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Activity Coefficients of NaBr in Aqueous Mixtures with High Relative Permittivity Cosolvent: Ethylene Carbonate + Water at 298.15 K

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The mean ionic activity coefficients of NaBr were experimentally determined in ethylene carbonate (EC) + water at 298.15 K from potential difference measurements of the following electrochemical cell containing two ion-selective electrodes (ISEs):

$$\text{Na-ISE}|\text{NaBr}(m), \text{EC}(w), \text{H}_2\text{O}(1-w)|\text{Br-ISE}$$

The molality (m) varied between 0.04 $\text{mol}\cdot\text{kg}^{-1}$ and almost saturation, while the mass fraction of EC in the mixture (w) was varied between 0 and 0.8 in 0.1 unit steps. Values of the standard potential difference, E^0 (molal scale), were determined using a routine method of extrapolation together with the extended Debye−Hückel, Pitzer−Rard−Archer, and Scatchard equations. The results obtained produced good internal consistency, within the normal limits of experimental error in these types of measurement. Once E^0 was determined, the mean ionic activity coefficients of NaBr (γ), the Gibbs energy of transfer of the NaBr from the water to the EC + water mixture (ΔG_t^0), the standard solubility product of NaBr in EC + water (K_{sp}^0), the NaBr primary hydration number (n_{hyd}), Gibbs energy interaction parameters (g_{EN}), and the salting constant (k_S) were estimated. The results were comparatively analyzed with those of NaF and NaCl previously obtained in similar mixtures.

1. Introduction

Aqua-organic electrolyte solutions are important in fields such as chemistry, chemical engineering, biology, biochemistry, the pharmaceutical industry, the environment, and so forth. Therefore, new data are always welcome. In previous work by our group, the behavior of NaF and NaCl has been studied in both organic + water mixtures with low relative permittivity cosolvents (i.e., methanol + water, ethanol + water),[1,2] as well as in organic-water mixtures with high relative permittivity cosolvents (i.e., ethylene carbonate (EC) + water, formamide + water).[3−6] The activity coefficients of these electrolytes were determined on the basis of potential difference measured in cells containing ion-selective electrodes (ISEs) for the F^- or Cl^- anions and the Na^+ cation. A simple methodology was developed and applied to obtain the maximum possible information about these systems. The objective of the present research is to carry out a similar study for NaBr in EC + water and to compare the results with those obtained previously with NaF and NaCl.

EC demonstrates some unusual properties which makes it of interest[7−10] also for industrial use. This compound is solid at 25 °C (t_{fus}: 36.2 °C) and miscible with water up to 0.8 mass fraction at this temperature. It is nearly inert in its acid−base properties and in other types of chemical reactions. It is a typical dipolar aprotic cosolvent and almost iso-dielectric with water, but with a dipolar moment much greater than water, which notably favors ion−dipole type solute−solvent interactions.

With regard to the electrolyte used, it is well-known that NaBr, unlike NaF and NaCl, is much more soluble in water (9.186 $\text{mol}\cdot\text{kg}^{-1}$ against 0.983 $\text{mol}\cdot\text{kg}^{-1}$ and 6.146 $\text{mol}\cdot\text{kg}^{-1}$ at 298.15 K, respectively)[11−13] and has a smaller capacity for the association and formation of ion pairs. Na^+ and Br^- ions are present in many natural systems, from seawater to biological fluids such as urine or blood (white cells), as well as in some drugs (sedatives). The Br^- ion is also widely used as mild germicidal agent and in veterinary medicine.

In the literature there are several potentiometric studies of NaBr in aqueous mixtures with a low relative permittivity cosolvent[14−23] but none that we know of in aqueous mixtures with a high relative permittivity cosolvent.

The present study includes the experimental determination of mean ionic activity coefficients of NaBr (γ), the Gibbs energy of transfer of NaBr from water to the EC + water mixture (ΔG_t^0), the standard solubility product of NaBr in EC + water (K_{sp}^0), the NaBr primary hydration number (n_{hyd}), Gibbs energy interaction parameters (g_{EN}), and the salting constant (k_S). The molality of NaBr was varied between 0.04 $\text{mol}\cdot\text{kg}^{-1}$ and almost saturation, while the mass fraction of EC in the mixture (w) was varied between 0 and 0.8 in 0.1 unit steps. All of the measurements were carried out at 298.15 K.

