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Activity Coefficients of $NaClO_4$ in Aqueous Solution

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ABSTRACT: The activity coefficients of $NaClO_4$ in water were experimentally determined at (288.15, 298.15, and 308.15) K from electromotive force (emf) measurements of the following electrochemical cell without transference containing two ion-selective electrodes (ISEs): Na-ISE|$NaClO_4$ (m)|ClO_4-ISE. The molality m varied between about (0.02 and 12) $mol \cdot kg^{-1}$. The determination of E^{0*}, which is necessary to calculate the activity coefficients, was carried out following a method similar to that of Hitchcock, using the Pitzer, extended Debye–Hückel, and Scatchard equations to represent the dependency of log γ on molality. The electrode system employed shows good Nernstian behavior. The activity and osmotic coefficients obtained in this study at 298.15 K were contrasted to those from the literature and show a good agreement.

1. INTRODUCTION

Although many investigations that have been carried out in recent decades have provided data to the literature on thermodynamic and transport properties, there are still electrolyte systems for which there is a lack of data and/or which have not been sufficiently contrasted. Hamer and Wu[1] reported osmotic coefficients and activity coefficients for $NaClO_4$ rounded molalities from (0.001 to 18) $mol \cdot kg^{-1}$ at 298.15 K. These authors used experimental osmotic coefficient data, obtaining by isopiestic vapor pressure method, reported by Jones[2] [(0.2 to 6.5) $mol \cdot kg^{-1}$], Miller and Sheridan[3] [(4 to 6) $mol \cdot kg^{-1}$], and Rush and Johnson[4] [(6 to 18) $mol \cdot kg^{-1}$]. For molalities higher than 6.0 $mol \cdot kg^{-1}$ the data calculated by Hamer and Wu present some uncertainty because the data reported by Miller and Sheridan[3] and Rush and Johnson[4] differ fairly widely. Figure 1 shows the information provided by Hamer and Wu, Miller and Sheridan, and Rush and Johnson.

Much has been written about the advantages and disadvantages of various methods used in the determination of activity coefficients,[5,6] especially the isopiestic method and the measurement of electromotive force. Although an agreement has not been reached, it appears that the potentiometric method is simpler and more rapid than the isopiestic method, although it has the definite limitation of requiring electrodes that are reversible for the ions of the studied electrolyte. In recent years this problem has been remedied by the development and improvement of new ion-selective electrodes (ISEs). Currently, these electrodes are not only valuable for analytical use but can also be employed in determining thermodynamic and transport magnitudes.[6−15] The bi-ISE system employed in this study is composed of a glass-membrane electrode selective for Na^+ ions and a liquid membrane electrode selective for ClO_4^- ions.

$NaClO_4$ is a highly soluble salt (almost 18 $mol \cdot kg^{-1}$ in water at 298.15 K). For many years, $NaClO_4$ has been widely used as an electrolyte support for adjusting the ionic strength of a medium, as in polarographics studies (metal−ligand systems),[16] studies of double-layers and electrode kinetics,[17,18] and potentiometric studies (adjusting the ionic strength to work with selective electrodes).[19] This extensive use is due not only to the high solubility of $NaClO_4$ but also to its weak tendency to form complexes with metals that may be present,[20,21] which makes it a good inert electrolyte.

This study presents data on mean ionic activity coefficients of the $NaClO_4 + H_2O$ system at temperatures of (288.15, 298.15, and 308.15) K over a broad range of molalities [ca. (0.1 to 12) $mol \cdot kg^{-1}$]. The $NaClO_4$ was measured because the literature thermodynamic data exist only at a temperature of 25 °C. The experimental data were analyzed using three thermodynamic models. Our data were then compared to literature data for results obtained at 298.15 K.

2. EXPERIMENTAL SECTION

Sodium perchlorate monohydrate, Merck pro analysis (w = 0.99), was stored on silica gel in a desiccators and used without further purification. The solutions were continually agitated by a magnetic stirrer during the measurements.

Na-ISE (mod. 8411) and ClO_4-ISE (mod. 9300) were obtained from Orion Corp. A double-wall vessel Metrohm cell was used to hold the electrodes and the solution. The temperature in the cell was kept constant at 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 relative temperature uncertainty was estimated to be 0.02 %.

