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

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ABSTRACT: The mean ionic activity coefficients of NaBr were experimentally determined in formamide + water mixtures at 298.15 K from potential difference measurements of the following electrochemical cell containing two ion selective electrodes (ISEs): Na-ISE|NaBr (m), formamide (w), H_2O ($1-w$)|Br-ISE. The molality (m) varied between 0.02 $\text{mol}\cdot\text{kg}^{-1}$ and almost saturation, whereas the mass fraction of formamide in the mixture (w) was varied between 0 and 1 in 0.1-unit steps. The determination of E^{0*} (molal scale) was carried out following a method similar to that proposed by Hitchcock and using the classical extended Debye–Hückel and Scatchard equations. We also use for this purpose a modification of the Pitzer equation proposed by Rard and Archer and the most recent modified three-characteristic-parameter-correlation model. 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 formamide + water mixture (ΔG_t^0), standard solubility product of NaBr in formamide + water (K_{sp}^0), and NaBr primary hydration number (n_{hyd}) 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 constantly required by researchers.

As a continuation of previous work by our group on the determination of thermodynamic properties of electrolyte systems in aqueous–organic media containing high relative permittivity cosolvents,[1−6] we now carry out the study of NaBr in water + formamide mixtures.

This study was conducted using the potentiometric technique which has been greatly improved in recent decades mainly due to the development and improvement of the ion-selective electrodes (ISEs). Activity coefficients of NaBr were determined based on potential difference measured of cells containing two ion selective electrodes: one of them of membrane solid crystalline for the ion Br^- and another one of glass membrane for ion Na^+. Our usual working method was applied to obtain the maximum possible information about this system. The activity coefficients were discussed in light of the solvent properties, especially its relative permittivity. The standard Gibbs energy of transfer from the water to the organic–water mixture, the standard solubility product, and the primary hydration number of the electrolyte were also calculated. The variations of all of them with the composition of the mixture have been comparatively discussed with those obtained previously for both NaF[2] and NaCl[3].

Formamide[7−9] is a highly ionizing polar liquid with a dipole moment and relative permittivity higher than water, with which it is completely miscible throughout the complete composition range and forms a hydrogen-bonded network. In the formamide–water mixtures the relative permittivity (static dielectric constant), the density, and the viscosity uniformly increase with the cosolvent content. The relative permittivity reaches a maximum value at 80–90%.

Moreover, formamide shows two other important characteristics. The first is its highly hygroscopic nature, which makes it difficult to maintain in a pure state for a long period. Fortunately, it has also been shown[7] that a water content change of 1–2% did not appreciably affect conductivity or potentiometric experiments and is probably negligible when working with formamide + water mixtures.

The second important feature of formamide is its notable capacity for hydrolysis,[7] especially in very acid or very basic media. Kinetic investigations[10] have shown that, under these experimental conditions, hydrolysis is too slow to affect the potentiometric measurements.

Aqueous mixtures containing amides (in particular, cyclic amides) constitute an important tool in the interpretation of behavior of complex molecules with biological interest.[11,12] A lot of work has been published on the amide + water system to learn the manner in which water exercises thermodynamic and kinetic control over the chemical activities of polypeptides. The abnormally high density of H-bonds in water (strongly self-associated) and the nature donor–acceptor (−CO−NH−peptide bond) give these water–amide systems a great interest from a structural perspective. The additional presence of an electrolyte further complicates the picture (structure making/breaking effects).

From studies of density and viscosity, Garcia et al.,[11] calculated excess volumes, mixing viscosities and excess Gibbs energies of activation of viscous flow of some amide–water mixtures. The values of these functions compared with those of the amide + alcohol mixtures, reveal an important hydration effect with strong amide–water interactions and formation of aggregates, the nature of which depends on the extent of substitution of the

