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Activity Coefficients of NaBF_4 in PEG4000 + Water Mixtures at (288.15, 298.15, and 308.15) K

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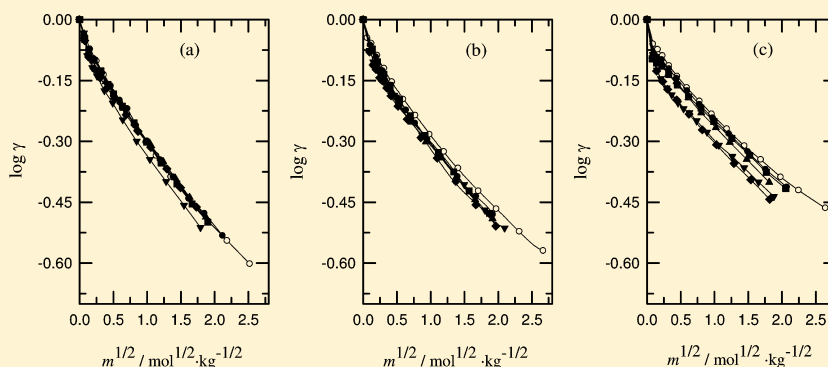
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ABSTRACT: The electromotive force of the cell containing two ion-selective electrodes (ISEs), $\text{Na-ISE}|\text{NaBF}_4(m), \text{PEG4000}(Y), \text{H}_2\text{O}(100 - Y)|\text{BF}_4\text{-ISE}$, has been measured at temperatures of (288.15, 298.15, and 308.15) K as a function of the weight percentage Y of PEG4000 (poly(ethylene glycol) 4000) in a mixed solvent. Y was varied between (0 and 25) % in five-unit steps, and the molality of the electrolyte (m) was between ca. (0.04 and 7) $\text{mol} \cdot \text{kg}^{-1}$. The values of standard electromotive force were determined using routine methods of extrapolation, together with Debye–Hückel and Pitzer equations. The results obtained produced good internal consistency for all of the temperatures studied. Once the standard electromotive force was determined, calculations were made of the mean ionic activity coefficients for NaBF_4 , the Gibbs energy of transfer from the water to the PEG4000–water mixture, and the primary NaBF_4 hydration number.

1. INTRODUCTION

Experimental values of activity coefficients of electrolytes in salt + water + polymer systems are important in studies oriented to the prediction of the liquid–liquid equilibrium of aqueous two-phase systems (ATPS's).^{1–5} In addition, they are relevant to the development of thermodynamic models and for the design, operation, and optimization of separation processes that involve ATPS's.^{2,3,6,7}

Activity coefficients are normally determined via one of two methods: electromotive force (emf) measurements of galvanic cells or isopiestic vapor pressure measurements. With the first method the determination is direct, while with the second method water activity is determined experimentally (the osmotic coefficient). The Gibbs–Duhem equation may also be used to obtain the value of the electrolyte activity coefficient.^{8–14}

Owing to the lack of bibliographic information on mean ionic activity coefficients of electrolytes in poly(ethylene glycol) (PEG) + H_2O , previous works^{15–25} have studied systems containing (NaCl , LiCl , KCl , NaNO_3) + PEG4000 + H_2O at temperatures of (288.15, 298.15, and 308.15) K, using an experimental methodology (measurement of the electromotive force, emf, of electrochemical cells containing two ion-selective electrodes without transport).

In this report, we present the corresponding study for a system of NaBF_4 + PEG4000 + H_2O . Since various salt beds in northern Chile contain boron, a fact which has driven our interest in studying the properties of some systems that contain boron compounds in recent years,^{26,27} the current study was

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Table 1. Experimental Electromotive Force E and Mean Ionic Activity Coefficients γ at Different NaBF_4 Molality and PEG4000 wt % in the PEG4000–Water Mixture at (288.15, 298.15, and 308.15) K

