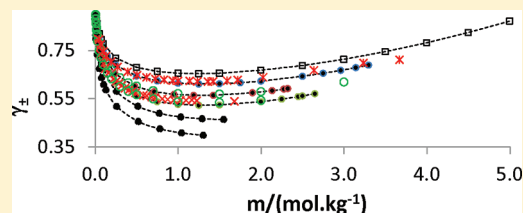


NaCl + CH₃OH + H₂O Mixture: Investigation Using the Pitzer and the Modified Pitzer Approaches To Describe the Binary and Ternary Ion–Nonelectrolyte Interactions

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ABSTRACT: In this work, NaCl electrolyte in different mass fractions of CH₃OH (x) + H₂O ($1 - x$) mixed solvents (where $x = 0.10, 0.20, 0.30, 0.40,$ and 0.50) were investigated by the Pitzer and the modified Pitzer equations. Since in mixed solvent electrolyte system the interactions of the ion–nonelectrolyte are absent in the Pitzer equation, the modified Pitzer equations were used for the determination of the binary and ternary ion–nonelectrolyte interaction parameters. The experimental data were obtained by using a galvanic cell using an Na⁺-glass membrane and Ag/AgCl electrodes for collecting the potentiometric data with a series of electrolyte solutions, at (298.15 ± 0.05) K.



INTRODUCTION

The determination of the thermodynamic properties of electrolytes such as solvent osmotic coefficients, activity coefficients, and excess Gibbs free energies in aqueous and in mixed solutions is necessary for understanding the nature of various ionic interactions and also for handling of various industrial and environmental processes such as desalination, chemical separation, marine chemistry, geology, and environmental problems. The use of the ion-selective electrodes (ISEs) proved to be an efficient method for the determination of the activity coefficients in electrolyte systems. For many years, we have used in our laboratory glass membrane^{1,2} and solvent polymeric membrane ISEs for the determination of mean activity coefficients of electrolytes in aqueous^{3,4} and mixed solvents.^{5,6}

In this work, the modified Pitzer equations were used for the investigation of NaCl electrolytes in different mass fractions of CH₃OH (x) in H₂O ($1 - x$), where $x = 0.10, 0.20, 0.30, 0.40,$ and 0.50 . The experimental data were obtained by using a galvanic cell containing an Na⁺-glass membrane electrode and an Ag/AgCl electrode for collecting the potentiometric data over the total electrolyte molality, ranging from about 0.001 mol·kg⁻¹ up to 3.3 mol·kg⁻¹, at (298.15 ± 0.05) K. The modified Pitzer equations permit the determination of the binary and ternary ion–nonelectrolyte interaction parameters which are absent in the Pitzer equation.

The available literature data for this mixture, specifically for the CH₃OH mass fractions $x = 0.10, 0.30,$ and 0.50 in H₂O,^{7,8} are limited up to the molality of 0.2 mol·kg⁻¹.^{7,8} Because of the used low concentration range of electrolytes in these investigations, the triple interaction Pitzer parameters were neglected by these authors.

The related experimental data at high concentrations were reported by Yan et al.¹¹ and Basili et al.¹² for CH₃OH mass fractions $x = 0.20, 0.40, 0.60, 0.80$ and 1.00 in H₂O. In addition, modeling NaCl electrolyte in CH₃OH + H₂O mixed solvent by

the Pitzer equation was also performed by Koh et al.,⁹ Boukhalfa and Méniat,¹⁰ and Yan et al.¹¹ Therefore, because of the unavailability of the Pitzer coefficients and the related data at relatively high concentrations for CH₃OH mass fractions $x = 0.10, 0.30,$ and 0.50 in H₂O, we have also determined in this work the Pitzer ion-interaction parameters $\beta^{(0)}, \beta^{(1)},$ and C^ϕ for NaCl at these CH₃OH mass fractions, along with the binary and ternary ion–nonelectrolyte interaction parameters based on the modified Pitzer equations.

