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Activity Coefficients of Electrolytes in the NaCl + Na_2SO_4 + H_2O Ternary System from Potential Difference Measurements at (298.15, 303.15, and 308.15) K

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ABSTRACT: Potential difference measurements have been used to obtain the mean ionic activity and osmotic coefficients of NaCl and Na_2SO_4 in their aqueous solutions. Also, the mean ionic activity coefficients of NaCl in NaCl−Na_2SO_4−H_2O ternary system with sodium as a common ion have been determined from cell potential measurements using: Na-ISE/NaCl (m_{NaCl}); Na_2SO_4 ($m_{Na_2SO_4}$)/Ag/AgCl combined with the reference cell: Na-ISE/NaCl ($I = m_{NaCl} + 3m_{Na_2SO_4}$), AgCl(s)/Ag. The measurements were made at ionic strength ratios for Na_2SO_4, $y_{Na_2SO_4}$, of (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0), at constant total ionic strengths, *I*, of (0.1, 0.5, 1.0, 2.0, 3.0, and 4.0) $mol\cdot kg^{-1}$ and at temperatures of (298.15, 303.15, and 308.15) K. The experimental mean ionic activity coefficients of NaCl were correlated and analyzed with the Harned rule and Scatchard and Pitzer models. The excess free Gibbs energies of mixing were calculated from the trace activity coefficient data of NaCl and analyzed versus system composition at different temperatures and total ionic strengths.

INTRODUCTION

The thermodynamic study of aqueous multicomponent electrolyte systems[1−3] is important to understand the chemistry of natural aqueous sources and to optimize equipment design of many industrial processes like seawater desalination, inorganic salt production, waste waters recovery, energy production from geothermal sources, and so forth.[3,4] These applications require a clear knowledge of the mean ionic activity coefficients of the salts and the interactions between them in aqueous electrolyte ternary mixtures.

A literature survey shows that the information regarding the mean ionic activity coefficients for the NaCl−Na_2SO_4−H_2O ternary system is still limited. In previous publications, several authors have reported experimental data for this ternary system. Thus, Platford[5] and Robinson et al.[6] have studied the system by the isopiestic method at 298.15 K; Lanier[7] at 298.15 K, Sarada and Ananthaswamy[8] at (298.15, 308.15, and 318.15) K and at constant total ionic strengths of (0.5 to 3.0) $mol\cdot kg^{-1}$, and Galleguillos-Castro et al.[9] at (0.1 to 6.0) $mol\cdot kg^{-1}$ and temperatures of (288.15, 298.15, 308.15, and 318.15) K have applied the potential cell method. The Harned rule,[10−13] Lim et al.,[14] Scatchard,[15] and Pitzer[16−19] models proved to be useful to correlate the experimental data.

To continue our research on aqueous electrolyte mixtures,[20−23] in the present work, the NaCl−Na_2SO_4−H_2O ternary system has been investigated by cell potential measurements using an electrochemical cell with a cation ion-selective electrode (sodium ISE) as an indicator electrode and the reference electrode AgCl(s)/Ag at ionic strength ratios for Na_2SO_4, $y_{Na_2SO_4}$, of (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0), at constant total ionic strengths, *I*, of (0.1, 0.5, 1.0, 2.0, 3.0, and 4.0) $mol\cdot kg^{-1}$ and at (298.15, 303.15, and 308.15) K temperatures. For the temperature of 303.15 K no data are reported in the literature. The new experimental data obtained for NaCl mean ionic activity and trace activity coefficients were correlated and analyzed by using the Harned rule and the Scatchard and Pitzer models, and these were used to characterize the Gibbs energy of mixing in the studied ternary system.

EXPERIMENTAL SECTION

Chemicals. All of the salts used in this work were supplied by Merck without further purification. The purity of these materials was 99.8 % for NaCl and Na_2SO_4, respectively. The salts were dried at 410 K for about 48 h before use. Both were stored and cooled in desiccators over silica gel. Stock aqueous solutions of NaCl and Na_2SO_4 were prepared by direct weighing.

Working solutions of different NaCl and Na_2SO_4 molalities were prepared using double-distilled and deionized water with a specific conductivity-grade water of $5\cdot 10^{-5}$ $S\cdot m^{-1}$ at 298.15 K. All of the solutions were prepared based on molality, and the water was also weighed using a Mettler Toledo (Switzerland) electronic balance with a precision of ± 0.0001 g. The molalities of the initial solutions were prepared with an accuracy of ± $2\cdot 10^{-4}$ $mol\cdot kg^{-1}$.

The densities of stock aqueous solutions were measured with an Anton Paar DSA 5000 digital (Austria) density meter to within ± 10^{-6} $g\cdot cm^{-3}$. The temperature for density measurements was controlled with a precision of ± 10^{-3} K. The density meter was calibrated with dried air and twice-distilled water. The density of water was measured as the 0.99708 $g\cdot cm^{-3}$ at

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Table 1. Pitzer Parameters for the $NaCl-H_2O$ and $Na_2SO_4-H_2O$ Binary Systems at Various Temperatures

T	A_Φ	$\beta^{(0)}/kg \cdot mol^{-1}$		$\beta^{(1)}/kg \cdot mol^{-1}$		$C_\Phi/kg^2 \cdot mol^{-2}$	
K	$kg^{1/2} \cdot mol^{-1/2}$	NaCl	Na_2SO_4	NaCl	Na_2SO_4	NaCl	Na_2SO_4
298.15	0.3917[a]	0.07545[a]	0.006536[b]	0.2775[a]	0.8743[b]	0.0015[a]	0.00755[b]
303.15	0.3952[c]	0.07880[c]	0.005900[c]	0.2820[c]	0.8813[c]	0.0010[c]	0.00760[c]
308.15	0.3987[a]	0.0820[a]	0.003197[b]	0.2859[a]	0.8917[b]	0.0005[a]	0.00765[b]

[a] From refs 9 and 25. [b] From refs 9 and 27. [c] Obtained from ref 9.

298.15 K, similarly with literature.[24] For NaCl with a molality value of 4 $mol \cdot kg^{-1}$, the density is 1.14713 $g \cdot cm^{-3}$ and for Na_2SO_4 with a molality value of 2 $mol \cdot kg^{-1}$, is 1.21015 $g \cdot cm^{-3}$ at 298.15 K.