m mol·kg ⁻¹	$-E$ mV	γ	m mol·kg ⁻¹	$-E$ mV	γ	m mol·kg ⁻¹	$-E$ mV	γ
288.15 K								
0 wt %			5 wt %			10 wt %		
0.0052	61.4	0.9152	0.0047	58.1	0.8965	0.0056	69.3	0.8927
0.0250	133.5	0.8439	0.0191	122.7	0.8408	0.0184	124.2	0.8406
0.0649	176.3	0.7889	0.0464	163.1	0.7990	0.0465	166.0	0.7932
0.1308	206.4	0.7301	0.1135	202.3	0.7373	0.0991	199.6	0.7473
0.2120	226.3	0.6807	0.2150	229.6	0.6853	0.1739	223.0	0.6917
0.3616	247.8	0.6233	0.3579	250.2	0.6311	0.2534	238.6	0.6561
0.4929	259.8	0.5866	0.5059	264.6	0.6020	0.3988	257.1	0.6117
0.6851	272.3	0.5469	0.7064	276.1	0.5472	0.6509	276.2	0.5570
0.9767	284.9	0.4982	1.0036	288.8	0.5013	0.9886	291.0	0.4985
1.2928	294.7	0.4612	1.4352	300.9	0.4505	1.4585	304.1	0.4434
1.8344	305.8	0.4092	1.9395	310.7	0.4085	2.0680	315.2	0.3936
2.6303	317.2	0.3615	2.6458	320.0	0.3631	2.7773	323.9	0.3511
3.6518	326.8	0.3177	3.4425	328.4	0.3322	3.6028	331.5	0.3168
4.7942	334.6	0.2845	4.5053	335.3	0.2929			
6.3720	342.0	0.2496						
15 wt %			20 wt %			25 wt %		
0.0045	60.0	0.9216	0.0040	61.3	0.9264	0.0057	78.3	0.8877
0.0164	117.9	0.8321	0.0132	112.3	0.8145	0.0180	129.4	0.8078
0.0396	158.0	0.7921	0.0351	156.2	0.7607	0.0470	172.6	0.7569
0.0797	188.5	0.7414	0.0670	185.2	0.7265	0.0928	202.8	0.7180
0.1501	216.5	0.7034	0.1349	214.9	0.6680	0.1643	227.6	0.6778
0.2566	239.0	0.6563	0.2395	239.2	0.6226	0.2734	249.3	0.6390
0.4234	259.2	0.6047	0.4081	260.3	0.5660	0.4734	271.3	0.5825
0.7238	279.4	0.5378	0.7165	281.6	0.5015	0.7534	289.2	0.5305
1.1059	295.5	0.4915	1.0796	296.4	0.4524	1.1112	303.5	0.4839
1.5299	306.6	0.4473	1.6471	310.7	0.3989	1.6706	317.3	0.4285
2.0039	315.1	0.4073	2.3906	322.2	0.3489	2.2348	326.2	0.3853
2.6568	323.4	0.3649	3.2153	330.4	0.3075	2.9943	335.0	0.3451
3.4891	331.1	0.3260						
298.15 K								
0 wt %			5 wt %			10 wt %		
0.0042	43.1	0.8993	0.0116	97.7	0.8636	0.0182	-122.4	0.8455
0.0155	107.2	0.8723	0.0378	153.7	0.8070	0.0437	-162.8	0.7869
0.0447	157.3	0.8147	0.0843	190.2	0.7466	0.0927	-197.1	0.7328
0.0986	193.4	0.7569	0.1607	218.6	0.6885	0.1576	-220.6	0.6872
0.1846	221.1	0.7004	0.2696	240.9	0.6389	0.2906	-247.3	0.6334
0.3550	249.1	0.6349	0.4034	257.8	0.5970	0.4886	-269.0	0.5794
0.6032	271.2	0.5794	0.5966	273.8	0.5546	0.8332	-290.2	0.5175
0.9718	289.8	0.5202	0.9103	290.4	0.5053	1.2407	-305.4	0.4699
1.4410	304.7	0.4715	1.3270	304.5	0.4585	1.7975	-318.6	0.4215
1.9872	316.2	0.4296	1.9622	318.5	0.4094	2.4562	-328.9	0.3784
2.9231	329.1	0.3773	2.8064	330.9	0.3661	3.5040	-340.4	0.3332
3.9055	338.6	0.3410	3.7041	339.7	0.3303			
5.3721	348.2	0.2999						
7.1339	357.0	0.2689						
15 wt %			20 wt %			25 wt %		
0.0167	122.2	0.8336	0.0097	99.3	0.8392	0.0090	99.3	0.8322
0.0491	172.0	0.7620	0.0220	137.5	0.7869	0.0217	139.6	0.7729
0.0943	201.6	0.7138	0.0385	164.6	0.7692	0.0364	164.4	0.7529
0.1718	228.3	0.6655	0.0617	186.0	0.7342	0.0595	186.9	0.7187
0.2850	250.3	0.6206	0.0995	208.1	0.7061	0.0795	200.6	0.7069
0.5085	274.2	0.5591	0.1505	226.6	0.6745	0.1217	220.0	0.6786
0.8638	295.2	0.4993	0.2098	241.5	0.6501	0.1714	235.0	0.6485
1.3385	312.7	0.4560	0.3807	267.4	0.5989	0.2672	254.4	0.6114
1.8967	324.7	0.4083	0.5001	278.3	0.5661	0.4270	274.3	0.5680
2.7502	337.1	0.3602	0.7633	295.3	0.5197	0.7315	296.2	0.5120