The emf measurements were carried out with a 614 Keithley electrometer, with inner impedance greater than $5 \cdot 10^{13}$ Ω with a resolution of ± 0.1 mV.

Depending on the concentration of the $NaClO_4$ studied, it was observed that, after approximately (30 to 45) min, the variation of the potential with time was very small [around 0.1 mV per (15 to 20) min]. The reading at this point in time was considered to

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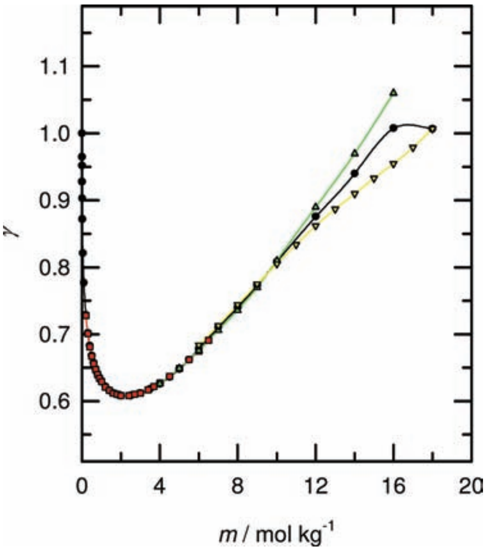

Figure 1. Comparison of γ versus m for aqueous $NaClO_4$ at 298.15 K: ●, Hamer and Wu;[1] ▲, Miller and Sheridan;[3] ▼, Rush and Johnson.[4]

represent the cell in equilibrium. Depending on the temperature, the emf uncertainty can be estimated between (0.1 and 0.3) mV, approximately.

3. RESULTS

Ionic mean activity coefficient values for $NaClO_4$ were determined from the emf measurements of the following galvanic cells without transference:

$$\text{Na-ISE}|NaClO_4(m)|ClO_4\text{-ISE} \qquad (I)$$

combined with that of the reference cell

$$\text{Na-ISE}|NaClO_4(m_r)|ClO_4\text{-ISE} \qquad (II)$$

The basis for using these ISEs and obtaining correct thermodynamic properties is the use of a reference cell in conjunction with the working cell.[22−25] The subtraction of the potentials from both cells resulted in the elimination of all of the nonthermodynamic potentials present. Thus, applying the equation of Nernst−Nikolsky to the cells (I) and (II) and subtracting, the following expression is obtained:

$$\Delta E = E_I - E_{II} = -2k \log[(m\gamma)/(m_r\gamma_r)] \qquad (1)$$

where m and m_r are the molalities of $NaClO_4$ in the working and reference solutions, respectively; E is the emf of cell, $k = (\ln 10)RT/F$ is the theoretical Nernst slope, and γ and γ_r are the mean ionic activity coefficients of $NaClO_4$ at molality m and m_r, respectively. In summary, although we are using a nonthermodynamic cell, the values of the potentials are obtained, and thus the activity coefficients are indeed thermodynamic. In no instance have we made extra-thermodynamic assumptions.

ΔE values as a function of the $NaClO_4$ molalities are shown in Table 1 for the three temperatures studied.

To use eq 1, to calculate γ, it is necessary first to know the values for γ_r. This is an important point since this it affects the accuracy of the activity coefficients and the other thermodynamic functions subsequently calculated.

Table 1. Experimental ΔE and γ at Different $NaClO_4$ Molalities[a]

