

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

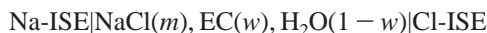
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The mean ionic activity coefficients of NaCl were experimentally determined in ethylene carbonate (EC) + water at 298.15 K from potential difference measurements of the following electrochemical cell containing two ion-selective electrodes (ISEs):



The molality ( $m$ ) varied between  $0.02 \text{ mol}\cdot\text{kg}^{-1}$  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, and Scatchard equations. The results obtained produced good internal consistency, within the normal limits of experimental error encountered in these types of measurement. Once  $E^0$  was determined, the mean ionic activity coefficients of the NaCl, the Gibbs energy of transfer of the NaCl from the water to the EC + water mixture, standard solubility product of NaCl in EC + water, and the NaCl primary hydration number were estimated. The results were comparatively analyzed with those of the NaF previously obtained in similar mixtures.

## 1. Introduction

It is well-known that in recent decades there has been a marked increase in interest in the understanding of thermodynamic properties of multicomponent systems, particularly for those which, due to their composition, are important in fields such as chemistry, chemical engineering, biology, biochemistry, pharmaceutical industry, and the environment, and so forth.

Aqua-organic electrolyte solutions are important for a wide number of applications, and therefore new data are always welcome. In previous works by our group, the behavior of NaF has been studied both in organic + water mixtures with low relative permittivity cosolvent (i.e., methanol + water, ethanol + water),<sup>1</sup> as in organic–water mixtures with high relative permittivity cosolvents (i.e., EC + water, formamide + water).<sup>2,3</sup> The activity coefficients of NaF were determined in these media based on the potential difference measured in cells containing an ion-selective electrode (ISE) for both  $\text{F}^-$  and  $\text{Na}^+$  ions. 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 NaCl in EC + water and to compare results with those obtained previously for NaF.

EC demonstrates some unusual properties which makes it of interest,<sup>4–7</sup> also for industrial use. This compound is solid at  $25 \text{ }^\circ\text{C}$  ( $t_{\text{fus}}$ :  $36.2 \text{ }^\circ\text{C}$ ) 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 used electrolyte, it is well-known that NaCl, unlike NaF, is much more soluble in water ( $6.146 \text{ mol}\cdot\text{kg}^{-1}$  against  $0.983 \text{ mol}\cdot\text{kg}^{-1}$  at 298.15 K) and has a smaller capacity for the association and formation of ion pairs. This electrolyte is present in many natural systems, from seawater to biological fluids such as urine. In the literature there are numerous potentiometric studies of NaCl in mixtures with low relative permittivity cosolvent<sup>8–23</sup> but very few in mixtures with high relative permittivity cosolvent.<sup>23</sup>

The present study includes the experimental determination of mean ionic activity coefficients in aqueous NaCl solutions containing EC, the Gibbs energy of transfer of the NaCl from the water to the EC + water mixture, standard solubility product of NaCl in EC + water, and the NaCl primary hydration number. The molality of NaCl varied between  $0.02 \text{ mol}\cdot\text{kg}^{-1}$  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

NaCl, Merck pro analysi ( $w = 0.99$ ), was dried in vacuo at 373 K for 72 h. Ethylene carbonate (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  $w$  of EC), working solutions were obtained by adding successive known masses of solid NaCl to a previously prepared solution of EC and double-distilled water ( $\kappa < 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ ). The solutions were stirred continuously by

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**Table 1. Values of the Molality ( $m$ ) and Potential Difference ( $E$ ) for the Cell Na-ISE|NaCl ( $m$ ), EC ( $w$ ), H<sub>2</sub>O ( $1 - w$ )|Cl-ISE, and Mean Ionic Activity Coefficients ( $\gamma$ ) Calculated for NaCl in the Different EC + Water Mixtures at 298.15 K**