Table 1. continued

m mol·kg ⁻¹	$-E$ mV	γ	m mol·kg ⁻¹	$-E$ mV	γ	m mol·kg ⁻¹	$-E$ mV	γ
15 wt %			20 wt %			25 wt %		
3.6695	346.2	0.3234	1.2804	315.3	0.4608	1.2035	315.4	0.4556
			2.2333	335.2	0.3921	1.8862	331.4	0.3993
			3.2409	346.7	0.3395	2.7887	344.4	0.3496
			4.3871	356.8	0.3065	3.8619	354.7	0.3097
			308.15 K					
0 wt %			5 wt %			10 wt %		
0.0088	79.2	0.8684	0.0090	80.0	0.8181	0.0064	62.6	0.8004
0.0263	134.0	0.8425	0.0239	129.2	0.8063	0.0190	117.4	0.7824
0.0544	169.3	0.8130	0.0502	166.5	0.7948	0.0478	163.8	0.7684
0.1091	202.1	0.7682	0.1087	203.4	0.7544	0.1027	200.5	0.7323
0.2028	230.8	0.7235	0.1955	230.7	0.7148	0.2000	231.6	0.6898
0.3526	255.8	0.6780	0.3587	258.2	0.6665	0.3788	260.9	0.6452
0.6151	280.4	0.6281	0.6046	281.0	0.6169	0.6359	284.2	0.6056
0.9257	297.6	0.5838	0.9570	300.6	0.5714	0.9816	302.5	0.5607
1.4079	314.8	0.5370	1.4768	318.2	0.5221	1.5745	321.8	0.5095
2.0936	330.2	0.4877	2.2375	334.3	0.4718	2.3092	336.5	0.4628
2.8551	342.1	0.4512	3.0957	345.8	0.4268	3.1206	347.0	0.4204
3.9412	353.5	0.4083	4.3075	357.6	0.3862	4.2245	357.8	0.3834
5.0621	362.5	0.3789						
7.0063	374.0	0.3426						
15 wt %			20 wt %			25 wt %		
0.0091	88.3	0.8346	0.0078	84.9	0.8206	7.6275e-3	87.3	0.8043
0.0276	142.3	0.7902	0.0212	131.6	0.7506	0.0206	134.4	0.7464
0.0503	172.2	0.7756	0.0415	163.5	0.7153	0.0535	180.3	0.7041
0.0999	204.5	0.7339	0.0850	197.5	0.6778	0.0935	206.6	0.6730
0.1923	235.9	0.7037	0.1340	218.9	0.6526	0.1925	240.5	0.6336
0.3752	265.5	0.6428	0.2106	239.7	0.6229	0.3873	272.2	0.5847
0.6451	288.8	0.5891	0.2928	254.9	0.6030	0.6721	295.9	0.5352
1.0363	308.8	0.5418	0.3958	269.2	0.5896	1.0604	314.9	0.4915
1.5064	323.7	0.4985	0.5397	282.7	0.5627	1.6592	332.4	0.4419
2.1752	337.6	0.4528	0.7927	299.1	0.5277	2.3647	345.8	0.4028
3.2823	352.0	0.3975	1.1354	313.7	0.4899	3.2989	357.2	0.3607
			1.5962	327.9	0.4597			
			2.0685	337.9	0.4312			
			2.7328	348.0	0.3975			
			3.5266	356.9	0.3665			

carried out between (288.15 and 308.15) K to approximate local conditions in this region where the annual temperature varies between (5 and 40) °C.

2. EXPERIMENTAL SECTION

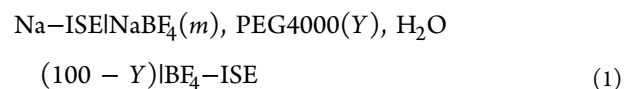
Sodium tetrafluoroborate (Aldrich pro analysis, 98 %) was vacuum-dried at 330 K for 2 days before use. It was then stored over silica gel in desiccators and used without further purification. Analytical grade (Fluka) PEG, with an average molar mass of 4000 and a minimum purity of 99 % was also used without further purification.

For each set of experiments (corresponding to a wt % of PEG4000), working solutions were obtained by adding successive known masses of solid NaBF₄ to a previously prepared solution of PEG4000 and bidistilled water ($\kappa \cdot 10^{-6}$ S·cm⁻¹). The uncertainties in the electrolyte molality and PEG wt % were ± 0.0003 and ± 0.02 , respectively. The solutions were continually stirred with a magnetic stirrer and the temperature was controlled at ± 0.03 K. The cells, apparatus, and temperature control system as well as the measurement

procedure employed in the present study have been described previously.^{16–18,23}

3. RESULTS

Mean ionic activity coefficient values for NaBF₄ in PEG4000–water mixtures were determined from the emf measurements of the following bi-ISE (ion-selective electrode) cells without transference:



In these cells, m is the molality of NaBF₄ (moles of NaBF₄/kilograms of mixed solvent) in the working solution of mixed solvent and Y the wt % of the PEG4000 in the mixture.