288.15 K			298.15 K			308.15 K		
m	ΔE	γ	m	ΔE	γ	m	ΔE	γ
0.0469	135.8	0.806	0.0283	163.3	0.873	0.0175	194.1	0.900
0.0873	107.8	0.776	0.0740	119.1	0.794	0.0642	132.0	0.800
0.1616	80.4	0.738	0.1255	94.8	0.758	0.1228	101.1	0.756
0.2526	60.7	0.712	0.2086	71. 8	0.720	0.1939	79.3	0.729
0.4103	39.3	0.681	0.3529	47.9	0.684	0.2821	61.3	0.709
0.6057	22.2	0.656	0.4325	38.5	0.673	0.4440	39.5	0.687
0.8878	5.4	0.633	0.6357	20.9	0.650	0.6367	22.1	0.671
1.0000	0.0	0.627	0.8761	6.1	0.634	0.8679	7.1	0.657
1.1986	−8.0	0.618	1.0000	0.0	0.629	1.0000	0.0	0.655
1.5855	−20.7	0.607	1.1272	−5.7	0.626	1.0774	−3.7	0.652
2.0210	−32.0	0.600	1.4430	−17.4	0.617	1.3615	−15.5	0.651
2.6401	−44.8	0.598	1.7981	−28.1	0.613	1.7155	−27.5	0.653
3.7032	−61.9	0.607	2.2518	−39.3	0.613	2.3486	−43.9	0.651
4.9760	−78.0	0.629	2.8849	−52.2	0.620	3.0499	−58.2	0.660
6.8544	−96.5	0.666	3.6706	−65.2	0.631	3.9694	−73.3	0.678
8.6445	−111.1	0.716	4.8085	−80.7	0.655	5.2720	−90.7	0.712
10.199	−122.0	0.760	6.0261	−94.5	0.689	7.4417	−113.2	0.777
10.889	−126.4	0.779	9.7621	−126.9	0.801	11.168	−141.0	0.884
			12.378	−143.1	0.881	12.938	−151.0	0.931

[a] Units: moles $NaClO_4$/kg water for m; mV for ΔE.

The determination of γ_r was performed using a similar method to that of Hitchcock[26] in combination with the Pitzer model,[27,28] whose mathematical form for a 1:1 electrolyte can be written as:

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

where

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

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

In these equations α and b are assumed to be fixed parameters with values of 2.0 $kg^{1/2}\cdot mol^{-1/2}$ and 1.2 $kg^{1/2}\cdot mol^{-1/2}$, respectively; β^0, β^1, and C^γ are solute-specific interaction parameters dependent on temperature, and A_ϕ is the Debye−Hückel constant for the osmotic coefficients defined by:

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

where all of the symbols maintain their usual meaning. The values of A_ϕ used were (0.3850, 0.3915, and 0.3986) $kg^{1/2}\cdot mol^{-1/2}$ at (288.15, 298.15, and 308.15) K, respectively.

To obtain a good estimation of γ_r, two additional equations were used. Thus, the extended Debye−Hückel[29,30] equation for 1:1 electrolytes can be written as:

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

Table 2. Summary of the Values Obtained for the Parameters of the Pitzer, Debye–Hückel, and Scatchard Equations for $NaClO_4$ and Average Values of γ_R and k

		288.15 K	298.15 K	308.15 K
Pitzer	γ_R	0.625	0.627	0.654
	$\beta^{(0)}/\mathrm{kg\cdot mol^{-1}}$	0.0514	0.0558	0.0657
	$\beta^{(1)}/\mathrm{kg\cdot mol^{-1}}$	0.2506	0.2765	0.3511
	$C^{\gamma}/\mathrm{kg^2\cdot mol^{-2}}$	−0.0019	−0.0018	−0.0035
	k/mV	55.96	57.90	59.84
			$\sigma = 0.24$ mV	
Debye–Hückel	γ_R	0.625	0.627	0.653
	a/Å	3.80	3.89	4.37
	$c/\mathrm{kg\cdot mol^{-1}}$	0.0331	0.0369	0.0424
	$d/\mathrm{kg^2\cdot mol^{-2}}$	0	−0.00004	−0.00067
	k/mV	55.87	57.81	59.75
			$\sigma = 0.23$ mV	
Scatchard	γ_R	0.630	0.632	0.658
	$a/\mathrm{kg\cdot mol^{-1}}$	1.3592	1.3991	1.5489
	$a^{(1)}/\mathrm{kg\cdot mol^{-1}}$	0.0212	0.0278	0.0484
	$a^{(2)}/\mathrm{kg^2\cdot mol^{-2}}$	0.00514	0.00624	0.00156
	$a^{(3)}/\mathrm{kg^3\cdot mol^{-3}}$	−0.000272	−0.000388	−0.000161
	k/mV	55.81	57.75	59.69
			$\sigma = 0.19$ mV	
	$\langle\gamma_R\rangle$	0.627 ± 0.003	0.629 ± 0.003	0.655 ± 0.003
	$\langle k\rangle$/mV	55.88 ± 0.08	57.82 ± 0.08	59.76 ± 0.08
	k_{teo}/mV	57.17	59.16	61.14
	% relative error in k	2.26%	2.27%	2.26%