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

m	$-E$		m	$-E$		m	$-E$	
$mol \cdot kg^{-1}$	mV	γ	$mol \cdot kg^{-1}$	mV	γ	$mol \cdot kg^{-1}$	mV	γ
	$w = 0^a$			$w = 0.1$			$w = 0.2$	
0.0517	218.13	0.819	0.0873	243.40	0.779	0.0249	185.37	0.879
0.2035	283.30	0.737	0.1593	272.57	0.771	0.2482	296.22	0.756
0.5536	331.59	0.691	0.3448	309.67	0.731	0.5320	334.13	0.736
0.9458	358.69	0.684	0.5712	334.61	0.716	0.9029	362.14	0.746
1.2965	375.54	0.692	0.9710	362.31	0.721	1.2328	379.53	0.766
1.7519	392.60	0.713	1.4892	387.39	0.764	1.7722	401.31	0.813
2.2153	406.86	0.743	2.1776	410.10	0.812	2.1523	413.70	0.851
3.1433	430.56	0.829	3.1063	435.24	0.927	3.5248	449.89	1.048
4.0317	449.74	0.938	3.9731	454.77	1.058	4.8151	477.23	1.304
5.5119	477.15	1.167	4.9631	474.48	1.242	5.8289	496.64	1.569
6.9125	499.90	1.447	6.0444	494.44	1.501	6.5430	509.29	1.787
8.4777	522.26	1.820	7.1078	511.82	1.788	7.2881	522.76	2.083
						7.9407	532.70	2.318
	$w = 0.3$			$w = 0.4$			$w = 0.5$	
0.0422	213.35	0.867	0.0347	206.66	0.883	0.0616	238.76	0.873
0.1500	274.69	0.801	0.1338	272.60	0.822	0.1357	277.49	0.839
0.3037	309.35	0.775	0.2145	295.93	0.806	0.4129	334.45	0.832
0.6410	347.43	0.768	0.3795	324.64	0.795	0.7202	365.40	0.870
0.9531	369.93	0.800	0.7704	363.67	0.835	1.1367	390.56	0.898
1.2905	387.53	0.831	1.1768	386.78	0.855	1.8471	421.29	1.002
1.5088	396.43	0.844	1.7278	410.50	0.923	2.5372	444.44	1.143
2.1005	417.54	0.913	2.3836	432.53	1.025	3.8898	481.22	1.522
2.6975	435.24	1.002	2.9134	447.95	1.131	4.8658	503.89	1.888
3.4737	455.33	1.149	3.4684	462.46	1.259	6.0442	527.85	2.419
4.9906	488.65	1.526	4.8694	496.77	1.744			
6.2933	513.52	1.961	6.4362	525.34	2.296			
7.2786	530.32	2.348						
7.8653	539.80	2.611						
	$w = 0.6$			$w = 0.7$			$w = 0.8$	
0.1261	278.27	0.877	0.0695	254.68	0.897	0.0633	255.17	0.895
0.2195	306.17	0.866	0.1498	292.86	0.873	0.1564	301.29	0.886
0.3864	336.92	0.893	0.2676	323.69	0.889	0.6228	374.39	0.918
0.5201	353.28	0.911	0.4065	345.91	0.900	0.9860	401.23	0.976
0.6744	366.52	0.908	0.8559	386.19	0.933	1.4530	426.01	1.070
0.8717	380.54	0.922	1.4173	417.21	1.029	1.9112	445.50	1.187
1.0772	392.94	0.949	2.5107	459.06	1.307	2.4229	463.91	1.339
1.4667	412.19	1.013	3.4845	488.06	1.653	3.3109	491.29	1.666
2.5586	452.22	1.261	4.0810	503.49	1.904	4.5120	525.64	2.380
3.8439	488.18	1.686	4.7199	518.90	2.219			
5.2319	520.51	2.319						
	$w = 0.9$			$w = 1.0$			$w = 0^b$	
0.0545	256.96	0.907	0.0541	264.51	0.963	0.0717	234.26	0.799
0.2140	328.00	0.916	0.0750	281.37	0.963	0.2323	289.95	0.726
0.4405	364.82	0.908	0.0945	293.55	0.972	0.4874	325.55	0.691
0.6924	389.87	0.939	0.1250	308.49	0.985	0.7485	346.87	0.680
1.0400	414.34	1.005	0.1709	325.24	0.998	0.9334	358.26	0.680
1.7085	448.22	1.180	0.2205	338.95	1.007	1.4136	380.68	0.693
2.1744	466.55	1.323	0.2882	353.55	1.017	1.7747	393.63	0.710
			0.4993	385.12	1.085	2.5200	415.42	0.763
						3.5329	439.30	0.865

Table 1. Continued

m mol·kg^{-1}	$-E$ mV	γ	m mol·kg^{-1}	$-E$ mV	γ	m mol·kg^{-1}	$-E$ mV	γ
						4.1691	452.45	0.946
						5.5212	477.27	1.156
						6.2339	489.18	1.289
						7.7859	512.60	1.626
						9.0461	529.60	1.946

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

amides. Only the behavior of the formamide—water mixture can be successfully predicted by a simple model.

Also, Papamatthaiakis et al.[12] measured both density and ultrasonic velocity for pure amides and their binary aqueous mixtures. From these data isentropic compressibility, apparent molar compressibility, intermolecular free length and relative association, as well as the corresponding excess quantities were calculated. The systematic study of these parameters reveals a large deviation from ideal behavior as a result of the strong amide—water interaction.

With regard to the electrolyte studied, it is well-known that NaBr, unlike NaF and NaCl, is much more soluble in water (9.186 mol·kg^{-1} against (0.983 and 6.146) mol·kg^{-1} at 298.15 K, respectively)[13−15] 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[16,25] but only one that we know of in aqueous mixtures with a high relative permittivity cosolvent.[5]

The main objective of this study includes the experimental determination of mean ionic activity coefficients of NaBr (γ), the Gibbs energy of transfer of NaBr from water to the formamide + water mixture (ΔG_t^0), standard solubility product of NaBr in formamide + water (K_{sp}^0), and NaBr primary hydration number (n_{hyd}). The molality of NaBr was varied between 0.02 mol·kg^{-1} and almost saturation, while the mass fraction of formamide in the mixture (w) was varied between 0 and 1 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 and stored over silica gel in desiccators. Formamide, Sigma puris (w = 0.995), was used without prior treatment. Correction for the very small water content of the original product was considered unnecessary. In each set of experiments (corresponding to a w of formamide), working solutions were prepared by adding successive known masses of solid NaBr to a previously prepared solution of formamide 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 formamide is estimated to be about 0.1 %.

The procedure to estimate the saturation molality of the NaBr, in each of the mixtures formamide + water studied, was as follows: (a) a solution (with excess of NaBr) was strongly shaken for 5 h and then decanted overnight, maintaining a constant temperature of 298.15 K; (b) approximately 2 g of sample was taken from the supernatant solution; (c) the samples were dried by solvent evaporation until a constant weight was reached. On the basis of the last weight and that of the initial sample, the saturation molality was then calculated. In order to obtain a good estimation, the process was quadruplicated and the average value subsequently calculated. The relative uncertainty of the saturation molality is estimated to be about 0.2%, approximately.

The electrodes, cells, apparatus, temperature control system, as well as the measurement procedure employed in the present study have been widely reported previously.[1−6] The temperature relative uncertainty was estimated to be 0.02 %. Depending on the mass fraction of formamide in the mixture, the potential difference uncertainty can be estimated between (0.08 and 0.26) mV, approximately. For mass fractions of formamide greater than 0.7, the stabilization times of the potential difference greatly increased due to the slow dissolution of NaBr, and therefore these uncertainties are somewhat higher.