$m$ mol·kg <sup>-1</sup>	$-E$ mV	$\gamma$	$m$ mol·kg <sup>-1</sup>	$-E$ mV	$\gamma$	$m$ mol·kg <sup>-1</sup>	$-E$ mV	$\gamma$
$w = 0$			$w = 0.1$			$w = 0.2$		
0.0627	37.54	0.809	0.0244	3.34	0.857	0.0693	58.55	0.787
0.1283	71.20	0.762	0.0801	59.06	0.773	0.2371	115.29	0.694
0.3550	118.74	0.695	0.2140	104.47	0.701	0.3848	138.15	0.668
0.5410	138.79	0.674	0.3234	123.68	0.674	0.8780	178.36	0.640
0.8378	160.06	0.658	0.4972	143.96	0.651	1.2220	195.48	0.642
1.0490	171.40	0.656	0.7275	162.38	0.637	1.4979	206.61	0.651
2.0101	205.83	0.669	1.2045	187.87	0.632	1.9926	222.99	0.673
2.9944	229.90	0.718	1.7000	206.52	0.644	2.4905	236.79	0.704
4.1197	251.72	0.798	2.0278	216.60	0.657	3.4648	259.21	0.783
5.0308	266.22	0.867	2.9999	240.67	0.709	4.0147	268.82	0.815
6.0100	281.97	0.986	4.0063	260.26	0.778	4.5986	277.97	0.850
			5.4259	282.23	0.881			
$w = 0.3$			$w = 0.4$			$w = 0.5$		
0.0681	65.44	0.784	0.0641	73.45	0.80	0.0475	72.94	0.825
0.2306	122.33	0.701	0.2123	129.54	0.719	0.0885	102.10	0.780
0.4182	150.28	0.667	0.419	161.72	0.682	0.1358	122.21	0.752
0.6988	175.13	0.647	0.4600	166.19	0.677	0.1678	132.25	0.740
0.9010	188.12	0.646	0.5591	175.76	0.672	0.2141	143.90	0.728
0.9702	191.99	0.647	0.6010	179.39	0.671	0.2778	156.35	0.715
1.0100	194.15	0.648	0.6787	185.59	0.670	0.3292	164.55	0.708
1.1896	203.07	0.655	0.7990	194.06	0.671	0.3808	171.63	0.702
1.4482	214.04	0.666	0.9277	201.84	0.673	0.4820	183.11	0.694
0.9552	231.56	0.694	1.1010	210.55	0.671	0.5527	189.91	0.691
2.4010	243.80	0.717				0.6570	198.54	0.688
$w = 0.6$			$w = 0.7$			$w = 0.8$		
0.0443	88.10	0.834	0.0394	106.51	0.833	0.0237	119.59	0.851
0.0783	114.54	0.789	0.0597	125.90	0.801	0.0280	127.17	0.836
0.1149	132.46	0.762	0.0843	142.00	0.776	0.0312	132.15	0.827
0.1507	145.19	0.745	0.0992	149.64	0.766	0.0408	144.54	0.805
0.1683	150.45	0.739	0.1131	155.83	0.758	0.0543	157.69	0.781
0.1790	153.36	0.735	0.1300	162.31	0.748	0.0670	167.40	0.765
0.2072	160.25	0.726	0.1448	167.31	0.740	0.0799	175.44	0.750
0.2333	165.87	0.720	0.1694	174.69	0.730	0.0950	183.28	0.735
0.2510	169.40	0.717	0.1850	178.78	0.724	0.1103	189.95	0.721
0.2984	177.68	0.708	0.1997	182.32	0.719	0.1285	196.78	0.707
0.3374	183.52	0.702	0.2353	189.90	0.707	0.1350	198.98	0.702
0.3887	190.25	0.694	0.2791	197.56	0.692	0.1416	201.14	0.698

magnetic stirring. The relative uncertainty both in the electrolyte molality and  $w$  of EC is evaluated to be about 0.1 %.

Na-ISE (model 6.0501.100) and Cl-ISE (model 6.0502.120) were obtained from Metrohm Corp. A double-walled vessel Metrohm cell was used to hold the electrodes and the solution. The temperature in the cell was maintained at  $(25.00 \pm 0.05)$  °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 inner impedance greater than  $5 \cdot 10^{13} \Omega$  with a resolution of  $\pm 0.1$  mV. To obtain more precise emf readings, the 2 V analog output of the electrometer was

connected to a Keithley model 197A Microvolt DMM with an input greater than  $1 \cdot 10^{12} \Omega$  and resolution of  $\pm 0.01$  mV. The correct functioning of this group was periodically checked by measuring potentials using a certified Leeds & Northrup Co. Weston standard cell.