EXPERIMENTAL SECTION

Materials. Methanol of analytical grade (purity >0.995) from Fluka was used as received. The analytical grade NaCl salts (mass percent fraction >0.995) were obtained from Fluka. Each time, prior to use, the analytical grade NaCl salt (mass percent fraction >0.995), from Fluka, was dried overnight in an oven (at 110 °C).

All primary stock solutions were prepared by weight using a Sartorius CPA225d electronic balance with a resolution of 0.01 mg in doubly distilled water. The Na⁺-glass membrane electrode (model 6.0501.100) was obtained from Metrohm, and Ag/AgCl wires, prepared essentially as described elsewhere by electrolysis,¹³ were used as internal reference electrodes. The lifetime of Ag/AgCl electrodes is limited and influenced by many effects such as the depletion of Ag, formation of complexes, and continuous dissolution of the AgCl layer and its oxidation due to the presence of trace of impurities and free dissolved O₂, respectively. The decreased operational performance of Ag/AgCl electrodes with increasing electrolyte concentration affects also its resulting potential.¹³ Therefore, in our work, pairs of Ag/AgCl electrodes were used to check against each other to ensure equivalent response. Under normal

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usage, in our experimental conditions, each Ag/AgCl electrode lasted about 8 weeks.

Potentiometric Measurement and Data Acquisition

Process. The experimental cell potentials were recorded using Metrohm ion-meter (model 619) with a high input impedance ($>1\text{ T}\Omega$) connected to a Topward multimeter equipped with a GPIB interface Bus option (model 1304, Taiwan, Korea). The output of the multimeter was finally connected to a personal computer (Samsung, 386/32 MHz processor) via the GPIB interface card (IEEE488, Keithley) for data acquisition and processing. The reading potential accuracy of instrumental setup was 0.1 mV. A laboratory written Basic program combined with Microsoft Excel (XP-Office 2007) software were also used for data acquisition and calculations. All measurements were performed under stirring conditions at a fixed temperature employing a double-wall container enabling the circulation of thermostatted water from a bath (Julabo thermostat MF12, Germany) with temperature kept constant at $(298.15 \pm 0.05)\text{ K}$. The electrodes and a glass thermometer were immersed in the solution through a lid, preventing solvent evaporation. In each mixed solvent system and for each molality, data acquisitions were performed at every 4 s interval and during 20 min (for concentrated solutions) to 60 min (for dilute solutions). From data processing, a resulting final potential mean value with a standard deviation never exceeding 0.1 mV during 1 min was accepted for each concentration.

METHOD

Pitzer Equation. For a $M_{\nu_+}X_{\nu_-}$ single electrolyte, the Pitzer equation is written as¹⁴

$$\ln \gamma_{\pm} = |z_+ z_-| f^{\gamma} + m \left(\frac{2\nu_+ \nu_-}{\nu} \right) B^{\gamma} + m^2 \left(\frac{2(\nu_+ \nu_-)^{3/2}}{\nu} \right) C^{\gamma} \quad (1)$$

where

$$f^{\gamma} = -A_{\phi} \left[\frac{\sqrt{I/m^0}}{1 + b\sqrt{I/m^0}} + \frac{2}{b} \ln(1 + b\sqrt{I/m^0}) \right] \quad (2)$$

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2(I/m^0)} [1 - \exp(-\alpha\sqrt{I/m^0})] (1 + \alpha\sqrt{I/m^0} - (1/2)\alpha^2(I/m^0)) \quad (3)$$

$$C^{\gamma} = (3/2)C^{\phi} \quad (4)$$

γ_{\pm} is the molality-scale mean ionic activity coefficient of the electrolyte $M_{\nu_+}X_{\nu_-}$; Z , the charge number of ions; $\nu = \nu_+ + \nu_-$, the number of ions dissociated in one unit electrolyte formula; m , the molality of electrolyte ($\text{mol}\cdot\text{kg}^{-1}$); I , the ionic strength on a molality scale; $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are the parameters of the Pitzer equation; $b = 1.2\text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ and $\alpha = 2\text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$. A_{ϕ} is the Debye–Hückel coefficient for the osmotic coefficient defined as

$$A_{\phi} = \frac{1}{3} (2\pi N_A \rho_A)^{1/2} \left(\frac{e^2}{4\pi \epsilon_0 D k T} \right)^{3/2} \quad (5)$$

where the constants ϵ_0 , k , N_A , D , and ρ_A are the vacuum permittivity, Boltzmann constant, Avogadro constant, dielectric constant, and density of the mixed solvent, respectively.