Applying the Nernst–Nikolsky equation,^{28,29} the following expression is obtained:

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

Table 2. Summary of Both Standard emf and the Parameter Values Obtained from the Debye–Hückel and Pitzer Equations, for Different PEG4000–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^a	$\langle E^{0*} \rangle$
wt %	mV	Å	kg·mol ⁻¹	kg ² ·mol ⁻²	mV	mV	kg·mol ⁻¹	kg·mol ⁻¹	kg ² ·mol ⁻²	mV	mV
Debye–Hückel Parameters						Pitzer Parameters					
288.15 K											
0	−320.02	3.02	−0.0378	−0.00368	0.14	−319.24	−0.0416	0.1586	0.00500	0.32	−319.63 ± 0.55
5	−321.94	4.65	−0.0678	0.00425	0.27	−321.92	−0.0510	0.3964	0.00966	0.24	−321.93 ± 0.01
10	−325.03	5.45	−0.0761	0.00338	0.17	−325.21	−0.0590	0.5693	0.01459	0.16	−325.12 ± 0.12
15	−324.68	6.20	−0.0590	−0.00521	0.10	−325.10	−0.0419	0.7952	0.00965	0.10	−324.89 ± 0.30
20	−330.78	5.17	−0.0578	0.00032	0.15	−331.13	−0.0193	0.6829	0.00317	0.18	−330.95 ± 0.25
25	−333.22	6.86	−0.0489	−0.01652	0.23	−333.61	−0.0430	1.1192	0.01527	0.15	−333.42 ± 0.25
298.15 K											
0	−321.21	3.56	−0.0369	0.00224	0.21	−324.13	−0.0224	0.1749	0.00200	0.20	−324.17 ± 0.05
5	−329.63	3.77	−0.0422	0.00347	0.12	−329.44	−0.0189	0.2656	0.00263	0.09	−329.53 ± 0.13
10	−332.54	5.03	−0.0564	0.00214	0.11	−332.63	−0.0308	0.5464	0.00765	0.13	−332.59 ± 0.06
15	−337.74	5.88	−0.0521	−0.00413	0.08	−337.74	−0.0280	0.8409	0.00909	0.14	−337.58 ± 0.22
20	−341.38	7.31	−0.0420	−0.02475	0.16	−342.39	−0.0322	1.2030	0.01165	0.19	−341.88 ± 0.71
25	−344.89	7.38	−0.0425	−0.02971	0.15	−346.48	−0.0119	1.2759	0.00850	0.31	−345.69 ± 1.13
308.15 K											
0	−329.44	4.87	−0.0253	−0.00054	0.19	−328.82	−0.0128	0.4425	0.0016	0.29	−329.13 ± 0.44
5	−331.73	5.69	−0.0287	−0.00315	0.13	−331.33	−0.0108	0.6152	0.00255	0.15	−331.53 ± 0.28
10	−332.78	6.98	−0.0170	−0.01646	0.17	−333.41	−0.0038	0.9390	0.00297	0.17	−333.09 ± 0.45
15	−337.88	7.88	−0.0003	−0.04211	0.08	−338.87	0.0056	1.3341	0.00318	0.09	−338.38 ± 0.70
20	−342.12	8.81	0.0145	−0.09196	0.20	−345.40	0.0120	1.8023	0.00804	0.31	−343.76 ± 2.32
25	−346.88	10.08	0.0418	−0.19940	0.47	−348.71	−0.0555	2.5537	0.04039	1.22	−348.30 ± 2.00

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

where E is the emf of the cell, $k = (\ln 10)RT/F$ is the Nernst theoretical slope, and m and γ are the molality and stoichiometric mean ionic coefficients of NaBF₄. E^{0*} is the apparent standard potential (molal scale) of the cell and contains the potential of asymmetry of both selective electrodes. It has been verified previously^{23,24} 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 PEG4000–water as a function of NaBF₄ molality. Since the activity coefficients of NaBF₄ in pure water are known for each temperature, the values of E that appear in Table 1 for 0 wt % of PEG4000 allow the calibration of the electrode system using eq 2. These were obtained based on the thermodynamic data reported by Galleguillos et al.³³

A very good linear relationship is obtained when E versus $-2 \log m\gamma$ is plotted at each temperature studied. The k values obtained, when applying a least-squares regression analysis to the previous plots, were $(55.51 \pm 0.06, 58.01 \pm 0.04, \text{ and } 59.17 \pm 0.09)$ 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 (0.10, 0.13, and 0.14) mV at (288.15, 298.15, and 308.15) K, respectively. These values are more than acceptable levels for a system containing two ISEs. In these calculations it has been assumed that $k_{\text{Na}} \cong k_{\text{BF}_4} \cong k \cong (k_{\text{Na}} + k_{\text{BF}_4})/2$.