The Cl-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 the 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.

**Table 2. Values of Average Molecular Mass ( $M$ ), Relativity Permittivity ( $\epsilon_r$ ), Density ( $\rho$ ), the Debye–Hückel ( $A$ ,  $B$ ), Pitzer ( $A_\phi$ ), and Scatchard ( $S$ ) Constants, and the Bjerrum Parameter ( $q$ ) as a Function of the Mass Fraction ( $w$ ) of EC in the EC + Water Mixture at 298.15 K**

$w$	$m$ g·mol <sup>-1</sup>	$\epsilon_r$	$\rho$ g·cm <sup>-3</sup>	$A$ kg <sup>1/2</sup> ·mol <sup>-1/2</sup>	$B$ kg <sup>1/2</sup> ·mol <sup>-1/2</sup> ·Å <sup>-1</sup>	$A_\phi$ kg <sup>1/2</sup> ·mol <sup>-1/2</sup>	$S$ kg <sup>1/2</sup> ·mol <sup>-1/2</sup>	$q$ 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

### 3. Results

Mean ionic activity coefficient values of the NaCl in EC + water were determined from the potential difference measurements of the following cells without transference:



In these cells,  $m$  is the molality of NaCl (moles NaCl/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:

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

where  $E$  is the potential difference of the cell,  $k = (\ln 10) \cdot (RT/F)$  is the Nernst theoretical slope, and  $m$  and  $\gamma$  are the molality and mean ionic activity coefficients of the NaCl.  $E^{0*}$  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<sup>1–3,24,25</sup> 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 NaCl molality. Since the activity coefficients of the NaCl in pure water are well-known,<sup>26</sup> the values of  $E$  that appear in Table 1 for  $w = 0$  allow carrying out a calibration of the electrode system, using eq 1. A very good linear relationship is obtained when  $E$  versus  $-\log m\gamma$  is plotted. The value obtained when applying a least-squares regression analysis to the previous representation was  $k = (59.12 \pm 0.08)$  mV, with a correlation coefficient of 0.999993 and standard deviation of 0.31 mV. This value of  $k$  differs only by about 0.1 %, from the theoretical value. This is above acceptable levels for a system containing two ISEs. In this calculation it has been assumed that  $k_{\text{Na}} \cong k_{\text{Cl}} \cong k \cong (k_{\text{Na}} + k_{\text{Cl}})/2$ .<sup>1–3</sup>

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 of Hitchcock,<sup>27</sup> using the extended Debye–Hückel,<sup>28,29</sup> Pitzer,<sup>30,31</sup> and Scatchard<sup>32,33</sup> equations to represent the dependency of  $\log \gamma$  on molality. For 1:1 electrolytes, these equations may be written as the following:

Extended Debye–Hückel equation:<sup>28,29</sup>

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

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

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

Pitzer equation:<sup>30,31</sup>

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

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

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

Table 3. Summary of Both Standard Potentials for the Cell Na-ISE|NaCl ( $m$ ), EC ( $w$ ), H<sub>2</sub>O (1 -  $w$ )|Cl-ISE and the NaCl Ionic Interaction Parameter Values Obtained for the Debye–Hückel (DH), Pitzer (P), and Scatchard (S) Equations, in the Different EC + Water Mixtures at 298.15 K