2. Experimental Section

NaBr, Riedel-de Haën ($w = 0.99$), was dried in vacuo at 373 K for 72 h. EC was Fluka microselect ($w = 0.99$) and used with no other treatment. Both were stored over silica gel in desiccators. In each set of experiments (corresponding to a w

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of EC), working solutions were obtained by adding successive known masses of solid NaBr to a previously prepared solution of EC and double-distilled water ($\kappa < 10^{-6}$ S·cm^{-1}). The solutions were stirred continuously by magnetic stirring. The relative uncertainty both in the electrolyte molality and w of EC is estimated to be about 0.1 %.

Na-ISE (model 6.0501.100) and Br-ISE (model 6.0502.100) were obtained from Metrohm Corp. A double-wall vessel Metrohm cell was used to hold the electrodes and the solution. The temperature in the cell was maintained at (25.00 ± 0.05) °C using a Hetofrig model 04 PT thermoregulator, and a platinum resistance thermometer (Guildline model 9540) was used to record the temperature. The temperature relative uncertainty was estimated to be 0.02 %.

The potential difference measurements were carried out with a 614 Keithley electrometer having an inner impedance greater than $5 \cdot 10^{13}$ Ω with a resolution of ± 0.1 mV. To obtain a more precise potential difference the 2 V analog output of the electrometer was connected to a Keithley model 197A Microvolt DMM with an input greater than $1 \cdot 10^{12}$ Ω and resolution of ± 0.01 mV. The correct functioning of this group was periodically checked by measuring potentials using a certified Leeds & Northrup Co. Weston standard cell.

The Br-ISE was connected to a low input (grounded) from the electrometer, since it has lower impedance than the Na glass electrode. Depending on the total ionic strength studied, it was observed that, after (30 to 40) min, the variation of the potential with time was very small [around 0.05 mV per (15 to 20) min]. The reading at this moment was considered representative of the cell in equilibrium. Depending on the mass fraction of EC in the mixture, the potential difference uncertainty can be estimated between (0.1 and 0.3) mV, approximately.

3. Results

Mean ionic activity coefficient values of the NaBr in EC + water were determined from the potential difference measurements of the following cells:

$$\text{Na-ISE}|\text{NaBr}(m), \text{EC}(w), \text{H}_2\text{O}(1 - w)|\text{Br-ISE} \qquad (1)$$

In these cells, m is the molality of NaBr (moles NaBr/kg mixed solvent) in the working solution in the mixed solvent and w the mass fraction of EC 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 potential difference of the cell, $k = (\ln 10) \cdot (RT/F)$ is the Nernst theoretical slope, and m and γ are the molality and mean ionic activity coefficients of the NaBr. $E^{0}*$ is the apparent standard potential difference (molal scale) of the cell and contains the asymmetry potential of both selective electrodes. In general, we have verified[1,3−5,24] that these asymmetric potentials are small and 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 mixtures of EC + water as a function of NaBr molality. Since the mean activity coefficients of the NaBr in pure water are well-known,[12] the two groups of E values that appear in Table 1 for $w = 0$ allow carrying out a calibration of the electrode system, using eq 2. The experiments were started with the first calibration and ended with the second one. A very good linear relationship is obtained when E versus $-\log m\gamma$ is plotted. The values obtained for the Nernst slope, when applying a least-squares regression analysis to the previous plots, were $k = (59.59 \pm 0.05)$ mV and $k = (59.60 \pm 0.03)$ mV, with correlation coefficients greater than 0.99999 in both cases and standard deviations of (0.09 and 0.12) mV, respectively. The average value of $k = (59.59 \pm 0.01)$ mV differs only by about 0.7 % from the theoretical value and will be taken heretofore as the value of k for the successive calculus achieved in this work. This is above acceptable levels for a system containing two ISEs. In this calculation it has been assumed that $k_{\text{Na}} \cong k_{\text{Br}} \cong k \cong (k_{\text{Na}} + k_{\text{Br}})/2$.[1−3]

Additionally, the intercepts in both cases are practically equal: $E^{0}* = (-368.77 \pm 0.02)$ mV and $E^{0}* = (-368.59 \pm 0.04)$ mV, respectively. This is very important since it indicates that the potential of asymmetry of the electrodes has scarcely varied in the 12 days that elapsed between both calibrations.

The most important and decisive point in this type of study is the determination of the apparent standard potential difference of the cell, $E^{0}*$, with the greatest possible precision for each mixture studied, since this affects the accuracy of the activity coefficients and the other thermodynamic functions subsequently calculated.