Once the electrodes have been calibrated and found to be operating correctly, the next important step is to determine E^{0*} for each temperature studied. The determination of E^{0*} was carried out following a method similar to that proposed by Hitchcock³⁰ 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 the following. The extended Debye–Hückel equation is:³¹

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

with a the ion size parameter, c and d the ion-interaction parameters, M the average molecular mass of the mixed solvent, and Ext the contribution of the extended terms. A and B are the Debye–Hückel constants given by:

$$A = 1.8247 \cdot 10^6 \rho^{1/2} / (\epsilon_r T)^{3/2} \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \quad (3a)$$

$$B = 50.2901 \rho^{1/2} / (\epsilon_r T)^{1/2} \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{\AA}^{-1} \quad (3b)$$

where ρ , ϵ_r , and T stand for the density, permittivity relative (static dielectric constant) of the solvent, and the temperature, respectively. The Pitzer equation is:³²

$$\ln \gamma = f^{\gamma} + B^{\gamma}m + C^{\gamma}m^2 \quad (4)$$

where

$$f^{\gamma} = -A_{\phi}m^{1/2} / (1 + bm^{1/2}) + (2/b) \ln(1 + bm^{1/2}) \quad (4a)$$

$$B^{\gamma} = 2\beta^0 + (2\beta^1/\alpha^2m)\{1 - (1 + \alpha m^{1/2} - \alpha^2m/2)\exp(-\alpha m^{1/2})\} \quad (4b)$$

$$C^{\gamma} = 3C^{\phi}/2 \quad (4c)$$

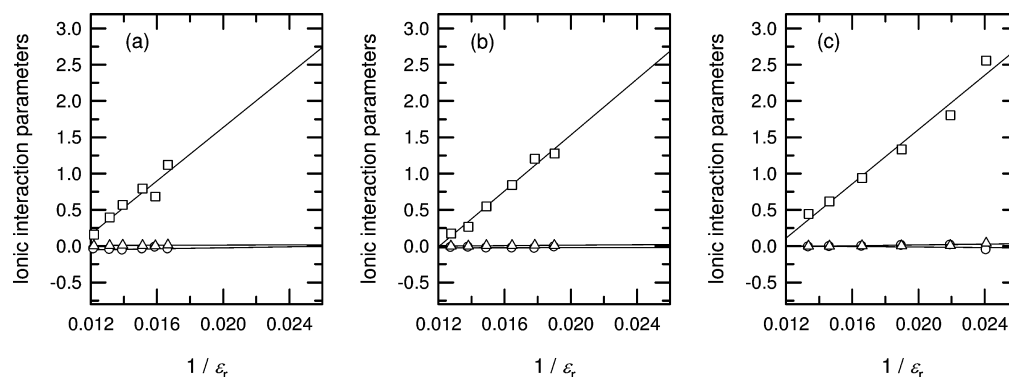


Figure 1. Plot of Pitzer parameters, β^0 , β^1 , C^ϕ , for NaBF_4 in PEG4000 + water mixtures as a function of the inverse of the relative permittivity at T/K : 288.15 (a), 298.15 (b), and 308.15 (c).

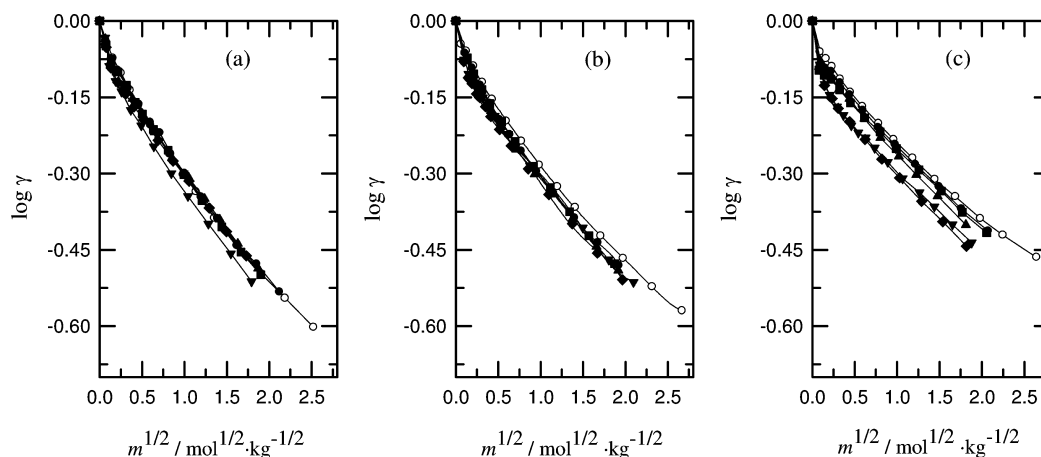


Figure 2. Plot of $\log \gamma$ vs $m^{1/2}$ for NaBF_4 in PEG4000 + water and PEG4000 different wt %: \circ , 0; \bullet , 5; \blacksquare , 10; \blacktriangle , 15; \blacktriangledown , 20; \blacklozenge , 25; at T/K : 288.15 (a), 298.15 (b), and 308.15 (c).

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 PEG4000–water mixtures; A_ϕ is the Debye–Hückel constant for the osmotic coefficients defined by:

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

where all symbols having their usual meaning. β^0 , β^1 , and C^ϕ are solute-specific interaction parameters.

By combining eqs 2 and 3 or 2 and 4, the values of E^{0*} can be optimized in accordance with the different models used and with the characteristic interaction parameters of each model. In Table 2, these values are presented along with the corresponding standard deviation of the fit.