$w$	$E^{0*}(\text{DH})$		$a$	$c$	$d$	$\sigma$	$E^{0*}(\text{P})$	$\beta^0$	$\beta^1$	$C^y$	$\sigma$	$E^{0*}(\text{S})$	$\sigma$	$\langle E^y \rangle^a$
	mV	mV												
0	-190.53 ± 0.35	-190.61 ± 0.35	4.04 ± 0.21	0.0520 ± 0.0034	0.0010 ± 0.0003	0.29	-190.61 ± 0.35	0.0765 <sup>a</sup>	0.2664 <sup>a</sup>	0.0019 <sup>a</sup>	0.28	-190.69 ± 0.42	0.21	-190.61 ± 0.05
0.1	-202.09 ± 0.09	-201.73 ± 0.13	2.68 ± 0.05	0.0884 ± 0.0016	-0.0020 ± 0.0002	0.10	-201.73 ± 0.13	0.1109 ± 0.0020	0.0422 ± 0.0140	-0.0082 ± 0.0006	0.15	-201.85 ± 0.13	0.13	-201.89 ± 0.10
0.2	-208.31 ± 0.25	-207.82 ± 0.22	2.47 ± 0.12	0.1056 ± 0.0050	-0.0039 ± 0.0006	0.18	-207.82 ± 0.22	0.1260 ± 0.0036	0.0111 ± 0.0247	-0.0122 ± 0.0012	0.18	-207.68 ± 0.27	0.17	-207.94 ± 0.19
0.3	-216.12 ± 0.31	-215.72 ± 0.22	2.37 ± 0.20	0.1243 ± 0.0119	-0.0073 ± 0.0025	0.16	-215.72 ± 0.22	0.1503 ± 0.0085	-0.0329 ± 0.0369	-0.0234 ± 0.0046	0.14	-215.79 ± 0.23	0.14	-215.88 ± 0.12
0.4	-226.22 ± 0.26	-225.92 ± 0.25	3.02 ± 0.17	0.1002 ± 0.0059		0.16	-225.92 ± 0.25	0.1227 ± 0.0055	0.1174 ± 0.0315		0.17	-226.03 ± 0.47	0.19	-226.06 ± 0.09
0.5	-239.46 ± 0.22	-239.27 ± 0.20	3.27 ± 0.23	0.1074 ± 0.0097		0.14	-239.27 ± 0.20	0.1342 ± 0.0106	0.1495 ± 0.0425		0.15	-239.30 ± 0.21	0.14	-239.34 ± 0.06
0.6	-257.61 ± 0.20	-257.42 ± 0.17	3.07 ± 0.25	0.1135 ± 0.0133		0.06	-257.42 ± 0.17	0.1391 ± 0.0145	0.1066 ± 0.0479		0.06	-257.45 ± 0.18	0.06	-257.49 ± 0.06
0.7	-282.09 ± 0.30	-281.94 ± 0.25	3.07 ± 0.54	0.0772 ± 0.0361		0.13	-281.94 ± 0.25	0.0936 ± 0.0428	0.1007 ± 0.1122		0.13	-281.96 ± 0.26	0.13	-282.00 ± 0.05
0.8	-319.87 ± 0.12	-320.37 ± 0.19	2.14 ± 0.07			0.16	-320.37 ± 0.19	0.4097 ± 0.0965	-0.9590 ± 0.1944		0.10	-319.64 ± 0.11	0.17	-319.96 ± 0.21

<sup>a</sup> Fixed values.<sup>30,31</sup>

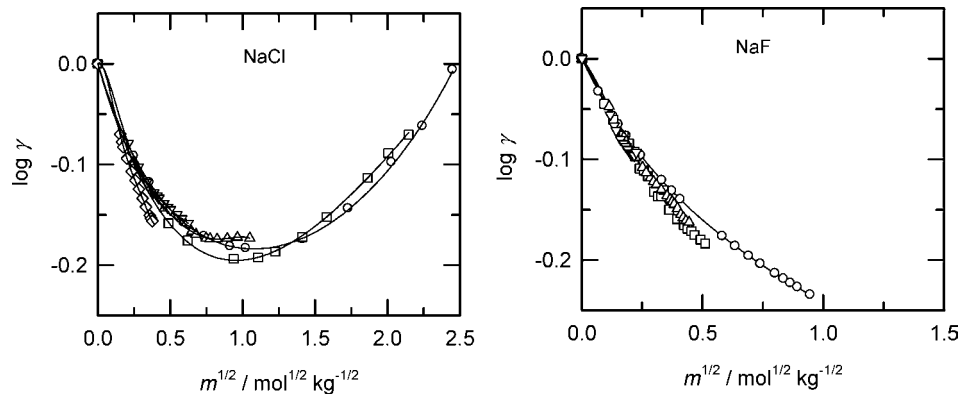


Figure 1. Plot of  $\log \gamma$  vs  $m^{1/2}$  for NaCl and NaF<sup>2</sup> in EC + water at 298.15 K.  $\circ$ ,  $w = 0$ ;  $\square$ ,  $w = 0.2$ ;  $\triangle$ ,  $w = 0.4$ ;  $\nabla$ ,  $w = 0.6$ ;  $\diamond$ ,  $w = 0.8$ .