The determination of $E^{0}*$ was carried out following a similar method to Hitchcock,[25] using the extended Debye−Hückel,[26,27] Pitzer−Rard−Archer,[11,28,29] and Scatchard[30,31] equations to represent the dependency of log γ on molality. For 1:1 electrolytes, these equations may be written as the following:

Extended Debye−Hückel equation:[26,27]

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

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

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

Pitzer−Rard−Archer equation:[11,28,29]

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

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

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

$$C^{\gamma} = 3C^0 + \frac{4C^1}{\alpha_2{}^4 m^2}[6 - (6 + 6\alpha_2\sqrt{m} + 3\alpha_2{}^2 m + \alpha_2{}^3 m^{3/2} - \alpha_2{}^4 m^2/2)\exp(-\alpha_2\sqrt{m})] \qquad (4c)$$

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

Scatchard equation:[30,31]

$$\ln \gamma = \frac{1}{2}\left[\frac{2S\sqrt{m}}{1 + a\sqrt{m}} + 2a^{(1)}m + \frac{3}{2}a^{(2)}m^2 + \frac{4}{3}a^{(3)}m^3 + \frac{5}{4}a^{(4)}m^4\right] \qquad (5)$$

$$S = -3A_{\phi} \qquad (5a)$$

where $\alpha = 2.0$ kg$^{1/2}$·mol$^{-1/2}$, $b = 1.2$ kg$^{1/2}$·mol$^{-1/2}$, and $\alpha_2 = 1.7$ kg$^{1/2}$·mol$^{-1/2}$. All other symbols have their usual meaning. The values of density, ρ, and the relative permittivity, ε_r, for the EC + water mixtures were interpolated from those found in the literature[6−9] and appear together with the others constants in Table 2.

Table 1. Values of the Molality (m) and Potential Difference (E) for the Cell Na-ISE|NaBr (m), EC (w), H_2O ($1 - w$)|Br-ISE, and Mean Ionic Activity Coefficients (γ) Calculated for NaBr in the Different EC + Water Mixtures at 298.15 K

$m/\mathrm{mol \cdot kg^{-1}}$	$-E/\mathrm{mV}$	γ	$m/\mathrm{mol \cdot kg^{-1}}$	$-E/\mathrm{mV}$	γ	$m/\mathrm{mol \cdot kg^{-1}}$	$-E/\mathrm{mV}$	γ
	$w = 0^{a}$			$w = 0.1$			$w = 0.2$	
0.1895	267.75	0.751	0.1533	259.24	0.769	0.1115	246.46	0.780
0.3052	290.37	0.721	0.3259	295.63	0.730	0.1921	271.90	0.740
0.3863	301.70	0.709	0.4666	313.99	0.727	0.3344	298.33	0.709
0.4945	313.69	0.699	0.7872	341.03	0.727	0.4983	318.03	0.696
0.5000	314.21	0.698	1.1227	360.99	0.749	0.7282	338.90	0.713
0.6466	326.91	0.690	1.4862	377.19	0.774	0.8386	346.27	0.713
0.8083	338.10	0.685	1.9808	394.79	0.816	0.9883	354.46	0.709
1.0289	350.66	0.686	2.9433	422.40	0.936	1.3984	373.79	0.728
2.0111	388.51	0.729	3.9931	447.09	1.112	2.2913	405.21	0.815
3.2194	420.19	0.840	5.1212	470.42	1.361	3.6845	442.08	1.034
4.5326	447.25	1.006	6.1004	488.91	1.633	4.7388	465.45	1.262
5.8062	470.08	1.221	6.9764	504.45	1.928	5.8892	488.82	1.596
6.9069	487.91	1.449	7.5482	513.84	2.137	6.7791	505.42	1.910
8.1873	506.77	1.760	7.9385	519.86	2.282	7.1998	512.94	2.080
			8.2960	525.48	2.434	7.4876	518.18	2.213
						7.5554	519.40	2.246
	$w = 0.3$			$w = 0.4$			$w = 0.5$	
0.0952	242.57	0.789	0.0952	252.07	0.797	0.0777	254.40	0.799
0.2340	285.44	0.735	0.2251	293.29	0.747	0.1795	295.05	0.758
0.4429	315.57	0.722	0.4137	324.38	0.741	0.2813	318.01	0.754
0.7350	344.09	0.726	0.5552	340.15	0.749	0.4223	338.32	0.744
1.0029	360.62	0.733	0.7391	354.73	0.746	0.5000	346.47	0.735
1.2785	374.98	0.759	1.0348	373.91	0.772	0.5421	350.49	0.733
1.5448	386.37	0.782	1.7630	407.64	0.869	0.8178	372.87	0.749
2.3167	413.90	0.888	2.5258	434.04	1.010	1.0605	388.50	0.781
3.7108	452.32	1.165	3.4171	459.80	1.228	1.9517	429.05	0.929
4.7060	475.65	1.441	4.4748	486.87	1.582	2.6887	454.04	1.092
5.5091	493.06	1.723	5.4296	509.30	2.011	3.7177	484.37	1.420
5.9859	503.04	1.923	5.8768	519.09	2.245	4.5212	506.05	1.774
6.5199	513.73	2.171	5.9857	521.52	2.310	4.7564	512.27	1.902
6.8645	520.34	2.343	6.0985	524.30	2.393	4.9108	516.18	1.987
	$w = 0.6$			$w = 0.7$			$w = 0.8$	
0.0950	299.30	0.823	0.0743	289.15	0.807	0.0418	293.48	0.833
0.2623	330.26	0.786	0.2091	339.45	0.758	0.0879	328.69	0.782
0.3910	350.97	0.787	0.2727	353.04	0.756	0.1287	347.11	0.762
0.5000	364.05	0.792	0.3904	372.05	0.762	0.2060	370.66	0.750
0.5063	364.67	0.792	0.5000	385.58	0.773	0.2447	379.43	0.748
0.7762	388.94	0.826	0.5380	389.73	0.778	0.2932	389.08	0.753
0.8800	396.28	0.839	0.6163	397.64	0.792	0.3329	395.92	0.756
0.9911	403.41	0.855	0.7388	408.68	0.818	0.3899	404.60	0.764
1.2891	420.25	0.910	0.8353	416.25	0.837	0.4318	410.67	0.776
1.8466	446.10	1.047	0.9577	425.01	0.865	0.4812	416.54	0.779
						0.5507	424.61	0.796
	$w = 0^{b}$							
0.1253	247.71	0.771						
0.2999	288.98	0.715						
0.5268	316.26	0.690						
0.8068	338.18	0.688						
1.0956	354.28	0.691						
2.0405	389.36	0.731						
3.2058	419.97	0.840						
4.6692	449.90	1.029						
5.9752	472.54	1.245						
7.0207	489.22	1.462						
8.5807	511.73	1.849						