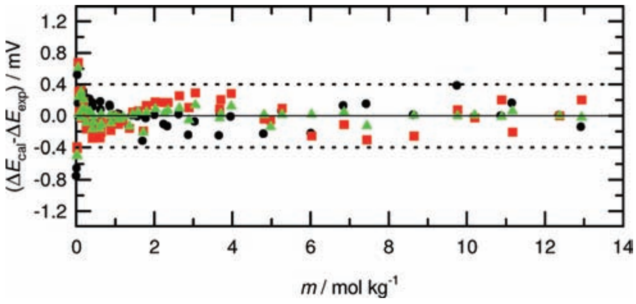

Figure 2. Fit residual values of ΔE versus m for the ●, Pitzer, ■, Debye–Hückel, and ▲, Scatchard models.

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

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

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

where all of the symbols maintain their usual meaning. The values of A and B used were (0.5016, 0.5100, and 0.5193) $\mathrm{kg^{1/2}\cdot mol^{-1/2}}$ and (0.3269, 0.3285, and 0.3301) $\mathrm{kg^{1/2}\cdot mol^{-1/2}}$ at (288.15, 298.15, and 308.15) K, respectively.

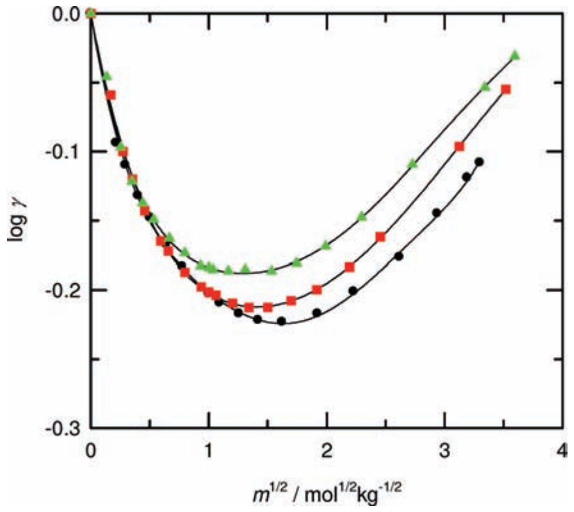

Figure 3. Plot of experimental log γ versus $m^{1/2}$ for aqueous $NaClO_4$ at ●, 288.15 K, ■, 298.15 K, and ▲, 308.15 K. The solid curves are guides for the eye.

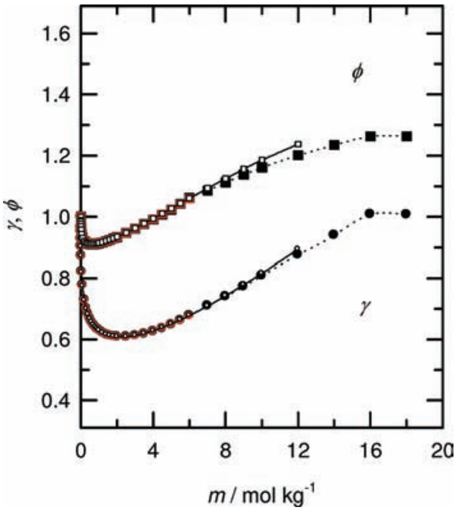

Figure 4. Comparison of γ and ϕ versus m for aqueous $NaClO_4$ at 298.15 K: black (●, ■) Hamer and Wu;[4] red (●, ■) Pitzer;[22] (○, □) this work.

An additional parameter, d, has been included in the eq 3 to cover the entire range of studied concentrations.

Furthermore, for 1:1 electrolytes, the Scatchard[31,32] equation can be written as:

$$\ln \gamma = \{2Sm^{1/2}/(1 + am^{1/2}) + 2a^{(1)}m + (3/2)a^{(2)}m^2 + (4/3)a^{(3)}m^3 + (5/4)a^{(4)}m^4\}/2 \tag{4}$$

where $S = -3A_\phi$ (1.1550, 1.1745, and 1.5579) $\mathrm{kg^{1/2}\cdot mol^{-1/2}}$ at (288.15, 298.15, and 308.15) K, respectively. a, $a^{(1)}$, $a^{(2)}$, $a^{(3)}$, and $a^{(4)}$ are the characteristic interaction parameters of the model.