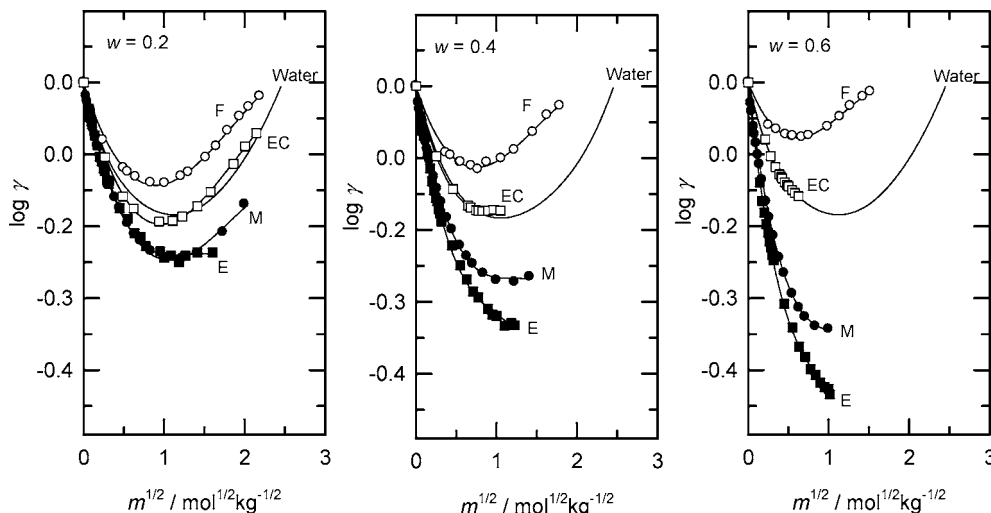


Figure 2. Plot of  $\log \gamma$  vs  $m^{1/2}$  for NaCl both in water and in different  $w$  of various cosolvents. EC, ethylene carbonate<sup>this work</sup>; F, formamide;<sup>24</sup> M, methanol;<sup>11</sup> E, ethanol.<sup>8</sup>

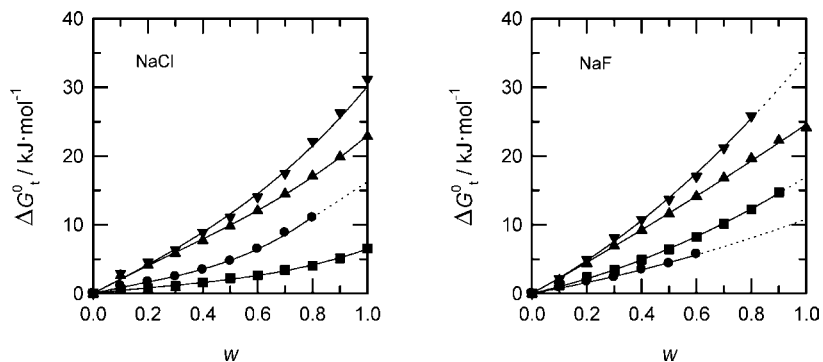


Figure 3. Variation of the standard Gibbs energy of transference with  $w$  of cosolvent for NaCl and NaF.  $\bullet$ , EC + water<sup>this work,2</sup>;  $\blacksquare$ , formamide + water;<sup>3,24</sup>  $\blacktriangle$ , methanol + water;<sup>1,11</sup>  $\blacktriangledown$ , ethanol + water.<sup>1,8</sup>

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

Scatchard equation:<sup>32,33</sup>

$$\ln \gamma = \frac{1}{2} \left[ \frac{2Sm^{1/2}}{1 + am^{1/2}} + 2a^{(1)}m + \frac{3}{2}a^{(2)}m^2 + \frac{4}{3}a^{(3)}m^3 + \frac{5}{4}a^{(4)}m^4 \right] \quad (5)$$