[a] First calibration. [b] Second calibration.

By combining eqs 2 and 3, 2 and 4, or 2 and 5, the values of E^{0*} can be optimized, as well as the interaction parameters characteristic of each model. In Table 3, these values are presented as well as the corresponding standard deviation of the fit. The values of the adjustable parameters of the Scatchard equation are not included, as they do not provide any additional significant information.

4. Discussion

As can be observed from Table 3, the values of E^{0*} obtained with each one of the tried models are in very good agreement (standard errors less than 0.5 mV). The standard deviations of the fits are also comparable.

Optimization using the Debye−Hückel extended equation (DH) with the inclusion of the additional parameter d allows the fit to be made in the entire range of molality of NaBr with a very good standard deviation for $0 \leq w \leq 0.6$. As the solubility of NaBr decreases significantly with the increase of w of EC, the inclusion of the extra parameter d is not necessary for $w > 0.6$, since the maximum molality is less than 1.0 mol·kg^{-1}, approximately.

Table 2. Values of Average Molecular Mass (*M*), Relativity Permittivity (ε_r), Density (ρ), the Debye−Hückel (*A*, *B*), Pitzer (A_ϕ), and Scatchard (*S*) Constants, and the Bjerrum Parameter (*q*) as a Function of the Mass Fraction (*w*) of EC in EC + Water Mixture at 298.15 K

w	M / $\mathrm{g \cdot mol^{-1}}$	ε_r	ρ / $\mathrm{g \cdot cm^{-3}}$	A / $\mathrm{kg^{1/2} \cdot mol^{-1/2}}$	B / $\mathrm{kg^{1/2} \cdot mol^{-1/2} \cdot Å^{-1}}$	A_ϕ / $\mathrm{kg^{1/2} \cdot mol^{-1/2}}$	S / $\mathrm{kg^{1/2} \cdot mol^{-1/2}}$	q / Å
0	18.0150	78.38	0.9971	0.5100	0.3285	0.3915	−1.1745	3.58
0.1	19.5718	79.22	1.0263	0.5092	0.3315	0.3909	−1.1726	3.54
0.2	21.4231	79.97	1.0560	0.5093	0.3347	0.3909	−1.1728	3.50
0.3	23.6612	80.70	1.0866	0.5096	0.3380	0.3912	−1.1736	3.47
0.4	26.4215	81.48	1.1181	0.5095	0.3412	0.3911	−1.1734	3.44
0.5	29.9109	82.36	1.1508	0.5087	0.3443	0.3905	−1.1714	3.40
0.6	34.4623	83.41	1.1848	0.5064	0.3471	0.3887	−1.1662	3.36
0.7	40.6472	84.69	1.2201	0.5023	0.3496	0.3856	−1.1567	3.31
0.8	49.5379	86.27	1.2569	0.4959	0.3515	0.3806	−1.1419	3.25