By combining eqs 1 and 2, 1 and 3, or 1 and 4, the γ_R values can be optimized, as well as the interaction parameters characteristic of each model and the real Nernst slope. In all cases the

Table 3. Activity Coefficients (γ) and Osmotic Coefficients (ϕ) for $NaClO_4$ Rounded Molalities

m/mol·kg^{-1}	288.15 K		298.15 K		308.15 K	
	γ	ϕ	γ	ϕ	γ	ϕ
0.000	1.000	1.000	1.000	1.000	1.000	1.000
0.001	0.966	0.989	0.965	0.988	0.965	0.988
0.002	0.952	0.984	0.952	0.984	0.951	0.984
0.005	0.928	0.976	0.927	0.976	0.927	0.976
0.010	0.903	0.968	0.902	0.968	0.902	0.968
0.020	0.872	0.958	0.871	0.958	0.871	0.958
0.050	0.820	0.943	0.819	0.943	0.821	0.944
0.100	0.775	0.930	0.775	0.931	0.779	0.934
0.200	0.727	0.919	0.727	0.920	0.736	0.926
0.300	0.699	0.913	0.700	0.915	0.711	0.923
0.400	0.679	0.910	0.681	0.913	0.695	0.922
0.500	0.665	0.909	0.667	0.911	0.683	0.922
0.600	0.653	0.908	0.656	0.911	0.674	0.923
0.700	0.644	0.908	0.648	0.911	0.667	0.925
0.800	0.636	0.908	0.640	0.912	0.662	0.926
0.900	0.629	0.908	0.634	0.913	0.657	0.928
1.000	0.624	0.909	0.629	0.914	0.654	0.930
1.200	0.615	0.911	0.622	0.917	0.648	0.934
1.400	0.609	0.914	0.616	0.921	0.645	0.939
1.600	0.604	0.918	0.612	0.925	0.643	0.944
1.800	0.600	0.921	0.610	0.929	0.642	0.949
2.000	0.598	0.925	0.608	0.934	0.643	0.955
2.500	0.596	0.937	0.608	0.948	0.647	0.969
3.000	0.597	0.950	0.612	0.962	0.654	0.985
3.500	0.601	0.963	0.619	0.978	0.664	1.001
4.000	0.607	0.977	0.628	0.994	0.675	1.017
4.500	0.615	0.992	0.638	1.010	0.688	1.033
5.000	0.624	1.006	0.651	1.027	0.702	1.048
5.500	0.634	1.020	0.664	1.044	0.716	1.063
6.000	0.644	1.035	0.678	1.061	0.731	1.078
7.000	0.667	1.063	0.709	1.093	0.762	1.105
8.000	0.692	1.089	0.743	1.125	0.793	1.130
9.000	0.719	1.115	0.778	1.156	0.823	1.150
10.000	0.746	1.138	0.816	1.185	0.852	1.167
11.000	0.773	1.159	0.854	1.212	0.877	1.180
12.000	0.799	1.179	0.893	1.237	0.899	1.189

fit was carried out simultaneously for all of the experimental data measured at the three temperatures, assuming that $k_{Na} \cong k_{ClO_4} \cong k \cong (k_{Na} + k_{ClO_4})/2$ and that k varies linearly with temperature.

Table 2 shows the values of the parameters obtained in the optimization, as well as their deviations.

4. DISCUSSION

In Figure 2 the fit residual values of ΔE for the three models are plotted. No significant difference is observed. Table 2 shows that the three models are in close agreement. For each temperature, a standard deviation of $\pm$ 0.003 units in $\langle\gamma_R\rangle$ is obtained. The standard deviations of the fits are similar (approximately 0.2 mV), as well as the deviations of the Nernst slopes compared to the theoretical values (2.3 %). The latter confirms the excellent behavior of the electrodes used, in spite of the broad range of concentrations employed in the study.