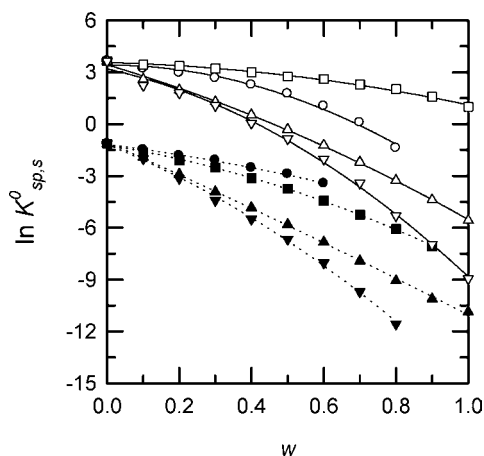
$$S = -3A_\phi \quad (5a)$$

All symbols having their usual meaning. The values of density,  $\rho$ , and the relative permittivity,  $\epsilon_r$ , for the EC + water mixtures were interpolated from those found in the literature<sup>4-6</sup> and appear together with the other constants in Table 2.

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. The standard deviations of the fits are also comparable.



**Figure 4.** Variation of  $\ln K^0_{sp,s}$  of NaCl and NaF with  $w$  of cosolvent. O, NaCl + EC + water<sup>this work</sup>; □, NaCl + formamide + water;<sup>24</sup> △, NaCl + methanol + water;<sup>11</sup> ▽, NaCl + ethanol + water;<sup>8</sup> ●, NaF + EC + water;<sup>2</sup> ■, NaF + formamide + water;<sup>3</sup> ▲, NaF + methanol + water;<sup>1</sup> ▼, NaF + ethanol + water.<sup>1</sup>

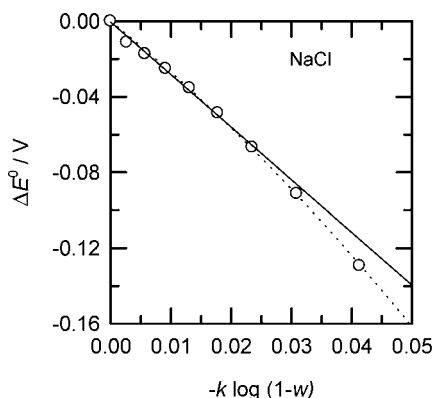
**Table 4.** Increments of Standard Potential Difference,  $\Delta E^0$ , and Standard Gibbs Energy of Transference,  $\Delta G^0_t$ , for the NaCl + EC + Water System at 298.15 K

$w$	$\Delta E^0$	$\Delta G^0_t$
	mV	$\text{kJ}\cdot\text{mol}^{-1}$
0	$0.00 \pm 0.09$	$0.00 \pm 0.01$
0.1	$-11.28 \pm 0.15$	$1.09 \pm 0.01$
0.2	$-17.33 \pm 0.24$	$1.67 \pm 0.02$
0.3	$-25.27 \pm 0.17$	$2.44 \pm 0.02$
0.4	$-35.45 \pm 0.13$	$3.42 \pm 0.01$
0.5	$-48.73 \pm 0.10$	$4.70 \pm 0.01$
0.6	$-66.88 \pm 0.10$	$6.45 \pm 0.01$
0.7	$-91.39 \pm 0.09$	$8.82 \pm 0.01$
0.8	$-129.35 \pm 0.26$	$12.48 \pm 0.03$

Optimization using the Debye–Hückel extended equation with the inclusion of the parameter  $d$  allows the fit to be made in the entire range of molality of NaCl with a very good standard deviation for  $0 < w < 0.3$ .

As the solubility of NaCl decreases significantly with the increase of  $w$  of EC, the inclusion of the additional parameter  $d$  is not necessary for  $w > 0.3$ , since the maximum molality is less than  $1.1 \text{ mol}\cdot\text{kg}^{-1}$ , approximately. Even more, for  $w = 0.8$ , where the maximum molality is  $0.14 \text{ mol}\cdot\text{kg}^{-1}$ , a good standard deviation in the fit can be obtained without taking into account the parameter  $c$ .