Measurements of Cell Potential. The measurement of potential difference was realized in electrochemical cells with one ion selective electrode, the cation ISE as an indicator electrode:

$$\text{NaISE/NaCl}(m_{\text{NaCl}}), \text{Na}_2\text{SO}_4(m_{\text{Na}_2\text{SO}_4}), \text{AgCl(s)/Ag} \qquad (1)$$

The asymmetry potential of the Na−ISE electrode was canceled by combining cell 1 with cell 2:

$$\text{NaISE/NaCl}(I = m_{\text{NaCl}} + 3m_{\text{Na}_2\text{SO}_4}), \text{AgCl(s)/Ag} \qquad (2)$$

In the two cells, m_{NaCl} and $m_{\text{Na}_2\text{SO}_4}$ represent the molality of NaCl and Na_2SO_4, respectively; I represents the constant total ionic strength in the mixture.

The experiments were done by measuring the potential difference of the Na ion selective electrode of type "pHoenix Sodium Ion Combination Epoxy Electrode, Cat. No. NA71503" (Germany, NaISE), with high stability and reproducibility, against a reference electrode Ag/AgCl incorporated in a jacketed glass cell containing 100 mL of solution under stirring. In all of the experiments, the conditioning procedure for the electrode was followed exactly according to the manufacturer instructions.[23] The potential difference of the electrochemical cells was measured with a Crison micropH/ISE 2002 electrometer with a resolution of ± 0.1 mV. For each series of measurements, the temperature from jacket of the cell was kept constant to within ± 0.1 K using a thermostatic water bath. The temperature in the sample was measured with a platinum wire resistive thermometer, metrologically verified, with a precision of ± 0.1 K.

For each solution, two to four reproducible readings were repeated, thus calculating the mean measured value. The readings of the potentiometer were registered, only when the drift was less than ± 0.1 mV. Consequently, the 95 % confidence interval for the values of the mean ionic activity coefficients of NaCl in the presence and in the absence of the Na_2SO_4, respectively, at the same NaCl concentration was calculated as ± 0.003.

From the potential difference between two electrochemical cells 2 and 1, the mean ionic activity coefficients of NaCl, γ_{NaCl}, were calculated with:[9]

$$\log \gamma_{\text{NaCl}} = \log \gamma^0_{\text{NaCl}} + \frac{1}{2}\log\frac{I^2}{m_{\text{NaCl}}(m_{\text{NaCl}} + 2m_{\text{Na}_2\text{SO}_4})} - \frac{\Delta E}{2k} \qquad (3)$$

where, E_1 and E_2 are the cell potentials for cells 1 and 2, respectively; $\Delta E = E_1 - E_2$ is the difference in potential between cells 1 and 2; γ^0_{NaCl} is the mean activity coefficient in the single-electrolyte solution of NaCl at the same ionic strength as that of the mixed−electrolyte solution; γ_{NaCl} is the mean ionic activity coefficient of NaCl in the mixtures with Na_2SO_4; $S = 2k = (\ln 10)RT/F$ is the Nernstian slope, whose theoretical value is described by the Nernst equation, where $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $F = 96485 \text{ C} \cdot \text{mol}^{-1}$, and T is the absolute temperature. Mean activity coefficients for sodium chloride in the mixtures were calculated using the rearranged form of the Nernst eq 3.

The experimental values for Nernstian slope, S, were obtained in the cell 2 by calibration with aqueous NaCl solutions only versus constant salt concentrations of (0.01, 0.1, and 1) $mol \cdot kg^{-1}$ and have been read the cell potentials repeatedly at all of the studied temperatures.

The obtained experimental results for cell potential against the NaCl concentration represents electrode response in a straight line with a slope of (53.2, 54.4, and 55.1) mV per decade (of the salt concentration) at T = (298.15, 303.15, and 308.15) K, respectively.

These values of S differ from the theoretical ones[26] by about 3.38 %, 3.97 %, and 3.61 %, respectively, and confer a Nernstian good behavior of the Na−ISE electrode at the studied temperatures.

The values of γ^0_{NaCl} for NaCl (electrolyte 1:1) were calculated with the Pitzer model for a single electrolyte:[2,18,19]

$$\ln \gamma^0_{\text{NaCl}} = |z_{\text{Na}}z_{\text{Cl}}|f^{\gamma} + \frac{2v_{\text{Na}}v_{\text{Cl}}}{v} m_{\text{NaCl},0}B^{\gamma} + \frac{2(v_{\text{Na}}v_{\text{Cl}})^{3/2}}{v} m^2_{\text{NaCl},0}C^{\gamma} \qquad (4)$$

$$f^{\gamma} = f^{\Phi} + \left(\frac{2}{b}\right)A_{\Phi} \ln(1 + bI^{1/2}) \qquad (5)$$

$$f^{\Phi} = -A_{\Phi}\left[\frac{I^{1/2}}{1 + bI^{1/2}}\right] \qquad (6)$$

$$A_{\Phi} = \frac{1}{3}\left(\frac{2\pi N_0 d_{\text{w}}}{1000}\right)^{1/2}\left(\frac{e^2}{\varepsilon kT}\right)^{3/2} \qquad (7)$$

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{x^2}[1 - e^{-x}(1 + x - 0.5x^2)] \qquad (8)$$

$$x = \alpha I^{1/2} \qquad (9)$$

$$C^{\gamma} = \frac{3}{2}C^{\Phi} \text{ kg} \cdot \text{mol}^{-2} \qquad (10)$$

$\alpha = 2 \text{ mol}^{-1/2} \cdot \text{kg}^{1/2}$; $b = 1.2 \text{ mol}^{-1/2} \cdot \text{kg}^{1/2}$, where z_{Na} and z_{Cl} are the charges of ions; $z_{\text{Na}} = 1$ and $z_{\text{Cl}} = -1$ are the stoichiometric coefficients of ions; v is the total stoichiometric

Table 2. Experimental Data of the Potential Differences and Mean Ionic Activity Coefficients for NaCl (γ_{NaCl}) in the $NaCl-Na_2SO_4-H_2O$ Ternary System versus Ionic Strength Ratio of Na_2SO_4 ($y_{Na_2SO_4}$) at Various Total Ionic Strength and Various Temperatures

