mathrm{calcd}})^2/(N - n)]^{1/2}$ where N is the number of experimental points and n is the number of adjustable parameters.

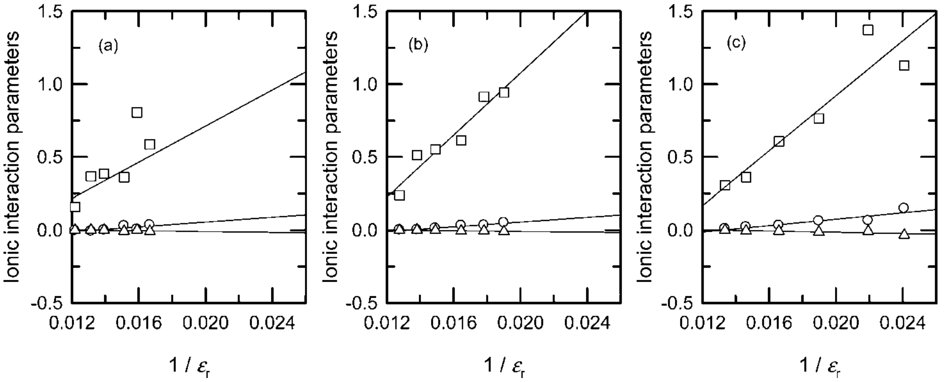

Figure 1. Plot of Pitzer parameters, ○, β^0; □, β^1; Δ, C^γ, for $NaNO_3$ in PEG 4000 + water mixtures as a function of the inverse of the relative permittivity at several temperatures: (a) 288.15 K; (b) 298.15 K; and (c) 308.15 K.

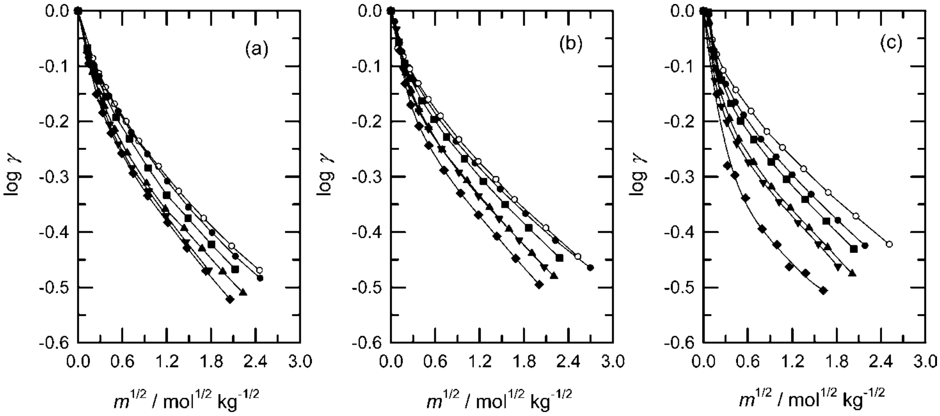

Figure 2. Plot of log γ vs $m^{1/2}$ for $NaNO_3$ in PEG 4000 + water at (a) 288.15 K, (b) 298.15 K, and (c) 308.15 K, for different mass fractions of PEG 4000: ○, 0.00; ●, 0.05; ■, 0.10; ▲, 0.15; ▼, 0.20; ♦, 0.25.

where *a* is the ion size parameter; *c* and *d* are the ion-interaction parameters; *M* is the average molecular mass of mixed solvent; and Ext is the contribution of the extended terms. *A* and *B* are the Debye−Hückel constants given by

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

$$B = 50.2901\rho^{1/2}/(\varepsilon_r T)^{1/2}\ \mathrm{kg^{1/2}\cdot mol^{-1/2}\cdot Å^{-1}} \qquad (3b)$$

where ρ, ε_r, and T stand for the density, the relative permittivity (static dielectric constant) of the solvent, and the temperature, respectively. An additional parameter, *d*, has been included in the eq 3 to cover the entire concentration range studied.

- Pitzer equation[24]

$$\ln \gamma = f^{\gamma} + B^{\gamma} m + C^{\gamma} m^2 \tag{4}$$

where

$$f^{\gamma} = -A_{\phi}\left[\frac{\sqrt{m}}{1 + b\sqrt{m}} + \frac{2}{b}\ln(1 + b\sqrt{m})\right] \tag{4a}$$

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

In these equations α and b are assumed to be constant with values of 2.0 and 1.2 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$, respectively, both in water and in PEG 4000 + water mixtures; β^0, β^1; and C^{γ} are solute-specific interaction parameters; and A_{ϕ} is the Debye−Hückel constant for the osmotic coefficients defined by

$$A_{\phi} = 1.4006\cdot 10^6 \rho^{1/2}/(\varepsilon_r T)^{3/2}\ \text{kg}^{1/2}\cdot\text{mol}^{-1/2} \tag{4c}$$

where all symbols have their usual meaning.

The values of the physical properties (ρ and ε_r) and the average molecular mass (M) of the mixture (PEG 4000 + water), together with the values of the constants A, B, and A_{ϕ}, are shown elsewhere.[8]

By combining eqs 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 interaction parameters of each model. These values are presented in Table 3, as well as the corresponding standard deviation of the fit.

Discussion

As can be observed in Table 3, the values of E^{0*} obtained with the studied models are in good agreement, and the standard deviations of the adjustments (σ) are also comparable. The two models require the same number of adjustable parameters. It was observed that for the different PEG + water mixtures parameter a of the extended Debye−Hückel equation has higher values than those obtained in pure water. This behavior is verified at the three studied temperatures. As well, the values of a (both in pure water and in PEG + water mixtures) are always higher than the sum of the Na^+ and NO_3^- radii,[25] i.e., 2.84 Å, which can be explained by ion solvation.

The values of β^0, β^1, and C^{γ} obtained in the fit using the Pitzer model are outlined in Figure 1 versus the reciprocal value of the relative permittivity of the PEG 4000 + water mixture, for the three studied temperatures. We can observe from the figure that the parameters generally present a linear tendency with $1/\varepsilon_r$, the NaNO_3 following a behavior similar to that observed with NaCl in the PEG 4000 + H_2O mixture.[8]

The average values for E^{0*}, which appear in the last column of Table 3, were calculated considering the studied models. These average values were used for calculating the mean ionic activity coefficients γ, which are shown in Table 1 for different molalities of NaNO_3 and mass fractions of PEG 4000 at the three studied temperatures. Using Pitzer parameters for aqueous solutions of sodium nitrate at 298.15 K,[24] the mean ionic activity coefficient values for the molalities of this work were calculated (from (0.03 to 4.99) $\text{mol}\cdot\text{kg}^{-1}$ because the parameters reported[24] are valid up to a molality of 6 $\text{mol}\cdot\text{kg}^{-1}$). Comparing these calculated values with our experimental values (at $w = 0$) gives an absolute mean deviation of 0.005. A similar procedure was done with the Pitzer parameters reported by El Guendouzi and Marouani.[26] The absolute mean deviation obtained was 0.003.

Figure 2 show log γ vs $m^{1/2}$ for the three temperatures and for the six studied mass fractions of PEG 4000. It can be observed in the figure that for a fixed concentration of NaNO_3 the log γ values decrease with the increase of PEG 4000. As it is already known, to explain the variation of log γ vs $m^{1/2}$ in electrolyte solutions, two kinds of interactions are taken into account: ion−ion (tends to decrease log γ values) and ion−solvent (tends to increase log γ values) interactions. In accordance with the preceding behavior, it can be assumed that the ion−ion interactions are much more significant than the ion−solvent interactions when the PEG 4000 concentration increases.

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