The parameter  $a$  (related to the ionic size) remains almost constant at  $(2.90 \pm 0.20) \text{ \AA}$ , with a value slightly superior than the sum of the crystallographic radii of  $\text{Na}^+$  and  $\text{Cl}^-$  ( $2.76 \text{ \AA}$ )<sup>34</sup>



and slightly inferior than the  $q$  parameter of Bjerrum,<sup>35</sup> shown in the last column of Table 2. This could indicate that there is little solvation and slight ionic association, although this last one is not clear since, as it occurred with NaF in EC + water,<sup>2</sup> the difference ( $a - q$ ) is very small and practically constant in the whole range of mass fraction of EC under study.

Optimization using the Pitzer equation allowed obtaining reasonable values for  $\beta^0$  (which can be identified with interactions of like and unlike charged ions),  $\beta^1$  (which can be identified with the interactions between unlike-charged ions) and  $C^{\gamma}$  (which represents triple ionic interactions). For  $w > 0.3$ , it can be considered  $C^{\gamma} = 0$ , without losing accuracy,<sup>30,31</sup> because the molality of NaCl is less than  $2 \text{ mol}\cdot\text{kg}^{-1}$ .

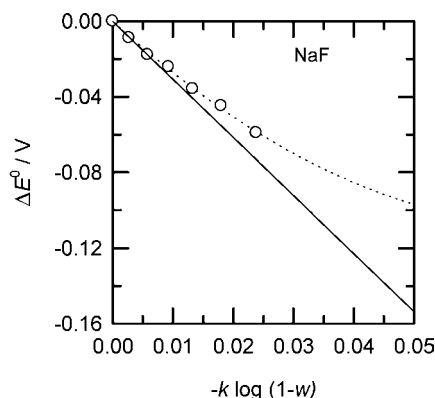
The average values for  $E^{0*}$  which appear in the last column of Table 3 were calculated considering the three models studied. These average values were used to calculate the mean ionic coefficient activity,  $\gamma$ , which is listed in Table 1 for each  $m$  of NaCl and each  $w$  of EC. The standard deviations of our activity coefficients compared to those reported in the literature were calculated to be less than  $\pm 0.004$  in pure water, showing good agreement between both sets of data, particularly if the wide range of concentrations studied is taken into account.

Figure 1 is an example of the dependence of  $\log \gamma$  versus  $m^{1/2}$  at various mass fractions of EC in the mixture. For comparison purpose, the corresponding plot for NaF in EC + water<sup>2</sup> also is shown. All of the curves show a typical profile of the variation  $\log \gamma$  with the root square of the molality which, as is well-known, is governed by two types of interactions: ion–ion and ion–solvent.<sup>28,29</sup>

Given that all measurements were carried almost to saturation molality, it is clearly observed that the solubility of both NaCl and NaF decreases significantly in all cases with the increase of  $w$  of EC.

Another aspect to emphasize is the small difference observed between the values of  $\log \gamma$  in the mixture and in pure water. Probably, this takes place because the water ( $\epsilon_r = 78.38$ ) and the EC ( $\epsilon_r = 89.78$  at  $40 \text{ }^\circ\text{C}$ ) are almost iso-dielectric. For comparison, Figure 2 shows the variation of  $\log \gamma$  with the molality of electrolyte (NaCl or NaF) for three different  $w$  of various cosolvents,<sup>1–3</sup> and it is observed as for formamide ( $\epsilon_r = 109.57$ ), methanol ( $\epsilon_r = 32.66$ ), or ethanol ( $\epsilon_r = 24.55$ ) the differences of  $\log \gamma$  with respect to the water are great.

Table 4 shows the standard Gibbs energy of transference,  $\Delta G^0_t$ , probably one of the magnitudes most commonly used for the understanding of differences in behavior of the solution. It can be easily calculated from the values of  $E^{0*}$  according to the expression:<sup>1–3,9,36</sup>