$y_{Na_2SO_4}$	ΔE/mV	γ_{NaCl}	ΔE/mV	γ_{NaCl}	ΔE/mV	γ_{NaCl}
	I/mol·kg^{-1} = 0.1		I/mol·kg^{-1} = 0.5		I/mol·kg^{-1} = 1	
			T/K = 298.15			
0	0.0	0.77761 (0.7773)[a]	0.0	0.68122 (0.68140)[a]	0.0	0.65728 (0.65740)[a]
0.2	3.4	0.77675 (0.7752)[a]	3.8	0.66881 (0.67343)[a]	4.0	0.63972 (0.64380)[a]
0.4	7.7	0.77272 (0.7717)[a]	8.2	0.66245 (0.66504)[a]	8.7	0.62548 (0.06272)[a]
0.6	13.4	0.76966 (0.7718)[a]	14.1	0.65414 (0.65761)[a]	14.8	0.61232 (0.61142)[a]
0.8	22.5	0.76676 (0.7692)[a]	23.5	0.64327 (0.6497)[a]	24.4	0.59694 (0.59826)[a]
			T/K = 303.15			
0	0.0	0.77644	0	0.68102	0.0	0.65916
0.2	3.5	0.77457	3.9	0.66825	4.1	0.64272
0.4	7.9	0.77101	8.4	0.66179	9.0	0.62755
0.6	13.7	0.76860	14.5	0.65169	15.4	0.61225
0.8	23.0	0.76553	24.0	0.64396	25.4	0.59546
			T/K = 308.15			
0	0.0	0.77523 (0.77534)[a]	0.0	0.68060 (0.68074)[a]	0.0	0.65916 (0.65925)[a]
0.2	3.7	0.76835 (0.77339)[a]	3.8	0.67205 (0.67369)[a]	4.2	0.64003 (0.64522)[a]
0.4	8.1	0.76664 (0.76961)[a]	8.5	0.66159 (0.66434)[a]	9.0	0.62755 (0.62913)[a]
0.6	13.9	0.76663 (0.7682)[a]	14.7	0.65092 (0.65602)[a]	15.3	0.61481 (0.61390)[a]
0.8	23.3	0.76419 (0.76656)[a]	24.4	0.64112 (0.64676)[a]	25.3	0.59794 (0.59820)[a]
	I/mol·kg^{-1} = 2		I/mol·kg^{-1} = 3		I/mol·kg^{-1} = 4	
			T/K = 298.15			
0	0.0	0.66888 (0.66868)[a]	0.0	0.71456 (0.71372)[a]	0.0	0.78399 (0.78204)[a]
0.2	4.5	0.63709 (0.64174)[a]	5.3	0.65745 (0.6756)[a]	5.6	0.71200 (0.71849)[a]
0.4	9.7	0.60956 (0.612167)[a]	10.7	0.62361 (0.62819)[a]	11.7	0.65521 (0.66115)[a]
0.6	16.4	0.58143 (0.58596)[a]	17.9	0.58210 (0.58777)[a]	19.6	0.59335 (0.60281)[a]
0.8	26.4	0.55711 (0.55830)[a]	28.4	0.54581 (0.54750)[a]	30.2	0.55396 (0.55335)[a]
			T/K = 303.15			
0	0.0	0.67227	0.0	0.71971	0.0	0.79026
0.2	4.5	0.64307	5.1	0.67120	5.9	0.71244
0.4	10.0	0.61054	11.0	0.62654	12.1	0.65667
0.6	16.7	0.58611	18.2	0.58888	20.2	0.59413
0.8	27.1	0.55746	29.2	0.54605	30.7	0.56269
			T/K = 308.15			
0	0.0	0.67509 (0.67484)[a]	0.0	0.72407 (0.72314)[a]	0.0	0.79544 (0.79338)[a]
0.2	4.6	0.64463 (0.64718)[a]	5.2	0.67428 (0.67850)[a]	6.2	0.71044 (0.72833)[a]
0.4	10.1	0.61385 (0.61786)[a]	11.2	0.62880 (0.63507)[a]	12.4	0.65701 (0.66813)[a]
0.6	17.0	0.58649 (0.59100)[a]	18.6	0.58834 (0.5943)[a]	20.6	0.59452 (0.61132)[a]
0.8	27.5	0.55860 (0.56221)[a]	29.7	0.54650 (0.552344)[a]	31.2	0.56391 (0.55882)[a]

[a] From ref 9.

coefficient; $\upsilon_{NaCl} = 2$; $m_{NaCl,0}$ is the molality of the single-electrolyte solution at the same ionic strength as that of mixed-electrolyte solution; A_Φ is the Debye−Huckel coefficient; $\beta^{(0)}$, $\beta^{(1)}$, and C^Φ are the Pitzer parameters for NaCl.

Similarly, the values of $\gamma^0_{Na_2SO_4}$ for Na_2SO_4 (electrolyte 1:2) were calculated with the Pitzer model for pure electrolytes (eqs 4 to 10), being necessary in the following, where $z_{Na} = 1$, $z_{SO_4} = -2$, and $\upsilon_{Na_2SO_4} = 3$.

The values for the Pitzer parameters, used for the $NaCl-H_2O$ and $Na_2SO_4-H_2O$ systems were taken from literature at (298.15 and 308.15) K[2,9,25,27] and calculated with polynomial regression from experimental data at 303.15 K.[9] The used values for interaction parameters are presented in Table 1. The mean relative deviations (eq 12 per number of data) for these activity coefficients were checked with existing data from literature[24,26] with ± 0.06 % for NaCl, ± 6.29 % (versus Robinson and Stokes[26]), and ± 6.65 % (versus Zaytev and Aseyev[24]) for Na_2SO_4. The difference between Robinson and Zaytev values for $\gamma^0_{Na_2SO_4}$ is significant for $I = 1$ mol·kg^{-1} and $T = 298.15$ K (respectively 0.237 and 0.320411), and by comparison, our value

Table 3. Harned Parameter for NaCl in the NaCl−Na_2SO_4−H_2O Ternary System at Various Total Ionic Strengths and Various Temperatures

I	α		α		α	
$mol \cdot kg^{-1}$	$kg \cdot mol^{-1}$	σ	$kg \cdot mol^{-1}$	σ	$kg \cdot mol^{-1}$	σ
	T/K = 298.15		T/K = 303.15		T/K = 308.15	
0.1	0.0743 (0.0620)[a]	0.0003	0.0763	0.0001	0.0807 (0.0702)[a]	0.0008
0.5	0.0611 (0.0564)[a]	0.0006	0.0622	0.0006	0.0645 (0.0580)[a]	0.0003
1	0.0523 (0.0514)[a]	0.0005	0.0533	0.0008	0.0539 (0.0519)[a]	0.0003
2	0.0504 (0.0483)[a]	0.0005	0.0508	0.0007	0.0514 (0.0487)[a]	0.0003
3	0.0493 (0.0473)[a]	0.0016	0.0500	0.0007	0.0509 (0.0480)[a]	0.0004
4	0.0487 (0.0469)[a]	0.0024	0.0503	0.0043	0.0519 (0.0473)[a]	0.0052

[a] From ref 9.