3. RESULTS

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

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

In these cells, m is the molality of NaBr (moles NaBr/kg mixed-solvent) in the working solution and w the mass fraction of formamide 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 respectively 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[1−6] 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 formamide + water as a function of NaBr molality. Since the mean activity coefficients of the NaBr in pure water are well-known,[14] the two groups of E values that appear in Table 1 for w = 0 allow a calibration of the electrode system to be carried out, using eq 2. The experiments were started with the first calibration and ended

Table 2. Values of Average Molecular Mass (M); Relativity Permittivity (ε_r); Density (ρ); Debye−Hückel (A, B), Pitzer (A_ϕ), and Scatchard (S) Constants; and Bjerrum Parameter (q) as a Function of the Mass Fraction (w) of Formamide in Formamide + 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	18.015	78.38	0.99705	0.5100	0.3285	0.3915	−1.1745	3.57
0.1	19.165	82.99	1.01116	0.4714	0.3215	0.3618	−1.0856	3.37
0.2	20.472	87.31	1.02506	0.4398	0.3156	0.3376	−1.0129	3.21
0.3	21.970	91.62	1.03879	0.4119	0.3101	0.3162	−0.9486	3.06
0.4	23.704	96.02	1.05233	0.3864	0.3049	0.2966	−0.8898	2.92
0.5	25.736	100.44	1.06568	0.3635	0.3000	0.2790	−0.8370	2.79
0.6	28.149	104.67	1.07886	0.3438	0.2957	0.2639	−0.7916	2.68
0.7	31.061	108.32	1.09185	0.3285	0.2924	0.2522	−0.7565	2.59
0.8	34.645	110.85	1.10466	0.3192	0.2907	0.2450	−0.7350	2.53
0.9	39.165	111.56	1.11728	0.3179	0.2915	0.2440	−0.7322	2.51
1	45.040	109.57	1.12972	0.3284	0.2957	0.2521	−0.7564	2.56

with the second one. A very good linear relationship is obtained when E versus $-\log m\gamma$ is plotted. The value obtained for the Nernst slope, when applying a least-squares regression analysis to the previous plots, were $k = (59.44 \pm 0.02)$ mV and $k = (59.31 \pm 0.02)$ 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 $k = (59.37 \pm 0.02)$ mV differs only by about 0.4 %, from the theoretical value and will be taken now as the value of k for the following calculations achieved in this work. This is above acceptable levels for a system containing two ISEs. In this calculation it has been assumed that $k_{\mathrm{Na}} \cong k_{\mathrm{Br}} \cong k \cong (k_{\mathrm{Na}} + k_{\mathrm{Br}})/2$.[1−6]

Additionally, the intercepts in both cases are practically equal: $E^{0*} = (-381.03 \pm 0.03)$ mV and $E^{0*} = (-381.21 \pm 0.03)$ mV, respectively. This is very significant because it indicates that the potential of asymmetry of the electrodes has scarcely varied in the 15 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,[26] and using the classical extended Debye−Hückel (DH) and Scatchard (S) equations. We also use for this purpose a modification of the Pitzer equation proposed by Rard and Archer (PRA) and the most recent modified three−characteristic−parameter−correlation (TCPC) model. For 1:1 electrolytes, these equations may be written as follows:

Extended Debye−Hückel equation:[27,28]

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

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

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

Scatchard equation:[29,30]

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

$$S = -3A_\phi \tag{4a}$$

Pitzer−Rard−Archer equation:[13,31,32]

$$\ln \gamma = f^\gamma + B^\gamma m + C^\gamma m^2 \tag{5}$$

$$f^\gamma = -A_\phi\left[\frac{\sqrt{m}}{1 + b\sqrt{m}} + \frac{2}{b}\ln(1 + b\sqrt{m})]\right. \tag{5a}$$

$$B^\gamma = 2\beta^0 + \frac{2\beta^1}{\alpha^2 m}[1 - (1 + \alpha\sqrt{m} - \alpha^2 m/2)\exp(-\alpha\sqrt{m})] \tag{5b}$$

$$C^\gamma = 3C^0 + \frac{4C^1}{\alpha_2^4 m^2}[6 - (6 + 6\alpha_2\sqrt{m} + 3\alpha_2^2 m + \alpha_2^3 m^{3/2} - \alpha_2^4 m^2/2)\exp(-\alpha_2\sqrt{m})] \tag{5c}$$

$$A_\phi = 1.4006 \cdot 10^6 \rho^{1/2}/(\varepsilon_r T)^{3/2} \quad \mathrm{kg^{1/2} \cdot mol^{-1/2}} \tag{5d}$$

where $\alpha = 2.0\ \mathrm{kg^{1/2} \cdot mol^{-1/2}}$, $b = 1.2\ \mathrm{kg^{1/2} \cdot mol^{-1/2}}$, and $\alpha_2 = 1.7\ \mathrm{kg^{1/2} \cdot mol^{-1/2}}$.

Modified three-characteristic-parameter correlation model (TCPC)[33−35]

$$\ln \gamma = -A_\phi\left[\frac{\sqrt{m}}{1 + b\sqrt{m}} + \frac{2}{b}\ln(1 + b\sqrt{m})]\right. + \frac{S}{T}\frac{m^{2n}}{2} \tag{6}$$

b is treated as an adjustable parameter to represent the closest distance between the cation and anion; S is an electrolyte−specific parameter that describes the incorporate solvation effects of the cation and anion; n is the parameter which is related to the