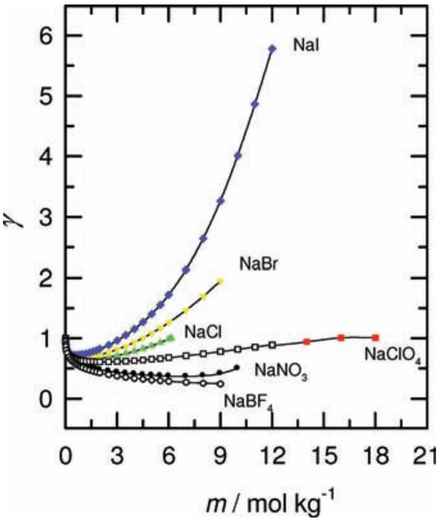

Figure 5. Plot of γ versus m for aqueous $NaClO_4$ at 298.15 K together with those for other very soluble sodium salts. □, this work; (●, ■, ▲, ▼, ◆) Hamer and Wu;[4] ○, Galleguillos et al.[25]

The values for the mean ionic activity coefficient of the $NaClO_4$ shown in Table 1 were calculated using eq 1 and the average values of γ_R and k summarized in Table 2. Figure 3 shows log γ versus $m^{1/2}$ for each temperature. For each molality, the activity coefficient value increases as the temperature increases. This behavior is less pronounced at low molalities.

Figure 4 compares activity and osmotic coefficients at 298.15 K to the Pitzer model (using the parameters obtained in this study and also those proposed directly by Pitzer[28]) and to the values of Hamer and Wu.[4] This figure shows good agreement between experimental and calculated data, especially the activity coefficients.

Table 3 shows both the activity coefficients and the osmotic coefficients obtained at rounded molalities using the equations of Pitzer and the parameters obtained in the present study, which were presented in Table 2 for the three temperatures studied.

Finally, Figure 5 plots our values of γ for $NaClO_4$ against m, together with those for other highly soluble sodium salts. The behavior of $NaClO_4$ is similar to those of $NaNO_3$ and $NaBF_4$, with an initial decrease followed by an almost constant value until the saturation molality, in contrast to the behavior of the alkaline halides. The behavior of these curves is defined by the ion−ion and ion−solvent interactions and the predominance of one over the other.

5. CONCLUSIONS

Using the bi-ISE cell Na-ISE|$NaClO_4$ (m)|ClO_4-ISE, we have determined the mean ionic activity coefficients of $NaClO_4$ in water at (288.15, 298.15, and 308.15) from emf measurements. A good fit of the experimental data was obtained with the use of Pitzer, Debye−Hückel, and Scatchard models.

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

Finally, the activity and osmotic coefficients obtained in this study at 298.15 K were contrasted to those from the literature and show a good agreement.

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REFERENCES

(1) 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.

(2) Jones, J. H. Osmotic and Activity Coefficients of Lithium and Sodium Perchlorates at 25 °C. *J. Phys. Chem.* **1947**, *51*, 516–521.

(3) Miller, M. L.; Sheridan, L. L. Concentrated Salt Solutions. I. Activity Coefficients of Sodium Thiocyanate, Sodium Iodide and Sodium Perchlorate at 25°. *J. Phys. Chem.* **1956**, *60*, 184–186.

(4) Rush, R. M.; Johnson, J. S. Isopiestic Measurements of Osmotic and Activity Coefficients for the System $HClO_4$-$LiClO_4$-H_2O, $HClO_4$-$NaClO_4$-H_2O, and $LiClO_4$-$NaClO_4$-H_2O. *J. Phys. Chem.* **1968**, *72*, 767–774.

(5) Pytkowicz, R. M. *Activity Coefficients in Electrolyte Solutions*; CRC Press: Boca Raton, FL, 1979.

(6) Haghtalab, A.; Vera, J. H. Mean Activity Coefficients in the Ternary Sodium Chloride-Sodium Nitrate-Water and Sodium Bromide-Sodium Nitrate-Water Systems at 298.15 K. *J. Chem. Eng. Data* **1991**, *36*, 332–340.

(7) Lanier, R. D. The Determination of Activity Coefficients of Sodium Chloride in Aqueous Three-Component Solutions by Cation-Sensitive Glass Electrodes. *J. Phys. Chem.* **1965**, *69*, 3992–3998.