Modified Pitzer Equation. To improve the fitting of experimental data containing polar nonelectrolyte, Estes and co-workers^{15–17} performed some modifications to the original Pitzer equation to include the dependence of the binary interaction parameters (containing the nonelectrolyte) on the ionic strength and the ion–nonelectrolyte interactions on the nonelectrolyte concentration. For an aqueous electrolyte system containing MX electrolyte (B) and polar nonelectrolyte (A), the modified Pitzer equation for the activity coefficient of the electrolyte can be written as:

$$\ln \left(\frac{\gamma_{MX}}{\gamma_{MX}^0} \right) = \ln \left(\frac{\gamma_B}{\gamma_B^0} \right) = \frac{2}{\nu_B} \chi_{BA} m_A + |z_{MX}| \chi'_{BA} m_A m_B + \frac{2}{\nu_B} \nu_M \nu_X \xi_{ABB} m_A m_B + \omega_{AAB} m_A^2 \quad (6)$$

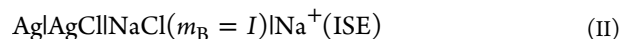
In eq 6, the ion–nonelectrolyte binary interaction parameter, χ , and its derivative, χ' , are expressed as^{16,17}

$$\chi_{BA} = \chi_{BA}^{(0)} + \left\{ (\chi_{BA}^{(1,0)} + \chi_{BA}^{(1,1)} m_A) \frac{2}{\alpha_0^2 I} \right\} [1 - (1 + \alpha_0 I^{0.5}) \exp(-\alpha_0 I^{0.5})] \quad (7)$$

$$\chi'_{BA} = (\chi_{BA}^{(1,0)} + \chi_{BA}^{(1,1)} m_A) \frac{2}{\alpha_0^2 I} \left[-1 + \left(1 + \alpha_0 I^{0.5} + \frac{1}{2} \alpha_0^2 I \right) \exp(-\alpha_0 I^{0.5}) \right] \quad (8)$$

ξ and ω are the ternary interaction parameters of non-electrolyte–ion–ion and nonelectrolyte–nonelectrolyte–ion, respectively. In principle, ξ and ω depend on the ionic strength of the solution, but their values are small, and their dependence on the ionic strength of the solution is not taken into account. $\chi^{(0)}$, $\chi^{(1,0)}$, and $\chi^{(1,1)}$ are the adjustable parameters; $\alpha_0 = 2\text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ is a fixed value, and I is the ionic strength.

Potentiometric Measurements. The following galvanic cells containing an Na⁺-glass membrane electrode and an Ag/AgCl electrode were used for collecting the potentiometric data and for elimination of the asymmetry potential¹⁸



The mean activity coefficients of NaCl in the mixtures were then determined at $T/\text{K} = 298.15$ by combining the potentiometric response of the cells I and II represented by the Nernst relation

$$\Delta E = E_{(\text{I})} - E_{(\text{II})} = 2s \ln \left(\frac{\gamma_B}{\gamma_B^0} \right) \quad (9)$$

where $s = (RT/F)$ is the Nernstian slope and in which the symbols have their usual meanings. γ_B and γ_B^0 are the mean activity coefficients of NaCl in the mixtures, in the presence and

Table 1. Experimental Mean Activity Coefficients (γ_{\pm}) of NaCl Electrolyte in Different Mass Fractions of CH₃OH ($x = 0.10, 0.20, 0.30, 0.40,$ and 0.50) in Water and the Corresponding Potentiometric Responses ($\Delta E/mV$) at 298.15 K