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

	$-E^{0*}$(DH)	a	c	d	σ	$-E^{0*}$(S)	σ	$-E^{0*}$(P)	β^0	β^1	C^0	C^1	σ	$-E^{0*}$(TCPC)	b	S		σ	$\langle -E^{0*} \rangle$
w	mV	Å	$kg \cdot mol^{-1}$	$kg^2 \cdot mol^{-2}$	mV	mV	mV	mV	$kg \cdot mol^{-1}$	$kg \cdot mol^{-1}$	$kg^2 \cdot mol^{-2}$	$kg^2 \cdot mol^{-2}$	mV	mV	$mol^{1/2} \cdot kg^{1/2}$	$K^{-1} \cdot mol^{2n} \cdot kg^{2n}$	n	mV	mV
0^a	381.93 ± 0.33	3.43	0.0830	0.00020	0.31	380.95 ± 0.07	0.05	380.34 ± 0.39	0.1526^c	0.2551^c	-0.00230^c	-0.1176^c	0.34	381.39 ± 0.39	1.904	111.03	0.496	0.32	381.15 ± 0.34
0.1	380.97 ± 0.36	3.65	0.0921	−0.00022	0.31	380.94 ± 0.60	0.31	380.53 ± 0.42	0.1152	0.2138	−0.00048	0.0024	0.32	380.37 ± 0.47	2.137	112.18	0.508	0.30	380.71 ± 0.15
0.2	382.63 ± 0.26	3.61	0.0970	−0.00012	0.26	382.67 ± 0.26	0.22	382.39 ± 0.31	0.1058	0.1881	0.00021	0.0262	0.29	382.29 ± 0.33	2.040	115.43	0.513	0.29	382.50 ± 0.09
0.3	384.24 ± 0.31	3.78	0.1070	−0.00083	0.42	384.05 ± 0.48	0.35	383.67 ± 0.40	0.1506	0.1831	−0.00178	−0.0606	0.39	383.81 ± 0.48	2.017	133.26	0.491	0.42	383.94 ± 0.13
0.4	386.48 ± 0.16	4.24	0.1092	−0.00047	0.43	386.76 ± 0.10	0.08	386.36 ± 0.19	0.0975	0.2369	0.00115	0.0646	0.21	386.21 ± 0.25	2.279	130.30	0.507	0.22	386.45 ± 0.12
0.5	389.97 ± 0.45	4.35	0.1191	−0.00069	0.41	389.32 ± 0.44	0.23	389.41 ± 0.21	0.2413	0.1055	−0.00573	−0.2273	0.19	389.40 ± 0.54	2.685	130.03	0.517	0.36	389.52 ± 0.15
0.6	392.79 ± 0.60	5.73	0.1166	−0.00016	0.40	390.61 ± 1.09	0.29	392.36 ± 0.35	0.3274	0.0469	−0.01000	−0.3945	0.26	391.41 ± 0.89	4.964	107.71	0.564	0.35	391.79 ± 0.49
0.7	398.59 ± 0.89	6.13	0.1202	0.00053	0.61	396.58 ± 1.31	0.44	398.50 ± 0.56	0.5175	−0.2456	−0.02050	−0.7490	0.45	397.39 ± 1.22	5.381	108.82	0.576	0.53	397.76 ± 0.48
0.8	403.04 ± 0.34	7.87	0.1162	0.00265	0.22	403.34 ± 0.49	0.22	403.32 ± 0.25	−0.0601	0.6073	0.01400	0.3587	0.21	403.23 ± 0.91	4.834	116.46	0.589	0.43	403.23 ± 0.07
0.9	411.83 ± 1.75	11.76	0.0913	0.01270	0.73	411.65 ± 1.86	0.72	412.68 ± 1.21	0.0940	0.4437	0.01280		0.78	412.05 ± 2.07	6.887	104.66	0.656	0.70	412.05 ± 0.22
1	417.85 ± 1.64	20.78	0.1771		0.34	415.75 ± 2.99	0.12	417.72 ± 0.41	−0.3088	1.6915	0.22780		0.10	415.42 ± 9.99	37.260	169.72	0.434	0.43	416.69 ± 0.64
0^b	382.62 ± 0.29	3.32	0.0837	0.00019	0.26	381.62 ± 0.11	0.06	380.44 ± 0.58	0.1526^c	0.2551^c	-0.00230^c	-0.1176^c	0.46	382.12 ± 0.42	1.694	123.57	0.477	0.33	381.70 ± 0.47

[a] First calibration. [b] Second calibration. [c] Fixed values.[13]

distance between the ion and solvent molecule. The other symbols have their usual meaning.

The values of density and relative permittivity for the formamide−water mixtures were taken from the literature[11,12,14] and they are shown in Table 2 together with those for M, A, B, A_ϕ, S, and q (Bjerrum parameter).[8,9,11]

By combining eqs 2 and 3, 2 and 4, 2 and 5, or 2 and 6, 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 0.6 mV). The standard deviations of the fits are also comparable.

Optimization using the DH extended equation 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 $0 \leq w \leq 0.9$. The inclusion of the extra parameter d is not necessary for $w = 1$ (maximum molality is less than 0.5 $mol \cdot kg^{-1}$, approximately).

Parameter a (related to the ionic size) increase between (3 and 8) Å, approximately, for w values between 0 and 0.8. For $w > 0.8$, we get unusually large a values, possibly due to the short-range of molalities. These values of a are greater than the sum of the crystallographic radii of Na^+ and Br^- (2.9 Å)[27,28,36] as a probable result of the solvation. Furthermore, these values of a are greater than those of q Bjerrum parameter[27,28,37] (last column of Table 2), suggesting that there is no ion association unlike what happens for NaF[2] in formamide + water mixtures, where $(a - q)$ is negative.

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.

In this study, we have used Pitzer's ion-interaction model,[31,32] with inclusion of an ionic strength dependence of the C^γ parameter (which represents triple ionic interactions) as has been suggested by Rard and Archer.[13] Optimization using this PRA equation, 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 $w \geq 0.9$, it can be considered $C^1 = 0$, without losing accuracy.