($\gamma^0_{Na_2SO_4} = 0.29838$) is situated just between those of Zaytev and Robinson.

RESULTS AND DISCUSSION

Cell potential measurements at constant total ionic strengths, I = (0.1, 0.5, 1.0, 2.0, 3.0, and 4.0) $mol \cdot kg^{-1}$, at total ionic strength ratio for Na_2SO_4, $y_{Na_2SO_4}$ between 0 and 1 and at T = (298.15, 303.15, and 308.15) K was made in the NaCl−Na_2SO_4−H_2O ternary system. From potential difference measurements, the mean ionic activity coefficients of the NaCl (experimental activity coefficient) were calculated with eq 3.

Table 2 presents the experimental potential differences data, the resulting mean ionic activity coefficients, γ_{NaCl}, which were compared with the existing data in literature[9] at (298.15 and 308.15) K. Note that the obtained data correspond with those in literature.

Also, the experimental data for γ_{NaCl} were compared to values resulting from the Harned rule[9,28−30] and Scatchard[14,29,31] and Pitzer models,[14,30,31] respectively.

Correlation with the Harned Rule. Harned's rule expresses the mean ionic activity coefficient of an electrolyte in the mixture as a function of the constant total ionic strength, I. Applied for NaCl:

$$\ln \gamma_{NaCl} = \ln \gamma^0_{NaCl} - \alpha_{NaCl} y_{Na_2SO_4} I - \beta_{NaCl} y^2_{Na_2SO_4} I^2 - \ldots \tag{11}$$

where α_{NaCl} and β_{NaCl} are the mixing parameters for the electrolyte NaCl, calculated from experimental data, and $y_{Na_2SO_4}$ is the ionic strength ratio of the second component of the system.

It was found that only one parameter, α_{NaCl}, is sufficient to fit the experimental data in all investigated conditions for the ternary system NaCl−Na_2SO_4−H_2O. Using two parameters provides no improvement. Results of the correlation with eq 11 for the mixture NaCl−Na_2SO_4−H_2O at different constant total ionic strengths and temperatures are presented in Table 3 and Figure 1: the Harned parameter values, α_{NaCl} (presented "α" in Table 3 and Figure 1), and the relative deviation, σ, calculated with eq 12:

$$\sigma = \frac{\gamma^{exp}_{NaCl} - \gamma^{calc}_{NaCl}}{\gamma^{exp}_{NaCl}} \cdot 100 \tag{12}$$

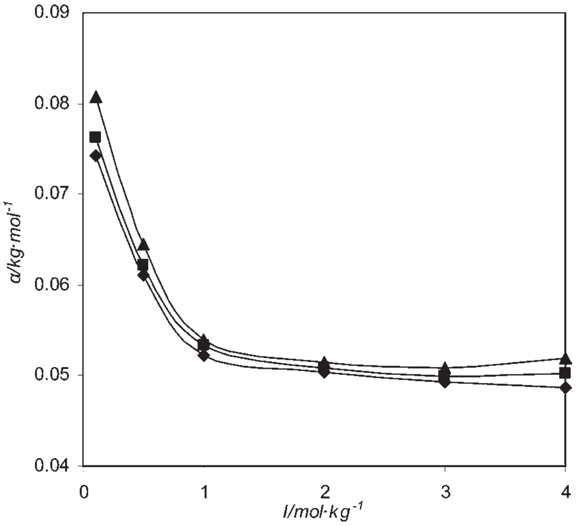

Figure 1. Harned parameter, α, versus total ionic strength, I, for the NaCl−Na_2SO_4−H_2O ternary system at various T/K: ◆, 298.15; ■, 303.15; ▲, 308.15.

where γ^{exp}_{NaCl} and γ^{calc}_{NaCl} represent the experimental and calculated mean ionic activity coefficients, respectively. Figure 1 show that the Harned parameter depends on the total ionic strength of system, stronger at low ionic strength (up to $I \cong 1$ $mol \cdot kg^{-1}$), and then becomes practically constant by increasing the total ionic strength. It should be noted that the Harned parameter, α, is positive for the studied ternary system, resulting in the fact that the mean ionic activity coefficient of NaCl in the ternary mixture is lower than in the NaCl−H_2O binary system: $\gamma_{NaCl} < \gamma^0_{NaCl}$. The Harned rule gives small values for σ, (eq 12) ranging from (0.01 to 0.52) %, in agreement with literature.[9]

Correlation with the Scatchard Model. The Scatchard model correlates the mean ionic activity coefficient of electrolyte in the mixture with the total ionic strength of the system, using the mixing parameters that are independent of total ionic strength: g_0, g_1, and g'_0:[31]

$$\ln \gamma^S_{NaCl} = \ln \gamma^0_{NaCl} + \frac{y_{Na_2SO_4} I}{2 \ln 10}\left[g_0 + \left(\frac{I}{2} + \frac{3YI}{2}\right) g_1 + \left(\frac{I}{2} + \frac{YI}{2}\right) g'_0 + \Phi\right] \tag{13}$$

Table 4. Scatchard Parameters for NaCl in the NaCl−Na_2SO_4−H_2O Ternary System at Various Temperatures[a]

T	b_{01}	b_{02}	b_{03}		
K	$kg \cdot mol^{-1}$	$kg^2 \cdot mol^{-2}$	$kg^3 \cdot mol^{-1}$	σ	N/p
298.15	−0.40746	0.00737		0.0030	30/2
	−0.40572	0.00616	0.00012	0.0030	30/3
303.15	−0.41741	0.00905		0.0036	30/2
	−0.41540	0.00756	0.00015	0.0037	30/3
308.15	−0.41844	0.00669		0.0041	30/2
	−0.41123	−0.00040	0.00082	0.0042	30/3

[a] N/p = number of experimental data/number of parameters.

$$Y = 1 - 2y_{Na_2SO_4} \tag{14}$$

$$\Phi = \frac{(2\Phi^0_{NaCl} - \Phi^0_{Na_2SO_4} - 1)}{I} \tag{15}$$

The Scatchard model[29,31] gives the following expressions for the mixing parameters:

$$g_0 = b_{01} + \frac{1}{2}b_{02}I + \frac{1}{3}b_{03}I^2 \tag{16}$$

$$g_0' = \frac{\partial g_0}{\partial I} = \frac{1}{2}b_{02} + \frac{2}{3}b_{03}I \tag{17}$$

$$g_1 = \frac{b_{12}}{2} \tag{18}$$

where b_{01}, b_{02}, and b_{03} represent the model parameters which are calculated by fitting the experimental data.