$x = 0.10$			$x = 0.20$			$x = 0.30$		
NaCl/mol·kg ⁻¹	$\gamma_{\pm}(\text{NaCl})$	$\Delta E/mV$	NaCl/mol·kg ⁻¹	$\gamma_{\pm}(\text{NaCl})$	$\Delta E/mV$	NaCl/mol·kg ⁻¹	$\gamma_{\pm}(\text{NaCl})$	$\Delta E/mV$
0.0010	0.9613	-115.7	0.0005	0.9677	-149.7	0.0005	0.9629	-148.7
0.0025	0.9413	-69.1	0.0010	0.9564	-114.6	0.0010	0.9504	-113.8
0.0050	0.9203	-34.3	0.0024	0.9352	-68.6	0.0025	0.9265	-67.9
0.0075	0.9053	-14.2	0.0048	0.9126	-34.0	0.0050	0.9014	-33.6
0.0100	0.8932	0.0	0.0095	0.8832	0.1	0.0100	0.8687	0.2
0.0250	0.8465	44.7	0.0239	0.8321	44.4	0.0250	0.8121	43.9
0.0500	0.8033	78.0	0.0477	0.7841	77.1	0.0500	0.7592	76.0
0.0750	0.7754	97.2	0.0716	0.7528	95.9	0.0750	0.7249	94.5
0.1000	0.7548	110.7	0.0954	0.7295	109.2	0.1000	0.6995	107.5
0.1500	0.7252	129.6	0.2385	0.6535	150.8	0.2500	0.6171	148.2
0.2000	0.7043	143.0	0.4766	0.6017	182.4	0.5000	0.5616	179.0
0.2500	0.6884	153.4	0.7145	0.5784	201.2	0.7500	0.5371	197.5
0.5000	0.6435	185.9	0.9520	0.5673	215.1	1.0000	0.5259	211.3
0.7500	0.6234	205.2	1.1892	0.5632	226.2	1.2500	0.5222	222.4
1.0000	0.6140	219.3	1.4261	0.5638	235.6	1.5000	0.5237	231.9
1.2500	0.6107	230.6	1.8989	0.5743	251.4	2.0000	0.5371	248.0
1.5000	0.6117	240.2	2.1348	0.5832	258.3	2.2500	0.5480	255.1
1.7500	0.6159	248.5	2.2762	0.5894	262.1	2.4500	0.5583	260.4
2.0000	0.6226	256.0	2.3234	0.5917	263.4	2.5000	0.5611	261.7
2.5000	0.6424	269.2				2.6500	0.5701	265.5
2.7500	0.6551	275.2						
2.9625	0.6672	278.0						
3.1433	0.6784	283.9						
3.2977	0.6887	287.2						

$x = 0.40$			$x = 0.50$		
NaCl/mol·kg ⁻¹	$\gamma_{\pm}(\text{NaCl})$	$\Delta E/mV$	NaCl/mol·kg ⁻¹	$\gamma_{\pm}(\text{NaCl})$	$\Delta E/mV$
0.0005	0.9585	-149.3	0.0005	0.9057	-235.4
0.0010	0.9444	-114.1	0.0008	0.8975	-213.0
0.0026	0.9178	-67.8	0.0010	0.8910	-197.7
0.0052	0.8900	-33.5	0.0025	0.8634	-148.9
0.0103	0.8537	0.3	0.0051	0.8346	-112.7
0.0258	0.7912	43.9	0.0076	0.8139	-91.8
0.0515	0.7330	75.9	0.0101	0.7973	-77.1
0.0773	0.6953	94.2	0.0253	0.7335	-31.3
0.1031	0.6675	107.0	0.0505	0.6744	2.3
0.2578	0.5772	147.1	0.0758	0.6364	21.4
0.5159	0.5155	177.2	0.1011	0.6084	34.8
0.7742	0.4868	195.3	0.1265	0.5863	45.0
1.0327	0.4720	208.6	0.2533	0.5178	76.4
1.2915	0.4648	219.5	0.5080	0.4551	107.5
1.5505	0.4627	228.7	0.7641	0.4248	126.1
			1.0217	0.4078	139.8
			1.2807	0.3981	150.9

in the absence of nonelectrolyte at same ionic strengths, respectively.