4. DISCUSSION

As can be observed in Table 2, the values of E^{0*} obtained with the studied models are in good agreement, and the standard deviations of the adjustments are also comparable. The two models require the same number of adjustable parameters. It was observed that for the different PEG–water mixtures that parameter a of the extended Debye–Hückel equation has higher values than those obtained in pure water. This behavior is verified at all three studied temperatures and is possibly due to the entry of PEG4000 molecules in the solvation sphere of ions, replacing the water molecules.

The values of β^0 , β^1 , and C^ϕ obtained in the fit using the Pitzer model are outlined in Figure 1 versus the reciprocal value

of the relative permittivity of the PEG4000–water mixture, for the three studied temperatures. It can be seen in this figure that the parameters generally present a linear tendency with $1/\epsilon_r$ and that NaBF_4 follows similar behavior to that observed with previous work.^{15–18}

The average values for E^{0*} , which appear in the last column of Table 2, were calculated considering the studied models. These average values were used for calculating the mean ionic coefficients γ , which are shown in Table 1 for the different molality values of NaBF_4 and the percentage weight of PEG4000 at the three studied temperatures. Figure 2 shows $\log \gamma$ versus $m^{1/2}$ for the three temperatures and for the six studied weight fractions of PEG4000. It can be observed that, for a fixed concentration of NaBF_4 , the $\log \gamma$ values decrease with the increase of PEG4000, following a similar behavior to that observed with NaNO_3 in the PEG4000 + H_2O mixture.¹⁸ 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 PEG4000 concentration increases.

The standard Gibbs energy of transfer, ΔG_t^0 , is defined as the difference between the standard Gibbs energy per mole of electrolyte in a pure solvent, usually water, in another pure or mixed solvent. It uses the values of E^{0*} to measure the change in the total energy of the solute when it is transferred from one solvent in accordance with the expression:

$$\begin{aligned}\Delta G_t^0 &= -zF(E_s^0 - E_w^0) \\ &= -zF[(E_s^{0*} - E_w^{0*}) - (E_s^{\text{asym}} - E_w^{\text{asym}})]\end{aligned}\quad (5)$$

where E^0 , E^{0*} , and E^{asym} correspond to standard potential, apparent standard potential, and the asymmetry potential ($\epsilon_{\text{Na}}^{\text{asym}} + \epsilon_{\text{BF}_4}^{\text{asym}}$), respectively. Subscript s refers to mixed solvent and w to water. All other symbols have their usual meaning. As mentioned above, in our case, E^{asym} is a constant value, small and independent of the composition of the solvent which allows us to state that $(E_s^{\text{asym}} + E_w^{\text{asym}})$ is negligible compared to $(E_s^{0*} - E_w^{0*})$, and thus eq 5 may be used without any problems.

Table 3 contains the values of ΔG_t^0 calculated for each temperature. In all cases an increase in the standard Gibbs

Table 3. Standard Gibbs Energy of Transference, ΔG_t^0 , for the System $\text{NaBF}_4 + \text{PEG4000} + \text{H}_2\text{O}$ at (288.15, 298.15, and 308.15) K

w	$\Delta G_t^0/\text{kJ}\cdot\text{mol}^{-1}$		
	288.15 K	298.15 K	308.15 K
0	0.00	0.00	0.00
0.05	0.22	0.52	0.23
0.10	0.53	0.81	0.38
0.15	0.51	1.29	0.89
0.20	1.09	1.71	1.41
0.25	1.33	2.08	1.85

energy of transfer is observed with the increase of PEG4000 in the mixture, which would indicate a decrease in solvation of the electrolyte in the mixture. This seems to be related to an increase in the hydration of the PEG4000.²⁴

As we have no primary hydration number from the Feakins and French equation,³⁴ an alternative is to make an estimation of the primary hydration number of the electrolyte based on the dependency that exists between the standard electromotive force of the cell and the logarithm of the mass fraction of water in the mixture, in accordance with:

$$\Delta E^0 = E_s^0 - E_w^0 \cong E_s^{0*} - E_w^{0*} = n_{\text{hydr}} k \log w \quad (6)$$

Figure 3 shows the relationship between ΔE^0 vs $-k \log w$, where excellent linear correlations can be observed for all cases. The values found for n_{hydr} were 1.9 ($r = 0.987$), 3.3 ($r = 0.994$), and 2.2 ($r = 0.995$) at temperatures of (288.15, 298.15, and 308.15) K, respectively, the variability of the hydration number

with temperature may be due to the effect of the values of ΔG_t^0 calculated for each temperature. The average value of (2.5 ± 0.4) Å is similar to those found for NaClO_4 (2.1) and KI (2.9), both having an a -value of 4 Å, approximately.³¹

5. CONCLUSIONS

Using the bi-ISE cell $\text{Na-ISE}|\text{NaBF}_4(m), \text{PEG4000}(Y), \text{H}_2\text{O}(100 - Y)|\text{BF}_4\text{-ISE}$, we have determined the mean ionic activity coefficients of NaBF_4 in water at (288.15, 298.15, and 308.15) K from emf measurements. A good fit of the experimental data was obtained with the equations of Pitzer and Debye–Hückel.