Φ^0_{NaCl} and $\Phi^0_{Na_2SO_4}$ are the osmotic coefficients in the single-electrolyte solution of NaCl and Na_2SO_4, respectively, at the same ionic strength as that of the mixed-electrolyte solution. The values of the osmotic coefficients were calculated with the Pitzer equation:

$$\begin{aligned}\Phi^0_{NaCl} = 1 + |z_{Na}z_{Cl}|\left[-A_\Phi\left(\frac{I^{1/2}}{1 + bI^{1/2}}\right)\right] \\ + \frac{2v_{Na}v_{Cl}}{v}m_{NaCl,0}(\beta^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2})) \\ + \frac{2(v_{Na}v_{Cl})^{3/2}}{v}m^2_{NaCl,0}C^\Phi\end{aligned} \tag{19}$$

The mean relative deviations (eq 12 per number of data) for these osmotic coefficients were checked with existing data from literature[26] with ± 0.06 % for NaCl and ± 3.4 % for Na_2SO_4 at a temperature of 298.15 K.

The correlations with the Scatchard model were made taking into account two and three parameters, respectively. The results obtained with Scatchard model are reported in Table 4: the parameters and standard deviations for the system at various temperatures. It was noted that two parameters are enough to describe the thermodynamic properties within the experimental error. The third parameter does not bring a significant improvement in correlation. The parameter values depend on temperature. The standard deviations, σ, are between (0.0030 and 0.0042) and increase by increasing the temperature with eq 26.

The Scatchard parameters depend on temperature but are independent of ionic strength and unique for both electrolytes. Parameter b_{01} represents the interactions between two ions, b_{02}, triple interactions, and so forth; b_{01} can be expressed in terms of equilibrium constants of ion association according to eq 20.[32]

$$\begin{aligned}b_{01} = K_{ClCl} + \frac{1}{9}K_{SO_4SO_4} - \frac{1}{3}K_{ClSO_4} + \frac{1}{3}K_{ClNa} \\ - \frac{1}{9}K_{NaSO_4} + \frac{10}{9}K_{NaNa}\end{aligned} \tag{20}$$

Taking into account that the interactions between different charged ions are much stronger than those between ions with the same task, consequently eq 20 becomes:

$$b_{01} \approx \frac{1}{3}\left[K_{ClNa} - \frac{K_{NaSO_4}}{3}\right] \tag{21}$$

b_{01} for the NaCl−Na_2SO_4−H_2O system is always negative, hence:

$$K_{ClNa} < \frac{K_{NaSO_4}}{3} \tag{22}$$

meaning that the value of association equilibrium constant, K_{NaSO_4}, is much higher than that for NaCl, K_{NaCl}.

This result is consistent with the values for K of Na−Cl, Na−SO_4^{2-} ion pairs, from the literature,[33−36] which confirms the negative values obtained for b_{01} in this paper.

This is due to an increase of the total interactions in the mixture, caused by a higher surface charge density of SO_4^{2-} ions from Cl^{1-} ions. The substitution of Cl^{1-} with SO_4^{2-} in a mixture leads to an increase of such interactions in the system. The result is a salting-in effect of the sulfate ions to the chloride ions.

Correlation with the Pitzer Model. The experimental mean ionic activity coefficient values were correlated with the Pitzer model,[16−19] one of the most currently used models:

$$\ln \gamma_{NaCl} = \ln \gamma^0_{NaCl} + \frac{y_{Na_2SO_4}I}{2\ln 10}\left[g_0 + g_0'\left(\frac{I}{2} + \frac{(1 - 2y_{Na_2SO_4})I}{2}\right) + \Phi\right] \tag{23}$$

$$g_0 = 2\theta + I\Psi \tag{24}$$

$$g_0' = \Psi \tag{25}$$

where g_0 and g_0' are the mixing parameters and θ and ψ are model parameters.

For both Scatchard and Pitzer models, the standard error was calculated with the equation:

$$\sigma = \left(\frac{\Sigma(\log \gamma^{exp}_{NaCl} - \log \gamma^{calc}_{NaCl})^2}{N - p}\right)^{0.5} \tag{26}$$

where N is the number of experimental data; p is the number of parameters.

In Table 5 the results from correlation with the Pitzer model (eqs 23 to 26) are presented.

The Pitzer parameters, θ and ψ, are the same signs with the Scatchard parameters, b_{01} and b_{02}, since they describe ionic interactions of the same type. The mean ionic activity coefficients calculated using the Pitzer model and the experimental values are illustrated in Figures 2 to 4 at all temperatures and total ionic strengths investigated.

Table 5. Pitzer Parameters in the NaCl−Na_2SO_4−H_2O Ternary System at Various Temperatures[a]

T	θ	ψ		
K	$kg \cdot mol^{-1}$	$kg^2 \cdot mol^{-2}$	σ	N/p
298.15	−0.20158	0.00411	0.0031	30/2
303.15	−0.20601	0.00500	0.0038	30/2
308.15	−0.20825	0.00405	0.0042	30/2

[a] N/p = number of experimental data/number of parameters.