RESULTS

The values γ_{\pm}^0 for the pure NaCl were calculated at the appropriate ionic strengths used in this work from the available Pitzer ion-interaction parameters for the pure NaCl.¹⁹ The obtained experimental mean activity coefficients of NaCl electrolyte in different mass fractions (x) of CH₃OH in water and the corresponding potentiometric responses, at $T/K = 298.15$, are presented in Table 1.

Table 2 shows the resulting Pitzer ion-interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} and particularly the related parameters at

relatively high concentrations for CH₃OH mass fractions $x = 0.10, 0.30,$ and 0.50 in H₂O (not reported previously) for this mixture and the corresponding standard deviation values ($\sigma = \text{rmsd}$)

$$\sigma = \left(\frac{\sum_{i=1}^n (E_{i,\text{exp}} - E_{i,\text{calc}})^2}{n - 1} \right)^{1/2} \quad (10)$$

where E is the emf (electromotive force) and n is the number of experimental data points.

The reported Pitzer parameters values^{9–11} were also included in Table 2 for comparison. The used values of A_{ϕ} , dielectric

Table 2. Comparison of Pitzer Ion-Interaction Parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ for NaCl in Different Mass Fractions of CH₃OH (x) in Water^a

MeOH	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	m_{\max}	σ	ref
x	kg·mol ⁻¹	kg·mol ⁻¹	kg ² ·mol ⁻²	mol·kg ⁻¹		
0	0.0771	0.2639	0.0011	6.144	1.323·10 ⁻⁵	19
0.1	0.08	0.2198	0.0023	3.298	2.35·10 ^{-1b}	this work
	0.068	0.312		0.2	7.3·10 ⁻⁴	9
	0.0966	0.1063	0.0015	2.323	3.64·10 ^{-1b}	this work
0.2	0.046	0.37799		0.2	2.07·10 ⁻³	9
	0.0985	0.3278	-0.0028	3.67	1.9·10 ⁻¹	11
	0.1067	0.0821	-0.0053	4	1.97·10 ^{-3c}	10
0.3	0.1036	0.0846	0.0028	2.65	6.64·10 ^{-1b}	this work
	0.037	0.468		0.2	2.7·10 ⁻³	9
0.4	0.1015	0.0685		1.55	3.52·10 ^{-1b}	this work
	0.062	0.524		0.2	1.09·10 ⁻³	9
	0.1349	0.2752	-0.0146	1.68	1.5·10 ⁻¹	11
0.5	0.1136	0.2785		2	3.81·10 ^{-3c}	10
	0.0999	0.1206		1.304	3.89·10 ^{-1b}	this work
	0.014	0.655		0.2	2.89·10 ⁻³	9

^a m_{\max} and σ are the maximum molality and the corresponding root-mean-squared deviation for each series, respectively, at 298.15 K. ^bStandard deviation values (rmsd) calculated using E/mV values. ^cPitzer parameters calculated by Boukhalfa and Ménéai¹⁰ using the experimental data of Feakins and Voice⁸ and Basili et al.¹²

constant (D), and density (ρ_A) for different solvent compositions⁹ are also presented in Table 3.

Table 3. Solvent Density (ρ_A), Dielectric Constant (D), and Debye–Hückel Coefficient for the Osmotic Coefficient Values (A_ϕ) in Different Mass Fractions of CH₃OH (x) in water, at 298.15 K, Taken from the Literature⁹

CH ₃ OH	$\rho_A/g\cdot mL^{-1}$	D	A_ϕ
0	0.9971	78.30	0.3921
0.10	0.9799	74.20	0.4214
0.20	0.9645	70.00	0.4562
0.30	0.9481	65.41	0.5008
0.40	0.9319	60.94	0.5521
0.50	0.9125	56.30	0.6152