Excellent behavior of the electrodes used, in spite of the broad range of concentrations employed in the study, is observed.

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REFERENCES

- (1) Wu, Y.-T.; Lin, D.-Q.; Zhu, Z.-Q.; Mei, L.-H. Prediction of liquid-liquid equilibria of polymer-salt aqueous two-phase systems by a modified Pitzer's virial equation. *Fluid Phase Equilib.* **1996**, *124*, 67–79.
- (2) Li, M.; Zhu, Z.-Q.; Wu, Y.-T.; Lin, D.-Q. Measurement of phase diagrams for new aqueous two-phase systems and prediction by a generalized multicomponent osmotic virial equation. *Chem. Eng. Sci.* **1998**, *53*, 2755–2767.
- (3) Li, W.; Lin, D.-Q.; Zhu, Z.-Q. Measurement of water activities and prediction of liquid-liquid equilibria for water + ethylene oxide-propylene oxide random copolymer + ammonium sulfate systems. *Fluid Phase Equilib.* **2000**, *175*, 7–18.
- (4) Salabat, A. The influence of salts on the phase composition in aqueous two-phase systems: experiments and predictions. *Fluid Phase Equilib.* **2001**, *187–188*, 489–498.

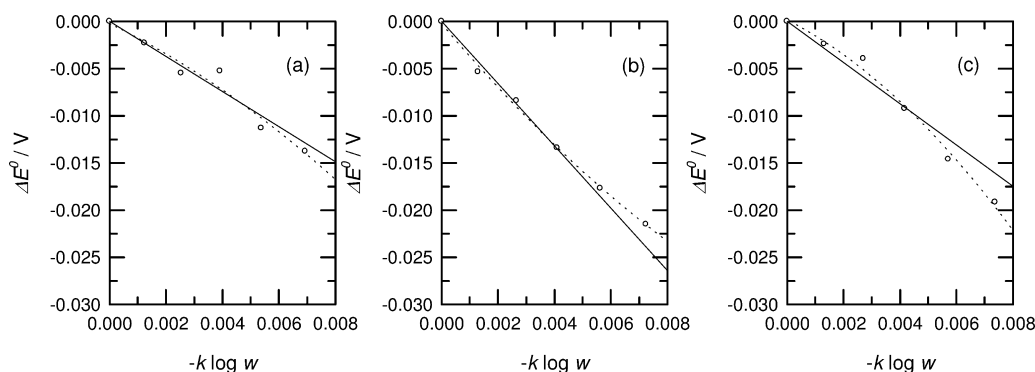


Figure 3. Variation of ΔE^0 with the mass fraction of water in PEG4000–water mixtures at T/K : 288.15 (a), 298.15 (b), and 308.15 (c).