Finally, the optimization using the most recent TCTP model shows good agreement with the above. Both E^{0*} values and fit standard deviation are very similar to previous ones. With respect to the characteristic parameters of the model, it is difficult to explain its variation with the mass fraction of formamide in the mixture. Thus, a slight increase of b (parameter that represent the closest distance between the cation and anion) is observed, which is consistent with the increase of the parameter a of the DH equation. In contrast, S (electrolyte−specific parameter that describes the incorporate solvation effects of the cation and anion) and n (parameter which is related to the distance between the ion and solvent molecule) do not show a clear trend and remain almost constant [(117.6 ± 3.0) and (0.537 ± 0.014), respectively]. The

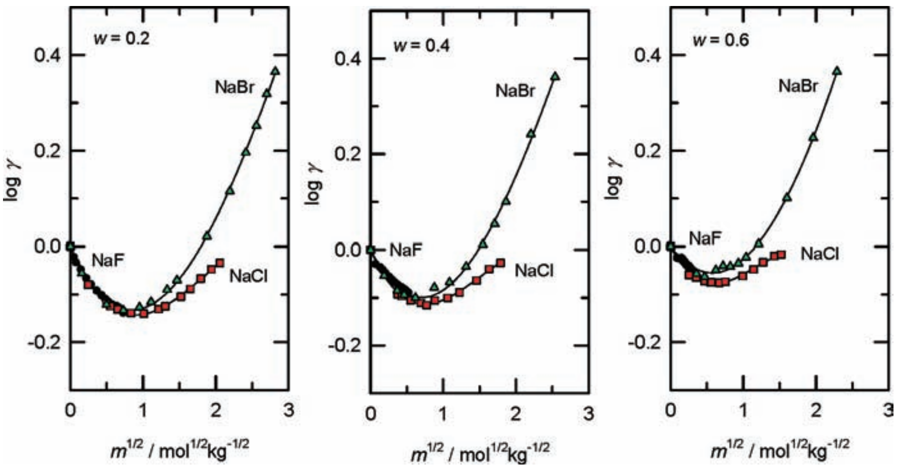

Figure 1. Plot of log γ vs $m^{1/2}$ for various formamide mass fractions (w) in formamide + water mixtures at 298.15 K. ●, NaF;[2] ■, NaCl;[3] and ▲, NaBr (this work).

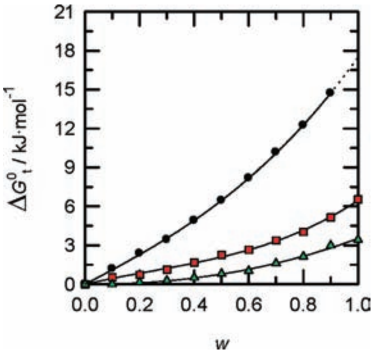

Figure 2. Variation of standard Gibbs energy of transfer with w in formamide + water mixtures at 298.15 K. ●, NaF;[2] ■, NaCl;[3] and ▲, NaBr (this work).

values for $w = 1$ show abnormally high values possibly due to the short-range of molalities measured, and they are not considered in the discussion. A more detailed interpretation of the sign and magnitude of these parameters can be found in the work of Ge et al.[33−35]

The average values for E^{0*} which appear in the last column of Table 3 were calculated considering the four 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 formamide (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 formamide in the mixture. For other values of w, the behavior is similar. For comparison purposes, the corresponding plots for NaF[2] and NaCl[3] are also shown. All of the curves show the 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.[27,28]

For a given molality, log γ increases with the w of formamide (increase of the relative permittivity of mixture) for the three electrolytes that are being compared.

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

$$\begin{aligned}\Delta G_t^0 &= -zF(E_s^0 - E_w^0) \\ &= -zF[(E_s^0* - E_w^0*) - (E_s^{asym} - E_w^{asym})]\end{aligned} \qquad (7)$$

where E^0, E^{0*}, and E^{asym} stand for the standard potential difference, the apparent standard potential difference and the total asymmetry potential ($\varepsilon_{Na}^{asym} + \varepsilon_{Br}^{asym}$), 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^{asym} is a small constant value, and independent of the composition of the solvent, which allows us to affirm, that ($E_s^{asym} - E_w^{asym}$) is negligible compared to ($E_s^{0*} - E_w^0*$), and thus eq 7 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_t^0, for NaF,[2] NaCl,[3] and NaBr against w of formamide in the formamide + water system. In all cases it is verified that $\Delta G_t^0 > 0$, indicating that the transfer is not energetically favorable.[8,9,27,28] For a given w, ΔG_t^0 always varies in the order NaF > NaCl > NaBr, indicating an increase of solvation in the same order. Since the cation is common to all three electrolytes, the order of solvation is determined by the properties of anion and especially its ionic radius.

According to Kalidas et al.,[38] the standard Gibbs energy of transfer to the whole salt, ΔG_t^0, is related to the standard solubility product, K_{sp}^0, of the electrolyte in the two solvents by

$$\Delta G_t^0 = RT \ln(K_{sp,w}^0 / K_{sp,s}^0) \qquad (8)$$

where $K_{sp,w}^0$ and $K_{sp,s}^0$ represent the standard solubility product of the salt in water (0.318 $mol^2 \cdot kg^{-2}$ for NaF, 38.051 $mol^2 \cdot kg^{-2}$ for NaCl, and 120.877 $mol^2 \cdot kg^{-2}$ for NaBr)[13,15] and in the formamide + water mixture, respectively. In Figure 3a, a considerable decrease of ln $K_{sp,s}^0$ calculated by eq 8 with w of the cosolvent