Figure 1 shows the obtained experimental mean activity coefficients of NaCl electrolyte versus molality in different mass fractions (x) of CH₃OH in water. The only available experimental data at relatively high concentrations that could be used for comparison are those of Yan et al.¹¹ and Basili et al.¹² at mass fractions $x = 0.20$ and 0.40 of CH₃OH in water which were also included in Figure 1 for comparison. As can be seen, only the data of Basili et al.¹² at mass fractions $x = 0.20$ of CH₃OH in water compare well with our results, while there are inconsistencies between our results and those of Yan et al.¹¹ and Basili et al.¹² at $x = 0.40$ mass fraction of CH₃OH. It has to be noted that the data of Yan et al.¹¹ and Basili et al.,¹² at mass fractions of $x = 0.20$ of CH₃OH in water diverge also between each other.

The inconsistencies between our results and those of Yan et al.¹¹ both at $x = 0.20$ and $x = 0.40$ and Basili et al.¹² at $x = 0.40$ mass fractions of CH₃OH appear also at low concentrations (see Figure 2). However, as shown in Figure 2, at lower concentrations, the general trends of our data compare well with those of Åkerlöf⁷ at all investigated mass fractions of CH₃OH and also with those of Basili et al.¹² at $x = 0.20$.

Table 4 shows the binary (ion–CH₃OH) and triple (ion–ion–CH₃OH, the ion–CH₃OH–CH₃OH) interaction param-

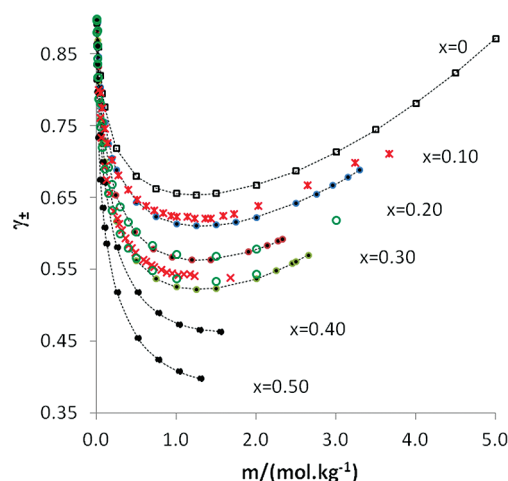


Figure 1. Experimental mean activity coefficients of NaCl electrolyte versus molality in different mass fractions (x) of CH₃OH in water, with $x = 0, 0.10, 0.20, 0.30, 0.40$, and 0.50 . The reported data of Yan et al.¹¹ and Basili et al.¹² at mass fractions of $x = 0.20$ and 0.40 are also included in this figure. □, mean activity coefficients of NaCl in water calculated using Pitzer parameters of Marshall et al.;¹⁹ ●, mean activity coefficients of NaCl obtained in this work; red *, mean activity coefficients of NaCl taken from Yan et al.;¹¹ and green ○, data taken from Basili et al.¹²

eter values of the modified Pitzer equations. From the comparison of the σ (rmsd) in the presence and in the absence of the ion–CH₃OH–CH₃OH triple interactions it can be concluded that the triple interactions are not negligible. The binary parameters $x_{AB}^{(0)}$ do not show any significant variation in the different mass fractions of CH₃OH, while $x_{AB}^{(1,1)}$ shows a decreasing trend with the increasing mass fraction of CH₃OH. The relatively large and negative values of the ion–alcohol binary interaction $x_{AB}^{(1,0)}$ was interpreted as responsible for some association phenomenon between the Na⁺ or Cl⁻ ions and the CH₃OH in these mixtures.^{16,17}