Table 3. Summary of Both Standard Potentials Different for the Cell Na-ISE|NaBr (*m*), EC (*w*), H_2O (1 − *w*)|Br-ISE and the NaCl Ionic Interaction Parameters Values Obtained for the Debye−Hückel (DH), Pitzer−Rard−Archer (PRA), and Scatchard (S) Equations, in the Different EC + Water Mixtures at 298.15 K

w	E^{0*}(DH) / mV	a / Å	c / $\mathrm{kg \cdot mol^{-1}}$	d / $\mathrm{kg^2 \cdot mol^{-2}}$	σ / mV	E^{0*}(P) / mV	β^0 / $\mathrm{kg \cdot mol^{-1}}$	β^1 / $\mathrm{kg \cdot mol^{-1}}$	C^0 / $\mathrm{kg^2 \cdot mol^{-2}}$	C^1 / $\mathrm{kg^2 \cdot mol^{-2}}$	σ / mV	E^{0*}(S) / mV	σ / mV	$\langle E^{0*} \rangle$ / mV
0	−368.68 ± 0.78	4.01	0.0750	0.00014	0.47	−368.01 ± 0.66	0.1526[a]	0.2551[a]	−0.00230[a]	−0.1176[a]	0.26	−369.38 ± 0.25	0.07	−368.69 ± 0.39
0.1	−370.68 ± 0.46	3.99	0.0971	−0.00063	0.32	−369.26 ± 0.46	0.1535	0.3367	−0.00176	−0.0730	0.24	−369.82 ± 0.59	0.19	−369.92 ± 0.41
0.2	−373.42 ± 0.55	3.50	0.0982	0.00085	0.45	−372.51 ± 0.61	0.1598	0.2118	−0.00152	−0.0822	0.45	−372.65 ± 1.08	0.47	−372.86 ± 0.28
0.3	−377.06 ± 0.31	3.58	0.1128	0.00046	0.25	−376.35 ± 0.30	0.1675	0.2253	−0.00143	−0.0620	0.21	−376.28 ± 0.54	0.22	−376.56 ± 0.25
0.4	−385.89 ± 0.41	3.98	0.1226	0.00027	0.29	−385.48 ± 0.42	0.1635	0.2860	−0.00051	−0.0263	0.29	−385.30 ± 0.82	0.32	−385.56 ± 0.17
0.5	−398.44 ± 0.50	3.82	0.1313	0.00166	0.37	−398.24 ± 0.47	0.1019	0.3397	0.00404	0.1138	0.38	−398.13 ± 0.68	0.38	−398.27 ± 0.09
0.6	−411.93 ± 0.97	5.54	0.1297	0.00555	0.10	−412.27 ± 0.69	0.1600	0.4421	0.00546		0.10	−411.71 ± 1.03	0.10	−411.97 ± 0.16
0.7	−434.95 ± 0.30	2.81	0.2311		0.14	−434.65 ± 0.25	0.2598	0.0835			0.15	−434.72 ± 0.24	0.15	−434.77 ± 0.09
0.8	−467.76 ± 0.41	1.51	0.3648		0.21	−467.11 ± 0.35	0.3898	−0.2794			0.23	−467.01 ± 0.31	0.24	−467.29 ± 0.24
0	−368.68 ± 0.57	3.83	0.0789	−0.00004	0.38	−367.84 ± 0.80	0.1526[a]	0.2551[a]	−0.00230[a]	−0.1176[a]	0.37	−369.49 ± 0.68	0.25	−368.67 ± 0.48

[a] Fixed values.[11]