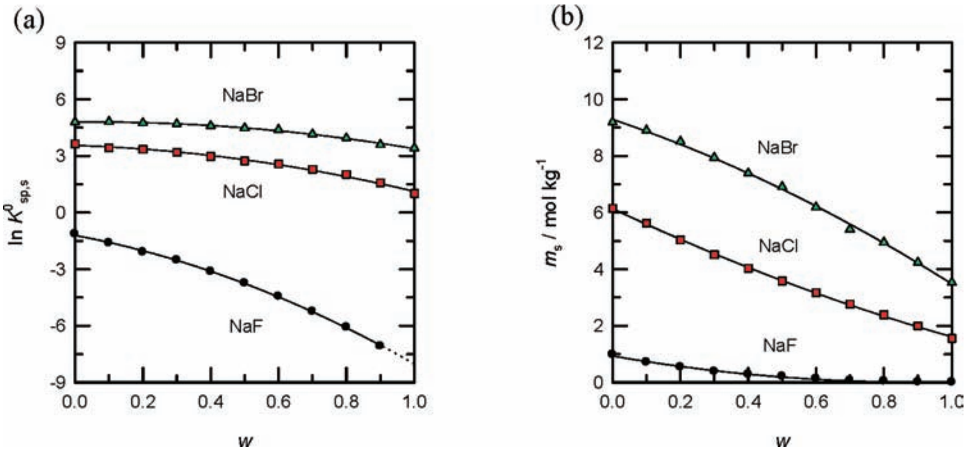

Figure 3. Variation of ln $K^0_{sp,s}$ and m_s with w in formamide + water mixtures at 298.15 K. ●, NaF;[3] ■, NaCl;[6] and ▲, NaBr (this work).

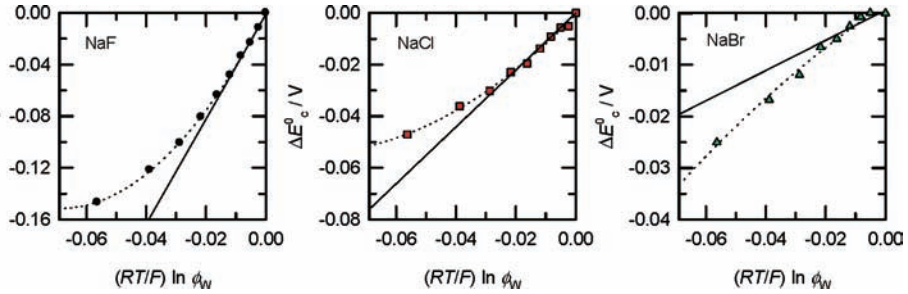

Figure 4. Variation of ΔE^0_c vs a function of water volume fraction in the formamide + water mixture at 298.15 K. ●, NaF;[3] ■, NaCl;[6] and ▲, NaBr (this work).

is clearly observed, for the three electrolytes. This agrees well with the order of solubility shown in the plots of Figure 3b where, in addition to the values obtained in this work for the saturation molality of NaBr in formamide—water mixtures, are presented those previously measured by us for both NaF[2] and NaCl[3] in similar mixtures.

Finally, in order to complete the thermodynamic description of NaBr dissolved in formamide + water, an interesting correlation deduced by Feakins and French[39] and widely discussed by Mussini et al.[40−42] will be used. This correlation allows for a rough estimate of the primary hydration number of the electrolyte, n_{hydr} (number of firmly bound moles of water per mol of electrolyte), based on the dependency which exists between the standard potential differences (molar scale) of the cell with the volume fraction of the water in the solvent mixture, ϕ_w, according to

$$\Delta E^0_c = E^0_{cs} - E^0_{cw} = n_{hydr}(RT/F)\ln\phi_w \qquad (9)$$

being

$$E^0_c = E^0_m + 2k\log d_s \qquad (10)$$

$$\phi_w = (w_w/d_w)/(w_w/d_w + w_F/d_F) \qquad (11)$$

E^0_m is the standard potential difference in the molal scale (up to now we have denoted it E^0 for simplicity), and all the other symbols have their usual meaning.

Although eq 9 is only fulfilled in mixtures rich in water and, in principle, is thermodynamically exact only if E^0 means standard potential difference of reversible cell,[40−42] our research group has applied the said equation to cells containing selective electrodes (cells that are not exactly reversible, due to the presence of the asymmetric potential, among others), and has obtained quite reasonable results.[1−6] This is possibly due to the fulfillment of the condition $(E_s^{asym} - E_w^{asym}) \ll (E_s^{0*} - E_w^{0*})$. Note that no extra-thermodynamic supposition has been imposed a priori for this research to be carried out.

Figure 4 is a plot of ΔE^0_c vs(RT/F) ln ϕ_w, for the three electrolytes being compared, showing a very good linear relation (r = 0.999) up to w = 0.4—0.5, approximately. The value of n_{hydr} obtained was 4.1, 1.3, and 0.5 for NaF, NaCl, and NaBr, respectively. These values are very low compared with those reported in the literature,[43] which have been measured by different experimental methods: (8 ± 2) for NaF and (6 ± 2) for NaCl and NaBr. This discrepancy has been fully justified[1−6,40−42] and is due to the high value of the dipole moment of formamide (μ = 3.37 D) with respect to water (μ = 1.83 D). Thus, the formamide is highly prone to preferentially solvate the ions, displacing water from the primary hydration sheath. In aqueous mixtures containing ethylene carbonate (μ = 4.87 D), the same effect is observed.[1,4,5] Since in both cases the value of n_{hydr} for the bromide ion is the most that deviates from the expected values, to differentiate the properties of this ion with respect to both fluoride and chloride ions would be necessary. However, many more studies should be made to rationalize this peculiar behavior and this is beyond the scope of this work.

5. CONCLUSIONS

Using the bi-ISE cell Na-ISE|NaBr (m), formamide (w), H_2O (1-w)|Br-ISE, we have determined the mean ionic activity coefficients of NaBr in the aqueous mixtures with a high relative permittivity cosolvent formamide + water. A good correlation of the experimental data was obtained with the used thermodynamic electrolyte models (Debye–Hückel, Scatchard, Pitzer–Rard–Archer, and the most recent modified three-characteristic-parameter correlation (TCPC) model).