(8) Weingärtner, H.; Braun, B. M.; Schmoll, J. M. Determination of Transference Numbers with Ion-Selective Electrodes. Transference Numbers and Activity Coefficients of Concentrated Aqueous Solutions of Potassium Fluoride. *J. Solution Chem.* **1987**, *16*, 419–431.

(9) Kozlowski, Z.; Bald, A.; Gregorowicz, J. Thermodynamic Studies of Sodium Chloride Solutions in Water + Methanol Mixtures by Means of a Galvanic Cell Containing a Glass Sodium Electrode. *J. Electroanal. Chem.* **1990**, *288*, 75–82.

(10) MacPherson, Y.; Palepu, R. Activity Coefficients and Standard Gibbs Free Energies of Transfer of NaCl and KCl from Water to Aqueous Solution of 2-Butoxyethanol by EMF Studies. *Can. J. Chem.* **1993**, *71*, 2038–2042.

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

(12) Zhuo, K.; Wang, J.; Wang, H. Activity Coefficients for NaCl-Monosaccharide (d-Glucose, d-Galactose, d-Xylose, d-Arabinose)-Water Systems at 298.15 K. *Carbohydr. Res.* **2000**, *325*, 46–55.

(13) Hernández-Luis, F.; Galleguillos, H. R.; Graber, T. A.; Taboada, M. E. Activity Coefficients of LiCl in Ethanol—Water Mixtures at 298.15 K. *Ind. Eng. Chem. Res.* **2008**, *47*, 2056–2062.

(14) Hernández-Luis, F.; Galleguillos, H. R.; Vázquez, M. V. Activity Coefficients of NaF in (Glucose + Water) and (Sucrose + Water) Mixtures at 298.15 K. *J. Chem. Thermodym.* **2004**, *36*, 957–964.

(15) Jiang, Y.; Hu, M.; Fan, P.; Wang, J.; Zhuo, K. Activity Coefficients and Thermodynamic Parameters for RbCl/CsCl + Amide (Acetamide, Propanamide, and n-Butanamide) + Water System at 298.15 K. *Biophys. Chem.* **2005**, *118*, 25–30.

(16) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1974.

(17) Delahay, P. *Double Layer and Electrode Kinetics*; Wiley: New York, 1965.

(18) Goodisman, J. *Electrochemistry: Theoretical Foundations*; Wiley: New York, 1987.

(19) Skoog, D. A.; Holler, F. J.; Nieman, T. A. *Principles of Instrumental Analysis*; Saunders College Publishing: Philadelphia, PA, 1992.

(20) Rodríguez-Placeres, J. C.; Ruiz-Cabrera, G. M.; Pastor, G.; Arévalo, A. Significado Real de las Constantes de Complejos Obtenidas por Métodos Potenciométricos Ajustando la Fuerza Iónica con Electrólitos Débilmente Complejantes. *Ann. Quim.* **1985**, *81*, 9–11.

(21) Rodríguez Placeres, J. C.; Alloza, A. M.; Borges, T. M.; Ruiz-Cabrera, G. M. Sobre el Significado Real de las Constantes de Complejos Obtenidas Ajustando la Fuerza Iónica con una Concentración Constante de Electrolitos Debilmente Complejantes. *Ann. Quim.* **1991**, *87*, 10–13.

(22) Covington, A. K.; Prue, J. E. Precise Measurements with the Glass Electrode. I. The Cell: Glass Electrode | HCl | AgCl | Ag. *J. Chem. Soc.* **1955**, 3696–3700.

(23) Zielen, A. J. The Elimination of Liquid Junction Potentials with the Glass Electrode. *J. Phys. Chem.* **1963**, *67*, 1474–1479.

(24) Hernández-Luis, F.; Amado-González, E.; Esteso, M. A. Activity Coefficients of NaCl in Trehalose-Water and Maltose-Water Mixtures at 298.15 K. *Carbohydr. Res.* **2003**, *338*, 1415–1424.

(25) Galleguillos, H. R.; Hernández-Luis, F.; Graber, T. A.; Morales, J. W. Activity Coefficients of $NaBF_4$ in Aqueous Solution. *J. Chem. Thermodyn.* **2007**, *39*, 1632–1636.

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

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

(28) Pitzer, K. S. *Thermodynamics*; McGraw-Hill: New York, 1995.

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

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

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

(32) 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.