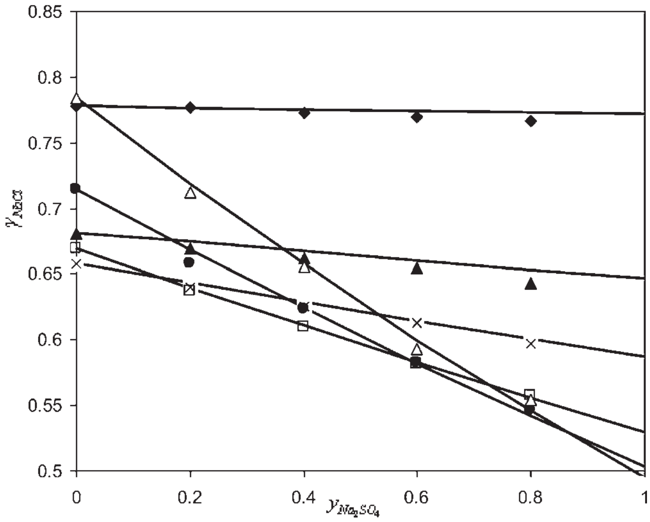

Figure 2. Experimental mean ionic activity coefficients for NaCl in the NaCl−Na_2SO_4−H_2O ternary system versus the ionic strength ratio of Na_2SO_4, $y_{Na_2SO_4}$, at 298.15 K and at various total ionic strengths, $I/mol \cdot kg^{-1}$: ◆, 0.1; ▲, 0.5; ×, 1; □, 2; ●, 3; △, 4; —, correlation with the Pitzer model.

The differences between the experimental and calculated results are approximately between (0.002 and 0.008) and increase with increasing temperature and ionic strength, respectively.

The standard deviations are higher at higher ionic strengths, (2.0, 3.0 and 4.0) $mol \cdot kg^{-1}$. The values for standard deviation, σ, between (0.0030 and 0.0042) with Scatchard and between (0.0031 and 0.0042) with Pitzer models, respectively, increase by increasing temperature. It is estimated that both models correlate the experimental data well.

The Pitzer parameters, as is known, represent the interactions between different ions in solution, independent of its concentration, and are not specific only to a given system.[37] These parameters are characteristic of the interactions between some ions, separated from other ions from the environment (the solution). Therefore, Pitzer parameters determined for a given mixture can be used in calculations for other systems in which the same ions are present.

Trace Mean Ionic Activity Coefficients. From the data presented in Table 3, the trace mean ionic activity coefficients for NaCl were calculated at $y_{Na_2SO_4} = 1$ with the Pitzer equation (eq 23) and are summarized in Table 6.

Figures 5 to7 present comparatively the mean ionic activity coefficients of NaCl, γ_{NaCl} in the ternary mixture, the mean ionic activity coefficients in binary mixtures, γ^0_{NaCl}, $\gamma^0_{Na_2SO_4}$, and the trace activity coefficients for NaCl, γ^∞_{NaCl}. The activity coefficients are presented versus the ionic strength, $I^{1/2}$, at various $y_{Na_2SO_4}$, and at temperatures of (298.15, 303.15, and 308.15) K.

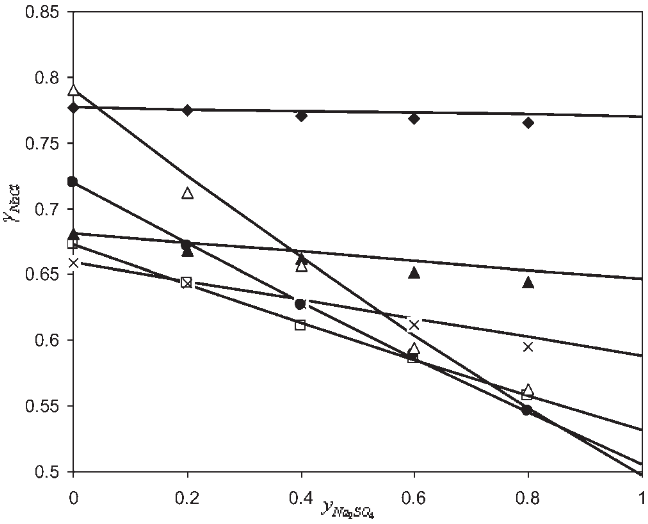

Figure 3. Experimental mean ionic activity coefficients for NaCl in the NaCl−Na_2SO_4−H_2O ternary system versus the ionic strength ratio of Na_2SO_4, $y_{Na_2SO_4}$, at 303.15 K and at various total ionic strengths, $I/mol \cdot kg^{-1}$: ◆, 0.1; ▲, 0.5; ×, 1; □, 2; ●, 3; △, 4; —, correlation with the Pitzer model.

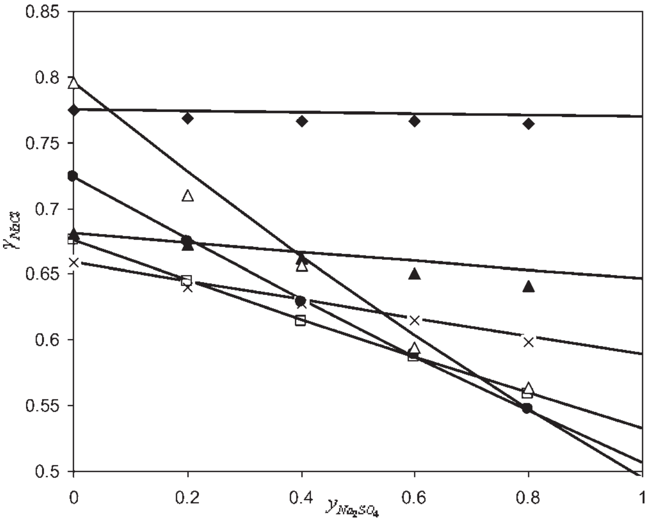

Figure 4. Experimental mean ionic activity coefficients for NaCl in the NaCl−Na_2SO_4−H_2O ternary system versus the ionic strength ratio of Na_2SO_4, $y_{Na_2SO_4}$, at 308.15 K and at various total ionic strengths, $I/mol \cdot kg^{-1}$: ◆, 0.1; ▲, 0.5; ×, 1; □, 2; ●, 3; △, 4; —, correlation with the Pitzer model.

The experimental and correlated data in Figures 5 to 7 show that the values for mean ionic activity coefficients of NaCl in ternary system, γ_{NaCl}, are between the mean ionic activity coefficients for both binary systems: $\gamma^0_{NaCl} > \gamma_{NaCl} > \gamma^0_{Na_2SO_4}$. Also, the curves γ^∞_{NaCl} versus I are the position between $\gamma^0_{Na_2SO_4}$ and γ^0_{NaCl}, in the order: $\gamma^0_{Na_2SO_4} < \gamma^\infty_{NaCl} < \gamma^0_{NaCl}$. This means that when the system goes from simple to mixed electrolyte at trace concentrations (infinite dilution), the ion−ion interactions increase for NaCl and decrease for Na_2SO_4.