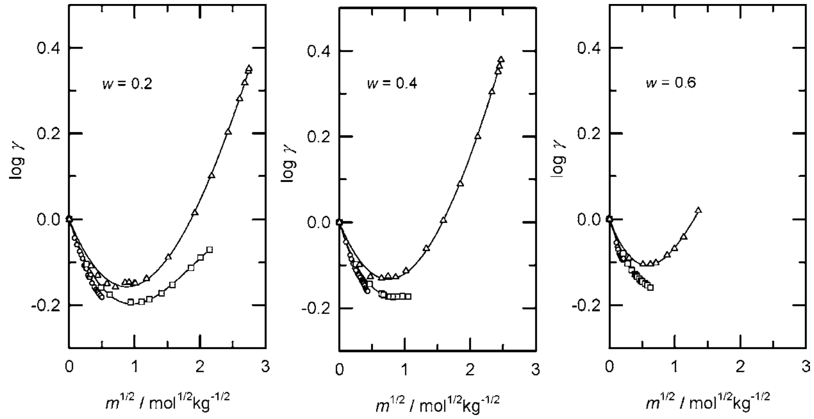

Figure 1. Plot of log γ vs $m^{1/2}$ for various EC mass fractions (*w*) in EC + water mixtures at 298.15 K. ○, NaF;[3] □, NaCl;[6] and △, NaBr[this work].

The parameter *a* (related to the ionic size) remains almost constant at (3.66 ± 0.32) Å, with a value superior than the sum of the crystallographic radii of Na^+ and Br^- (2.90 Å)[32] as a probable result of the solvation. These *a* values are also slightly higher than the *q* parameter of Bjerrum[33] (last column of Table 2), suggesting that there is no ion association unlike what happens for NaF[3] and NaCl[6] in EC + water mixtures, where ($a - q$) is negative.

In this study, we have used Pitzer's ion-interaction model,[28,29] with the inclusion of an ionic strength dependence of the C^γ parameter (which represents triple ionic interactions) as has been suggested by Rard and Archer.[11] Optimization using this Pitzer−Rard−Archer equation (PRA) allowed reasonable values for β^0 (which can be identified with interactions of like and unlike charged ions) and β^1 (which can be identified with the interactions between unlike-charged ions) to be obtained. For $w > 0.6$, it can be considered $C^\gamma = 0$, without losing accuracy,[28,29] because the molality of NaBr is less than 2 $\mathrm{mol \cdot kg^{-1}}$.

The Scatchard equation (S) was also used to carry out the optimization. A very good standard deviation was obtained, although as we said above its characteristic parameters have no physical meaning and therefore they are not shown.

The average values for E^{0*} which appear in the last column of Table 3 were calculated considering the three models studied. These average values were used to calculate the mean ionic coefficient activity, γ, which is listed in Table 1 for each molality of NaBr (*m*) and each mass fraction of EC (*w*). The standard deviations of our activity coefficients when compared to those reported in the literature were calculated to be less than ± 0.005 in pure water, showing good agreement between both sets of data, particularly if the very broad range of molalities studied is taken into account.

Figure 1 is an example of the dependence of log γ versus $m^{1/2}$ at various mass fractions of EC in the mixture. For comparison purposes, the corresponding plot for NaF[3] and NaCl[6] is shown. All of the curves show a typical profile of the variation log γ with the root square of the molality which, as is well-known, is governed by two types of interactions: ion−ion and ion−solvent.[26,27]

Given that all measurements were carried almost to saturation molality, it is clearly observed that the solubility of the three

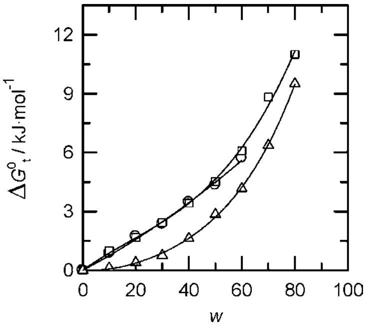

Figure 2. Variation of standard Gibbs energy of transfer with *w* in EC + water mixtures at 298.15 K. ○, NaF;[3] □, NaCl;[6] and △, NaBr$^{\text{this work}}$.

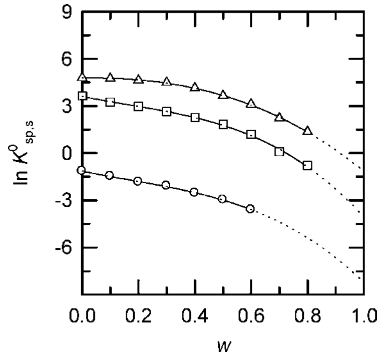

Figure 3. Variation of ln $K^0_{sp,s}$ with *w* in EC + water mixtures at 298.15 K. ○, NaF;[3] □, NaCl;[6] and △, NaBr$^{\text{this work}}$.

electrolytes studied decreases significantly in all cases with the increase of *w* of EC.