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

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LIST OF SYMBOLS

A, B	Debye–Hückel equation constants
A_ϕ	Debye–Hückel constant for the Pitzer equation
a	Ion size parameters
$a^{(i)}$	Characteristic parameters of Scatchard equation
b	Constant of Pitzer equation; constant of TCPC equation
c	Ion interaction parameter of Debye–Hückel equation; also molarity
C^γ	Triple-ion interaction parameter of Pitzer equation
d	Ion interaction parameter of Debye–Hückel equation
E	Potential difference
E^{asym}	Total asymmetry potential
E^0	Standard potential difference
E^{0*}	Apparent standard potential difference
Ext	Contribution of the extended terms of Debye–Hückel equation
F	Faraday constant
ΔG_t^0	Standard Gibbs energy of transfer
ISE	Ion selective electrode
K_{sp}^0	Standard solubility product constant
k	Nernst's theoretical slope [$(\ln 10)RT/F = 0.05916$ V at 25 °C]
M	Average molecular mass of mixed solvent
m	Molality
m_s	Saturation molality
n	Constant of TCPC equation
n_{hydr}	Primary hydration number
q	Bjerrum interionic distance parameter
R	Gas constant
r	Correlation index
S	Debye–Hückel constant for the Scatchard equation; constant of TCPC equation
T	Absolute temperature
w	Mass fraction
z	Ionic charge

GREEK LETTERS

β^0, β^1	Solute-specific interaction parameters of Pitzer equation
γ	Mean ionic activity coefficient
$\varepsilon^{\mathrm{asym}}$	Electrode asymmetry potential
ε_r	Relativity permittivity (relativity dielectric constant)
ϕ_w	Volume fraction of water in the mixed solvent
μ	Dipole moment
ρ	Density
σ	Standard deviation

SUBSCRIPTS

c	Molar scale
m	Molal scale
s	Mixed solvent
t	Transfer
w	Water

REFERENCES

(1) Hernández-Luis, F.; Vázquez, M. V.; Esteso, M. A. Activity Coefficients of NaF in Aqueous Mixtures with ε-Increasing Co-Solvent: Ethylene Carbonate-Water Mixtures at 298.15 K. *Fluid Phase Equilib.* **2004**, *218*, 295–304.

(2) Hernández-Luis, F.; Galleguillos, H. R.; Esteso, 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.

(3) Hernández-Luis, F.; Galleguillos, H. R.; Fernández-Mérida, L.; González-Diaz, 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.

(4) Hernández-Luis, F.; Rodríguez-Raposo, R.; Galleguillos, H. R.; Morales, J. W. Activity Coefficients of NaCl in Aqueous Mixtures with High Relative Permittivity Co-Solvent: Ethylene Carbonate + Water at 298.15 K. *J. Chem. Eng. Data* **2010**, *55*, 3349–3355.

(5) Hernández-Luis, F.; Rodríguez-Raposo, R.; Galleguillos, H. R.; Morales, J. W. Activity Coefficients of NaBr in Aqueous Mixtures with High Relative Permittivity Co-Solvent: Ethylene Carbonate + Water at 298.15 K. *J. Chem. Eng. Data* **2010**, *55*, 3786–3792.

(6) Hernández-Luis, F.; Rodríguez-Raposo, R.; Ruiz-Cabrera, G. Activity Coefficients of NaCl in Aqueous Mixtures with ε-Increasing Co-Solvent: N-Methylformamide-Water Mixtures at 298.15 K. *Fluid Phase Equilib.* **2011**in press.

(7) Riddick, J. A.; Bungerand, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*; John Wiley & Sons, Inc.: New York, 1986.

(8) Marcus, Y. *The Properties of Solvents*; John Wiley & Sons Ltd.: Chichester, U.K., 1998.

(9) Marcus, Y. *Solvent Mixtures: Properties and Selective Solvation*; Marcel Dekker Inc.: New York, 2002.

(10) Kozlowski, Z.; Wasiak, A. M. Electrochemical Studies on HCl Solutions in Formamide-Water Mixtures. *Pol. J. Chem.* **1983**, *57*, 497–506.

(11) García, B.; Alcalde, R.; Leal, J. M.; Matos, J. S. Solute-Solvent Interactions in Amide-Water Mixed Solvents. *J. Phys. Chem. B* **1997**, *101*, 7991–7997.

(12) Papamatthaiakis, D.; Aroni, F.; Havredaky, V. Isentropic Compressibilities of (Amide-Water) mixtures: A Comparative Study. *J. Chem. Thermodyn.* **2008**, *40*, 107–118.

(13) Rard, J. A.; Archer, D. G. Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous NaBr and the Solubility of NaBr·$2H_2O$ (cr) at 298.15 K: Thermodynamic Properties of the NaBr + H_2O System over Wide Ranges of Temperature and Pressure. *J. Chem. Eng. Data* **1995**, *40*, 170–185.

(14) Hamer, W. J.; Wu, Y.-C. Osmotic Coefficients and Mean activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099.

(15) Pitzer, K. S.; Peiper, J. C.; Busey, R. H. Thermodynamic Properties of Aqueous Sodium Chloride Solutions. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1–102.

(16) Zhuo, K.; Wang, W.; Chen, Y.; Wang, J. Activity Coefficients for NaBr in Aqueous D−Trehalose/D−Cellobiose Solutions at 298.15 K. *Chin. J. Chem.* **2009**, *27*, 707–712.

(17) Yang, L.; Zhuo, K.; Zhao, Y.; Wang, J. Thermodynamics of the Interaction Between Electrolytes ($CaCl_2$, NaCl, NaBr, NaI) and Monosaccharide (D-Mannose, D-Ribose) in Water at 298.15 K. *Z. Phys. Chem.* **2004**, *218*, 349–362.