Mean ionic activity coefficient variation versus the ionic strength, presented in Figures 5 to 7, show that NaCl is a strong

Table 6. Trace Mean Ionic Activity Coefficients for NaCl (γ^{∞}_{NaCl}) in the NaCl−Na$_2$SO$_4$−H$_2$O Ternary System versus Total Ionic Strength at Various Temperatures

I	γ^{∞}_{NaCl}		
mol·kg^{-1}	T/K = 298.15	T/K = 303.15	T/K = 308.15
0.1	0.77117	0.77007	0.76904
0.5	0.64607	0.64579	0.64586
1	0.58673	0.58804	0.58852
2	0.52919	0.53091	0.53283
3	0.50352	0.50558	0.50663
4	0.49494	0.49663	0.49527

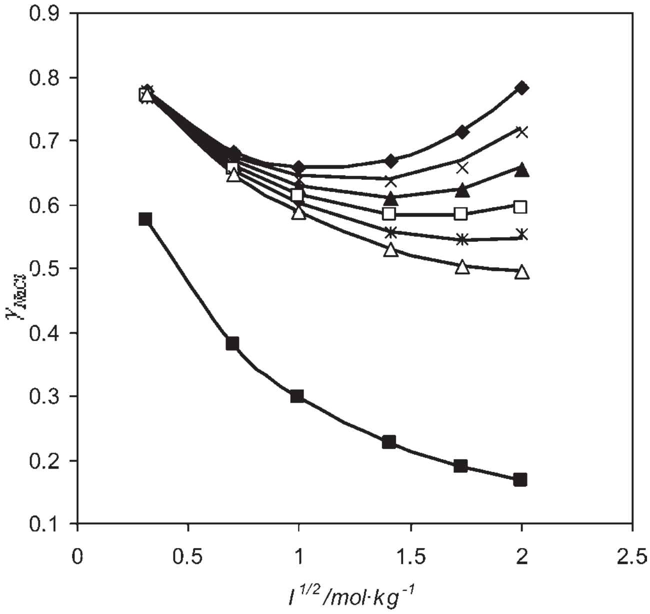

Figure 5. Mean ionic activity coefficients versus total ionic strength radical in binary electrolytes: ♦, γ^{0}_{NaCl}; ■, $\gamma^{0}_{Na_2SO_4}$ and in ternary electrolytes for NaCl at 298.15 K at various ionic strength ratios of Na$_2$SO$_4$, $y_{Na_2SO_4}$: ×, 0.2; ▲, 0.4; □, 0.6; ∗, 0.8; △, 1 (γ^{∞}_{NaCl}); —, correlation with the Pitzer model.

electrolyte. Initially the γ^{0}_{NaCl} decrease indicates a predominance of the ion−ion interactions up to an ionic strength of 1 mol·kg^{-1}, followed by an increase due to the increasing of the ion−solvent interactions, which become predominant at high ionic strengths. The variation of $\gamma^{0}_{Na_2SO_4}$ by the ionic strength is monotone decreasing with I, which indicates that the ion−ion interactions are predominant, which is typical for associating electrolytes;[9] the behavior is similar over the entire range of the studied ionic strengths.

From Figure 5 at a constant ionic strength ratio, the mean ionic activity coefficients of NaCl in the simple (γ^{0}_{NaCl}) and in the ternary (γ_{NaCl}) system decrease by increasing the ionic strength up to about $I \cong 1$ mol·kg^{-1}, then at higher ionic strengths, increase. Also, for the same constant total ionic strength of the mixture, the mean ionic activity coefficients of NaCl, γ_{NaCl}, in the ternary mixture, decreases with the increasing ionic strength ratio of Na$_2$SO$_4$. The behavior is similar at the three studied temperatures.

From Table 2 and Figures 5 to 7 the influence of the temperature can be observed: at the same ionic strength ratio, the mean ionic activity coefficients of NaCl decrease by increasing the temperature up to $I \cong 1$ mol·kg^{-1}, followed by an increase.

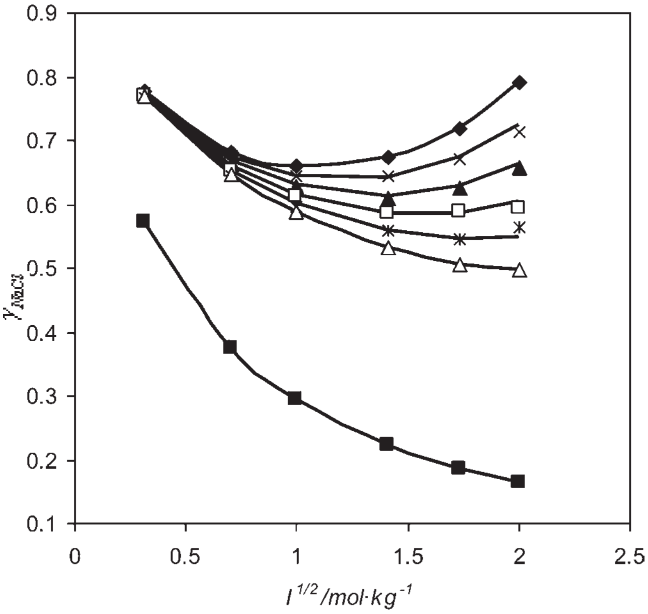

Figure 6. Mean ionic activity coefficients versus total ionic strength radical in binary electrolytes: ♦, γ^{0}_{NaCl}; ■, $\gamma^{0}_{Na_2SO_4}$ and in ternary electrolytes for NaCl at 303.15 K at various ionic strength ratios of Na$_2$SO$_4$, $y_{Na_2SO_4}$: ×, 0.2; ▲, 0.4; □, 0.6; ∗, 0.8; △, 1 (γ^{∞}_{NaCl}); —, correlation with the Pitzer model.