Another aspect to emphasize is the small difference observed, for a given electrolyte, between the values of log γ in the mixture at different mass fractions. Probably, this takes place because the water ($\varepsilon_r = 78.38$) and the EC ($\varepsilon_r = 89.78$ at 40 °C) are almost iso-dielectric.

The standard Gibbs energy of transfer, ΔG^0_t, 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:

$$\Delta G^0_t = -zF(E^0_s - E^0_w) = -zF[(E^{0*}_s - E^{0*}_w) - (E^{\text{asym}}_s - E^{\text{asym}}_w)] \quad (6)$$

where E^0, E^{0*}, and E^{asym} stand for the standard potential difference, the apparent standard potential difference, and the total asymmetry potential ($\varepsilon^{\text{asym}}_{\text{Na}} + \varepsilon^{\text{asym}}_{\text{Br}}$), respectively. Subscript "s" refers to mixed solvent and "w" to water. All of the other symbols have their usual meaning. As mentioned previously, in our case, E^{asym} is a constant value, small and independent of the composition of the solvent, which allows us to affirm, that ($E^{\text{asym}}_s - E^{\text{asym}}_w$) is negligible compared to ($E^{0*}_s - E^{0*}_w$), and thus eq 6 may be used without any inconvenience, 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).

Figure 2 shows a plot of the standard Gibbs energy of transfer, ΔG^0_t, for NaF,[3] NaCl,[6] and NaBr against *w* of EC in the EC + water system. In all cases it is verified that $\Delta G^0_t > 0$, which indicates that the transference process is not spontaneous. On the other hand, ΔG^0_t becomes more positive with an increase in *w* of EC, indicating that the thermodynamic stabilization of the sodium halide decreases in the mixed solvent, in the NaF ≅ NaCl < NaBr order.

According to Kalidas et al.,[34] the standard Gibbs energy of transfer to the whole salt, ΔG^0_t, is related to the standard solubility product, K^0_{sp}, of the electrolyte in the two solvents by:

$$\Delta G^0_t = RT \ln(K^0_{sp,w}/K^0_{sp,s}) \quad (7)$$

where $K^0_{sp,w}$ and $K^0_{sp,s}$ represent the standard solubility product of the salt in water (0.318 mol^2·kg^{-2} for NaF,[12] 38.051 mol^2·kg^{-2} for NaCl,[13] and 120.877 mol^2·kg^{-2} for NaBr[11]) and in the organic water mixture, respectively. In Figure 3 a considerable decrease of ln $K^0_{sp,s}$ calculated by eq 7 with *w* of the cosolvent is clearly observed, for the three electrolytes.

Since ΔG^0_t is fundamentally related to the changes in solvation undergone by the electrolyte in the presence of the cosolvent, it is of interest to calculate the primary hydration number. For this we may use the equation of Feakins and French[35] to make a rough estimate of the primary hydration number of the electrolyte based on the dependency which exists between the standard potential difference of the cell and the logarithm of the mass fraction of water in the mixture according to:

$$\Delta E^0 = E^0_s - E^0_w = n_{\text{hyd}} k \log(1 - w) \quad (8)$$

Figure 4 shows a plot of ΔE^0 versus $-k$ log (1 − *w*) where an excellent linear correlation is observed for both NaF ($n_{\text{hyd}} = 3.1$)[3] and NaCl ($n_{\text{hyd}} = 2.9$)[6] up to a 0.3 to 0.4 mass fraction of EC. For NaBr, the range of applicability is somewhat lower, being $n_{\text{hyd}} = 1.4$. These values are very low compared with those obtained from the literature[36] (8 ± 2 for NaF and 6 ± 2 for NaCl and NaBr). This can be due to the value of the dipole moment of EC ($\mu = 4.87$ D), which is much greater than that of water ($\mu = 1.83$ D). Thus, the EC is highly prone to preferentially solvate the cations, displacing water from the primary hydration sheath.