(18) Zhuo, K.; Zhang, H.; Wang, Y.; Liu, Q.; Wang, J. Activity Coefficients and Volumetric Properties for the NaBr + Maltose + Water System at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1589–1595.

(19) Gregorowicz, J.; Bald, A.; Szejgis, A.; Zurada, M. Gibbs Energy of Transfer and Conductivity properties of NaBr Solutions in Mixtures of Water with Propan-1-ol at 298.15 K. *J. Mol. Liq.* **1999**, *79*, 167–176.

(20) González-Díaz, O. M.; Fernández-Mérida, L.; Hernández-Luis, F.; Esteso, M. A. Activity Coefficients for NaBr in Ethanol−Water Mixtures at 298.15 K. *J. Solution Chem.* **1995**, *24*, 551–563.

(21) Han, S.; Pan, H. Thermodynamics of the Sodium Bromide−Methanol−Water and Sodium Bromide−Methanol−Water Two Ternary System by the Measurements of Electromotive Force at 298.15 K. *Fluid Phase Equilib.* **1993**, *83*, 261–270.

(22) Pan, H.; Han, S. Thermodynamic Properties for the Bromide−Methanol−Water System at 298.15 K by emf Measurements. *Huagong Xuebao* **1992**, *43*, 360–366.

(23) Parfenyuk, V. I.; Chankina, T. I. Electrochemical Study of Sodium Bromide Solution in Water−Acetone and Water−Isopropanol Mixtures. *Zh. Fiz. Khim.* **1992**, *66*, 2781–2782.

(24) Radosevic, J.; Mekjavic, I. Thermodynamic Studies of Sodium Bromide in 2-Propanol−Water Mixtures (10, 30, and 50%) from Electromotive Force Measurements. *Electrochim. Acta* **1983**, *28*, 1435–1438.

(25) Aleksandrov, V. V.; Izmailova, G. A.; Fisun, I. L. Activity Coefficients for Sodium Bromide in Mixtures of Dimethylformamide with Water at 25 °C. *Zh. Fiz. Khim.* **1980**, *54*, 790–791.

(26) Hitchcock, D. I. The Extrapolation of Electromotive Force Measurements to Unit Ionic Activity. *J. Am. Chem. Soc.* **1928**, *50*, 2076–2080.

(27) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1959.

(28) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold: New York, 1958.

(29) Scatchard, G. The Excess Free Energy and Related Properties of Solutions Containing Electrolytes. *J. Am. Chem. Soc.* **1968**, *90*, 3124–3129.

(30) Wu, Y. C.; Rush, R. M.; Scatchard, G. Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulphate, Magnesium Sulphate, and Magnesium Chloride in Water at 25 °C. I. Isopiestic Measurements on the Four Systems with Common Ions. *J. Chem. Phys.* **1968**, *72*, 4048–4053.

(31) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

(32) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*; CRC Press: Boca Raton, FL, 1991.

(33) Ge, X.; Wang, X.; Zhang, M.; Seetharaman, S. A New Three-Particle-Interaction Model to Predict the Thermodynamic Properties of Different Electrolytes. *J. Chem. Thermodyn.* **2007**, *39*, 602–612.

(34) Ge, X.; Wang, X.; Zhang, M.; Seetharaman, S. Correlation and Prediction of Activity and Osmotic Coefficients of Aqueous Electrolytes at 298.15 K by the Modified TCPC Model. *J. Chem. Eng. Data* **2007**, *52*, 538–547.

(35) Ge, X.; Zhang, M.; Guo, M.; Wang, X. Correlation and Prediction of Thermodynamic Properties of Nonaqueous Electrolytes by the Modified TCPC Model. *J. Chem. Eng. Data* **2008**, *53*, 149–159.

(36) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, N Y, 1940.

(37) Bjerrum, N. Ionic Association. I. Influence of Ionic Association on the Activity of Ions at Moderate Degrees of Association. *K. Dan. Vidensk. Selsk.* **1926**, *7*, 1–48.

(38) Kalidas, C.; Hefter, G.; Marcus, Y. Gibbs Energies of Transfer of Cations from Water to Mixed Aqueous Organic Solvents. *Chem. Rev.* **2000**, *100*, 819–852.

(39) Feakins, D.; French, C. M. Standard Potentials in Aqueous-Organic Media: A General Discussion of the Cell H_2 (Pt)|HCl|AgCl-Ag. *J. Chem. Soc.* **1957**, 2581–2589.

(40) Basili, A.; Mussini, P. R.; Mussini, T.; Rondinini, S. Thermodynamics of the Cell: $\{Na_xHg_{1-x}$ | NaCl (m) |AgCl | Ag$\}$ in (Methanol + Water) Solvent Mixtures. *J. Chem. Thermodyn.* **1996**, *28*, 923–933.

(41) Ceccattini, P. D.; Mussini, P. R.; Mussini, T. Thermodynamics of NaCl in Aqueous Ethylene Glycol, Acetonitrile, and 1,4-Dioxane Mixtures from Emf Measurements at 25°C. *J. Solution Chem.* **1997**, *26*, 1169–1186.

(42) Falciola, L.; Longoni, G.; Mussini, P. R.; Mussini, T. Thermodynamics of the Amalgam Cells {Cs-Amalgam | CsX (m) | AgX | Ag} (X = Cl, Br, I) and Primary Medium Effects in (Methanol + Water), (Acetonitrile + Water), and (1,4-Dioxane + Water) Solvent Mixtures. *J. Chem. Thermodyn.* **2006**, *38*, 788–798.

(43) Bockris, J. O'M.; Reddy, A. K. *Modern Aspect of Electrochemistry*; Plenum: New York, 1970; Vol. 1.