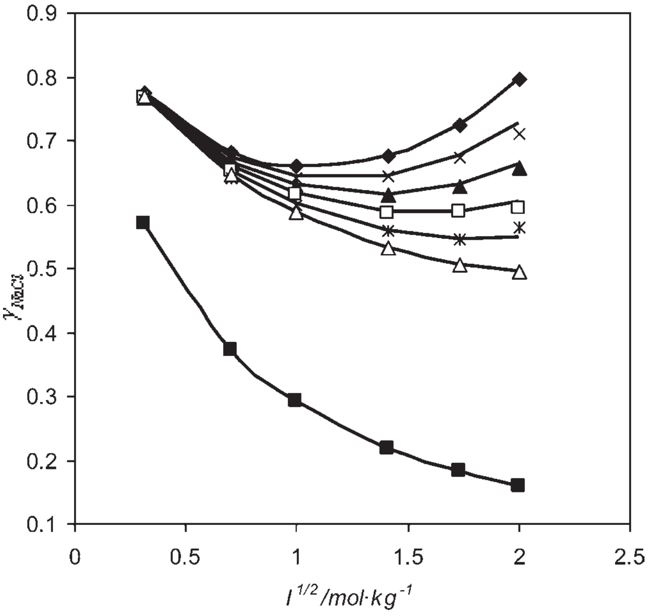

Figure 7. Mean ionic activity coefficients versus total ionic strength radical in binary electrolytes: ♦, γ^{0}_{NaCl}; ■, $\gamma^{0}_{Na_2SO_4}$ and in ternary electrolytes for NaCl at 308.15 K at various ionic strength ratios of Na$_2$SO$_4$, $y_{Na_2SO_4}$: ×, 0.2; ▲, 0.4; □, 0.6; ∗, 0.8; △, 1 (γ^{∞}_{NaCl}); —, correlation with the Pitzer model.

Excess Gibbs Free Energy of Mixing. The excess Gibbs free energy of mixing, ΔG^{E}, was calculated versus the ionic strength

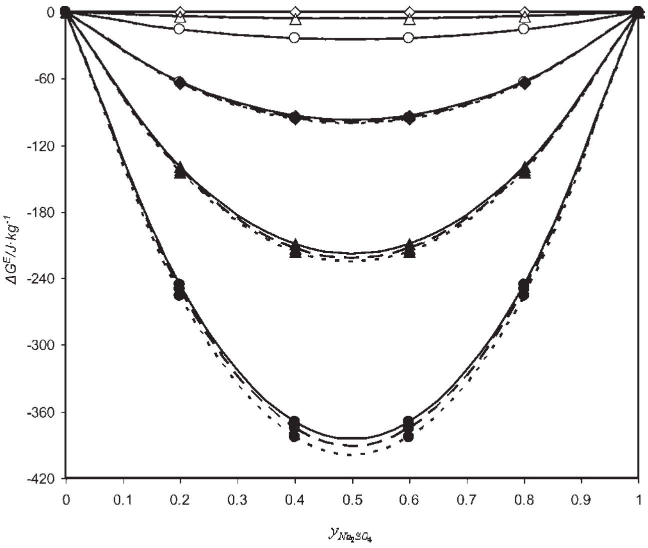

Figure 8. Excess Gibbs free energy of mixing, ΔG^{E}, for the NaCl−Na_2SO_4−H_2O ternary system versus the ionic strength ratio of Na_2SO_4, $y_{Na_2SO_4}$, at various total ionic strengths, I/mol·kg^{-1}: ◇, 0.1; △, 0.5; ○, 1; ◆, 2; ▲, 3; ●, 4; and at various temperatures, T/K: —, 298.15; — —, 303.15; - - -, 308.15.

ratio of Na_2SO_4 at all of the ionic strengths and studied temperatures by Friedmann's treatment:[38,39]

$$\Delta G^{E} = RTI^{2} y_{Na_2SO_4}(1 - y_{Na_2SO_4})[g_0 + I(1 - 2y_{Na_2SO_4})g_1] \tag{27}$$

$$g_0 = 2\theta + I\psi \tag{28}$$

where the mixing parameters, θ and ψ, are obtained with the Pitzer model (eq 23) and presented in Table 5; R = 0.8206 J·mol^{-1}·K^{-1}; T = (298.15, 303.15, and 308.15) K; g_1 represents the ternary interactions between ions, usually, less important than the binary interactions, neglected in this case, g_1 = 0.

The calculation results are shown in Figure 8. ΔG^{E} versus $y_{Na_2SO_4}$ curves are symmetrical at the same ionic strength ratio, $y_{NaCl} = y_{Na_2SO_4} = 0.5$.

As it can be observed the values for the excess Gibbs free energy of mixing are negative and increase in absolute value by increasing the ionic strength. The behavior is similar at all of the studied temperatures, with a stronger effect at higher ionic strengths and temperatures, respectively.

The ΔG^{E} negative values in the mixing process with Na_2SO_4 show that it has a stabilizing effect on the NaCl-H_2O system. The result is consistent with the sign and size of the mixing θ parameter. Given the imprecision of calculating the thermodynamic properties, it must be noticed that similar results were obtained in the literature for this system.[9]

Previous investigations[40,41] of the excess Gibbs free energy of mixing for the two-salt mixtures with a common ion have indicated that the heat of mixing is independent of the common ion. A similar behavior was reported in the literature for other ternary systems, such as the NaCl−Na_2CO_3−H_2O,[30] KI−KNO_3−H_2O,[42] NaBr−NaPro, and NaBr−NaButy systems.[31]

CONCLUSIONS

The results of the thermodynamic study of binary and ternary aqueous electrolyte systems with NaCl and Na_2SO_4 were presented for the range of constant ionic strengths of (0.1, 0.5, 1.0, 2.0, 3.0, and 4.0) mol·kg^{-1} and for the ionic strength ratios from 0 to 1 at temperatures of (298.15, 303.15, and 308.15) K.

The mean ionic activity coefficients for NaCl in the NaCl−Na_2SO_4−H_2O ternary system were obtained from the cell potential measurements.

The data correlation show that the Harned rule and Scatchard and Pitzer models, respectively, can be used to obtain a sufficiently precise description of the properties of the binary and ternary systems which contains Na_2SO_4 and NaCl electrolytes.

The mean ionic activity coefficients of salts and parameters obtained by Harned rule and Scatchard and Pitzer models agree with that of the experiment. The differences are within error limits of the studied models.

The Pitzer parameters, which represent the interactions between different ions in the solution, were obtained and can be used in calculations for the other systems with the same ions.

The traces mean ionic activity coefficients of NaCl were calculated and used in determination of the excess Gibbs free energy of mixing for ternary systems at all studied temperatures.

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