**Figure 5.** Variation of  $\Delta E^0$  vs a function of mass fraction of water in the EC + water mixture for NaCl and NaF.<sup>2</sup>

$$\Delta G_t^0 = -zF\Delta E^0 = -zF(E_s^0 - E_w^0) = -zF[(E_s^{0*} - E_w^{0*}) - (E_s^{\text{asym}} - E_w^{\text{asym}})] \quad (6)$$

where  $E^0$ ,  $E^{0*}$ , and  $E^{\text{asym}}$  stand for the standard potential difference, the apparent standard potential difference, and the total asymmetry potential ( $\varepsilon_{\text{Na}}^{\text{asym}} + \varepsilon_{\text{w}}^{\text{asym}}$ ), 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,  $E^{\text{asym}}$  is a constant value with time and is independent of the composition of the solvent (the asymmetry potential of an electrode depends on the characteristics of the membrane and not on the medium in which it is immersed<sup>27,38</sup>), which allows us to affirm that  $(E_s^{\text{asym}} - E_w^{\text{asym}})$  is negligible compared to  $(E_s^{0*} - E_w^{0*})$ , and thus eq 6 may be used without any problems. We must emphasize that, in no instance, we have made assumptions extra-thermodynamic.

Figure 3 shows a plot of the standard Gibbs energy of transfer obtained now against  $w$  of EC along with those obtained by us with other cosolvents.<sup>1–3</sup> For comparison purposes, the corresponding plot for NaF also is shown. The positive values of  $\Delta G_t^0$  suggest that the process of transference is not favored in any of the cases. Also, the increasing order of energies for a given  $w$  of cosolvent (formamide–water < EC–water < methanol–water < ethanol–water) for the NaCl and (EC–water < formamide–water < methanol–water < ethanol–water) for the NaF could indicate that both NaCl and NaF are more solvated in mixtures with high relative permittivity cosolvent than in mixtures with low relative permittivity cosolvent.

According to Kalidas et al.,<sup>39</sup> the standard Gibbs energy of transfer to the whole salt,  $\Delta G_t^0$ , is related to the standard solubility product,  $K_{\text{sp}}^0$ , of the electrolyte in the two solvents by:

$$\Delta G_t^0 = RT \ln(K_{\text{sp,w}}^0/K_{\text{sp,s}}^0) \quad (7)$$

where  $K_{\text{sp,w}}^0$  and  $K_{\text{sp,s}}^0$  represent the standard solubility product of the salt in water ( $38.051 \text{ mol}^2 \cdot \text{kg}^{-2}$  for the NaCl and  $0.318 \text{ mol}^2 \cdot \text{kg}^{-2}$  for the NaF)<sup>26</sup> and in organic–water mixture, respectively. In Figure 4 a significant decrease of  $\ln K_{\text{sp,s}}^0$  calculated by eq 7 with  $w$  of cosolvent is clearly observed, both for NaF and for NaCl.

Since  $\Delta G_t^0$  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 NaCl primary hydration number. For this we used the equation of Feakins and French<sup>40</sup> which allows the 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 weight fraction of water in the mixture according to:

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

Figure 5 shows a plot of  $\Delta E^0$  versus  $-k \log w$  where an excellent linear correlation is observed for both NaCl and NaF up to 0.3 to 0.4 mass fraction of water. The values found for  $n_{\text{hyd}}$  were 2.9 ( $r = 0.9991$ ) for NaCl and 3.1 ( $r = 0.9996$ ) for NaF. Both are very low compared with those obtained from the literature<sup>41</sup> ( $6 \pm 2$  for NaCl and  $8 \pm 2$  for NaF). This can be due to the value of the dipole moment of the EC ( $\mu = 4.87 \text{ D}$ ), which is much greater than the one of the water ( $\mu = 1.83 \text{ D}$ ). Thus, the EC is highly prone to preferentially solvate the cations, displacing water from the primary hydration sheath.

## 5. Conclusions

Using the bi-ISE cell Na-ISE|NaCl ( $m$ ), EC ( $w$ ),  $\text{H}_2\text{O}$  ( $1 - w$ )|Cl-ISE, we have determined the mean ionic activity coef-

ficients of NaCl in the aqueous mixtures with high relative permittivity cosolvent EC + water. A good correlation of the experimental data was obtained with the thermodynamic models used (Debye–Hückel, Pitzer, and Scatchard). Little variation of these coefficients with respect to those of the NaCl in pure water is observed, possibly because  $\varepsilon_r(\text{EC}) \cong \varepsilon_r(\text{H}_2\text{O})$ . The Gibbs energy of transfer of the NaCl from the water to the EC + water mixture, the standard solubility product of NaCl in EC + water, and the NaCl primary hydration number were also estimated and comparatively analyzed with those of the NaF previously obtained in similar mixtures.

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