- (5) Salabat, A. Prediction of liquid-liquid phase diagrams of aqueous salt + PEG systems using a thermodynamic model. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2006**, *30*, 296–300.
- (6) Zafarani-Moattar, M. T.; Sadeghi, R. A modified nonrandom factor model for the calculation of solvent activities in polymer solution. *Fluid Phase Equilib.* **2002**, *202*, 413–422.
- (7) Sadeghi, R.; Ziamajidi, F. Water activities of ternary mixtures of poly(ethylene glycol), NaCl and water over the temperature range of 293.15 to 313.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 1335–1343.
- (8) Ochs, L. R.; Kabiri-Badr, M.; Cabezas, H. An improved isopiestic method to determine activities in multicomponent mixtures. *AIChE J.* **1990**, *36*, 1908–1912.
- (9) Lin, D.-Q.; Mei, L.-H.; Zhu, Z.-Q.; Han, Z.-X. An improved isopiestic method for measurement of water activities in aqueous polymer and salt solutions. *Fluid Phase Equilib.* **1996**, *118*, 241–248.
- (10) Lin, D.-Q.; Zhu, Z.-Q.; Mei, L.-H.; Yang, L.-R. Isopiestic determination of the water activities of poly(ethylene glycol) + salt + water systems at 25 °C. *J. Chem. Eng. Data* **1996**, *41*, 1040–1042.
- (11) Zafarani-Moattar, M. T.; Salabat, A. Measurement and correlation of viscosities, densities, and water activities for the system poly(propylene glycol) + MgSO₄ + H₂O at 25 °C. *J. Solution Chem.* **1998**, *27*, 663–673.
- (12) Salabat, A.; Dashti, H.; Nasirzadeh, K. Measurement and correlation of water activities and refractive indices for the systems PPG425 + (NH₄)₂SO₄ + H₂O and PPG425 + Na₂SO₄ + H₂O at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 980–982.
- (13) Salabat, A.; Nasirzadeh, K. Measurement and prediction of water activity in PEG + (NH₄)₂SO₄ + H₂O systems using polymer scaling laws. *J. Mol. Liq.* **2003**, *103–104*, 349–358.
- (14) Sadeghi, R.; Hosseini, R.; Jamehbozorg, B. Effect of sodium phosphate salts on the thermodynamic properties of aqueous solutions of poly(ethylene oxide) 6000 at different temperatures. *J. Chem. Thermodyn.* **2008**, *40*, 1364–1377.
- (15) Morales, J. W.; Galleguillos, H. R.; Taboada, M. E.; Hernández-Luis, F. Activity coefficients of NaCl in PEG4000 + water mixtures at 288.15, 298.15 and 308.15 K. *Fluid Phase Equilib.* **2009**, *281*, 120–126.
- (16) Morales, J. W.; Galleguillos, H. R.; Graber, T. A.; Hernández-Luis, F. Activity coefficients of LiCl in (PEG4000 + water) at T = (288.15, 298.25, and 308.15) K. *J. Chem. Thermodyn.* **2010**, *42*, 1255–1260.
- (17) Hernández-Luis, F.; Rodríguez-Raposo, R.; Galleguillos, H. R.; Morales, J. W. Activity coefficients of KCl in PEG4000 + water mixtures at 288.15, 298.15 and 308.15 K. *Fluid Phase Equilib.* **2010**, *295*, 163–171.
- (18) Hernández-Luis, F.; Morales, J. W.; Graber, T. A.; Galleguillos, H. R. Activity coefficients of NaNO₃ in Poly(ethylene glycol) 4000 + water mixtures at (288.15, 298.15, and 308.15) K. *J. Chem. Eng. Data* **2010**, *55*, 4082–4087.
- (19) Hernández-Luis, F.; Amado-González, E.; Estes, M. A. Activity coefficients of NaCl in trehalose–water and maltose–water mixtures at 298.15 K. *Carbohydr. Res.* **2003**, *338*, 1415–1424.
- (20) Hernández-Luis, F.; Vázquez, M. V.; Estes, M. A. Activity coefficients for NaF in methanol–water and ethanol–water mixtures at 25 °C. *J. Mol. Liq.* **2003**, *108*, 283–301.
- (21) Hernández-Luis, F.; Grandoso, D.; Lemus, M. Activity Coefficients of NaCl in Fructose + Water at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 668–674.
- (22) Hernández-Luis, F.; Galleguillos, H. R.; Vázquez, M. V. Activity coefficients of NaF in (glucose + water) and (sucrose + water) mixtures at 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 957–964.
- (23) Hernández-Luis, F.; Galleguillos, H. R.; Estes, M. A. Activity coefficients of NaF in aqueous mixtures with ϵ -increasing co-solvent: formamide–water mixtures at 298.15 K. *Fluid Phase Equilib.* **2005**, *227*, 245–253.
- (24) Hernández-Luis, F.; Galleguillos, H. R.; Fernández-Mérida, L.; González-Díaz, O. Activity coefficients of NaCl in aqueous mixtures with ϵ -increasing co-solvent: formamide–water mixtures at 298.15 K. *Fluid Phase Equilib.* **2009**, *275*, 116–126.
- (25) Hernández-Luis, F.; Galleguillos, H. R.; Graber, T. A.; Taboada, M. E. Activity Coefficients of LiCl in Ethanol–Water Mixtures at 298.15 K. *Ind. Eng. Chem. Res.* **2008**, *47*, 2056–2062.
- (26) Galleguillos, H. R.; Flores, E. K.; Aguirre, C. E. Density and Refractive Index for Boric Acid + Potassium Chloride + Water and Disodium Tetraborate + Potassium Chloride + Water Systems at (20, 25, and 30) °C. *J. Chem. Eng. Data* **2011**, *46*, 1632–1634.
- (27) Galleguillos, H. R.; Molina, M. A.; Graber, T. A. Experimental Determination of Densities of Aqueous Electrolyte Mixtures Containing B(OH)₃ or Na₂B₄O₇ and Their Correlation with the Pitzer Model. *Ind. Eng. Chem. Res.* **2006**, *45*, 6604–6613.
- (28) Fry, C. H.; Langley, S. E. M. *Ion-selective electrodes for biological systems*; Harwood Academic Publishers: Amsterdam, 2001.
- (29) Guilbault, G. G. Recommendations for publishing on ion-selective electrodes. *Pure Appl. Chem.* **1981**, *53*, 1907–1912.
- (30) Hitchcock, D. The extrapolation of electromotive force measurements to unit ionic activity. *J. Am. Chem. Soc.* **1928**, *50*, 2076–2080.
- (31) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1959.
- (32) Pitzer, K. S. *Thermodynamics*; McGraw-Hill: New York, 1995.
- (33) Galleguillos, H. R.; Hernández-Luis, F.; Graber, T. A.; Morales, J. W. Activity coefficients of NaBF₄ in aqueous solution. *J. Chem. Thermodyn.* **2007**, *39*, 1632–1636.
- (34) Feakins, D.; French, C. M. Standard potentials in aqueous organic media: A general discussion of the cell H₂(Pt)|HCl|AgCl-Ag. *J. Chem. Soc.* **1957**, 2581–2589.