Finally, in accordance with Zhuo et al.,[37−40] it is possible to evaluate the Gibbs energy interaction parameters, based on the standard transfer Gibbs energy expressed in moles per kilogram of pure water, $\Delta G^{0m(\text{W})}_t$. It was first necessary to convert the standard transfer Gibbs energy expressed in moles per kilogram

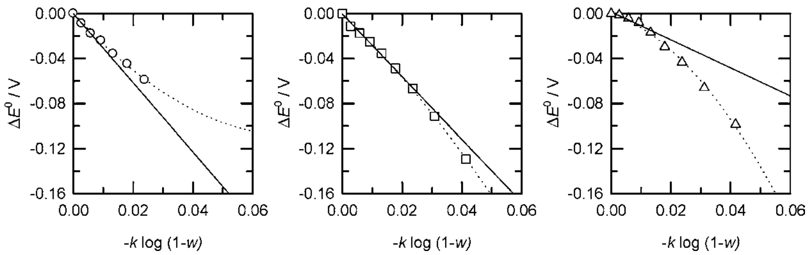

Figure 4. Variation of ΔE^0 vs a function of mass fraction of water (1 − *w*) in the EC + water mixture at 298.15 K. ○, NaF;[3] □, NaCl;[6] and △, NaBr$^{\text{this work}}$.

Table 4. Gibbs Energy Interaction Parameters (g_{EN}) and Salting Constant (k_S) for NaF, NaCl, and NaBr in the EC + Water System at 298.15 K

	g_{EN} / $J \cdot kg \cdot mol^{-2}$	k_S / $kg \cdot mol^{-1}$
NaF + EC + water[3]	231.5	0.093
NaCl + EC + water[6]	207.9	0.084
NaBr + EC + water	−220.6	−0.089

of the mixed solvent, $\Delta G_t^{0m(M)}$ (which until now we have termed for simplicity ΔG_t^0), in the standard transfer Gibbs energy expressed in moles per kilogram of pure water, $\Delta G_t^{0m(W)}$, in accordance with the expression:

$$\Delta G_t^{0m(W)} = \Delta G_t^{0m(M)} - \nu RT \ln(1 + 0.001 m_N M_N) \quad (9)$$

where m_N and M_N are the molality of the EC (in $mol \cdot kg^{-1}$ water) and its molecular mass, respectively.

According to the McMillan-Mayer theory, $\Delta G_t^{0m(W)}$, can be expressed as:[41−44]

$$\Delta G_t^{m(W)}(W \rightarrow W + N) = 2\nu g_{EN} m_N + 6\nu^2 g_{EEN} m_E m_N + 3\nu g_{ENN} {m_N}^2 + 12\nu^3 g_{EEEN} {m_E}^2 m_N + 12\nu^2 g_{EENN} m_E {m_N}^2 + 4\nu g_{ENNN} {m_N}^3 + ... \quad (10)$$

where g_{ij}, g_{ijk}, g_{ijkl} are pair, triple, and quadruple Gibbs energy interaction parameters, respectively. In dilute solution ($m_E \rightarrow 0$) eq 10 is reduced to:

$$\Delta G_t^{0m(W)}(W \rightarrow W + N) = 2\nu g_{EN} m_N + 3\nu g_{ENN} {m_N}^2 + 4\nu g_{ENNN} m^3 + ... \quad (11)$$

This removes any complicating effects of ion−ion interactions.

In a first approximation, only considering the ion pair interactions, the behavior of the three systems investigated here can be described by analyzing (sign and magnitude) of the g_{EN} parameter and the salting constant, k_S, defined as:[27,45]

$$k_S = \frac{2\nu}{RT} g_{EN} \quad (12)$$

As can be seen in Table 4, the values of both g_{EN} and k_S decrease going from NaF to NaBr. Positive values for NaF and NaCl indicate that the EC is salted-out by the electrolytes, while negative values for NaBr indicate that the EC is salted-in by the electrolyte. Given that the cation is common to the three electrolytes, the intensity of this effect should be marked by the properties of the anion (size, charge, polarizability, etc.).

5. Conclusions

Using the bi-ISE cell Na-ISE|NaBr (m), EC (w), H_2O ($1 - w$)|Br-ISE, we have determined the mean ionic activity coefficients of NaBr in aqueous mixtures with a high relative permittivity cosolvent (EC) + water. A good correlation of the experimental data was obtained with the used thermodynamic electrolyte models (Debye−Hückel, Pitzer−Rard−Archer, and Scatchard). Little variation of these coefficients in the mixture at different mass fractions of EC is observed, possibly because ε_r (EC) ≅ ε_r (H_2O).

The Gibbs energies of transfer of the NaBr from the water to the EC + water mixture were calculated. In all cases it is verified that $\Delta G_t^0 > 0$, which indicates that the transference process is not spontaneous. The standard solubility product of NaBr in EC + water and NaBr primary hydration number were also estimated and comparatively analyzed with those of NaF and NaCl previously obtained in similar mixtures.

Lastly, the Gibbs energy parameters and salting constant were determined. Their values indicate that both NaF and NaCl have a salting-out effect on EC, while NaBr has a salting-in effect.

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