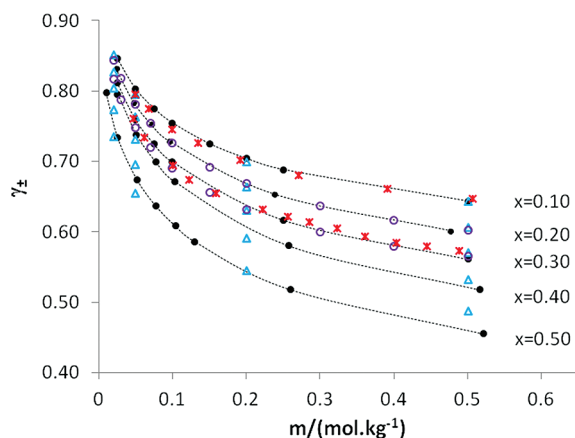


Figure 2. Obtained experimental mean activity coefficients of NaCl electrolyte versus molality, at low concentrations, in different mass fractions (x) of CH_3OH in water, with $x = 0.10, 0.20, 0.30, 0.40,$ and 0.50 , compared to the corresponding results reported in literature. ●, mean activity coefficients of NaCl obtained in this work; red *, mean activity coefficients of NaCl taken from Yan et al.¹¹ with $x = 0.20$ and 0.40 ; purple ○, data taken from Basili et al.¹² with $x = 0.20$ and 0.40 ; and green △, data taken from Åkerlöf⁷ with $x = 0.10, 0.20, 0.30, 0.40,$ and 0.50 .

CONCLUSION

The Pitzer and the modified Pitzer equations were used in this work for the investigation of NaCl electrolytes in different mass fractions (x) of CH_3OH in H_2O , where $x = 0.10, 0.20, 0.30, 0.40,$ and 0.50 and in the molality range of $(0.001 \text{ to } 3.3) \text{ mol}\cdot\text{kg}^{-1}$. A galvanic cell containing an Na^+ -glass membrane and Ag/AgCl electrodes were also used for collecting the potentiometric experimental data at $(298.15) \text{ K}$.

The Pitzer ion-interaction parameters $\beta^{(0)}, \beta^{(1)},$ and C^ϕ (not previously reported) for NaCl in different mass fractions $x = 0.10, 0.20, 0.30, 0.40,$ and 0.50 of CH_3OH in water at relatively high concentrations were determined, and the results were reported. The available literature data, specifically for the CH_3OH mass fractions $x = 0.10, 0.30,$ and 0.50 in H_2O , are mainly limited up to the molality of $0.2 \text{ mol}\cdot\text{kg}^{-1}$, in which the triple interaction Pitzer parameter C^ϕ are neglected. The obtained experimental data at relatively high concentrations at mass fractions $x = 0.20$ and 0.40 of CH_3OH in water were compared to those of Yan et al.¹¹ and Basili et al.¹² and at lower concentrations also to those of Åkerlöf⁷ at $x = 0.10, 0.20, 0.30, 0.40,$ and 0.50 .

Using the modified Pitzer equations,^{15–17} the binary ($\chi^{(0)}, \chi^{(1,0)},$ and $\chi^{(1,1)}$) and ternary ion–nonelectrolyte interaction parameters (ξ and ω) were determined for this mixture for different mass fractions of CH_3OH in H_2O . The results showed that the triple interactions are not negligible and should be taken into account. The results showed also that the binary

parameters $x_{\text{AB}}^{(0)}$ do not present any significant variation in different mass fractions series of CH_3OH , while $x_{\text{AB}}^{(1,1)}$ shows a decreasing trend with increasing CH_3OH mass fraction. Finally, the relatively large and negative values of the ion–alcohol binary interaction $x_{\text{AB}}^{(1,0)}$ was interpreted as responsible for some association phenomenon between the Na^+ or Cl^- ions and the CH_3OH in these mixtures.^{16,17}

The modified Pitzer approach permitted the determination of various binary ion–solvent and ternary ion–ion–solvent interaction coefficients (not reported previously) which represent complementary data to the Pitzer binary and ternary ion–ion interaction coefficients. A comparison of the two models shows that the modified Pitzer approach presents a better fit of the mean activity coefficients for NaCl in $\text{MeOH}-\text{H}_2\text{O}$ mixtures based on the resulting roots of mean square deviation of their fits.

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Table 4. Binary ($\chi^{(0)}, \chi^{(1,0)},$ and $\chi^{(1,1)}$) and Ternary (ξ and ω) Ion– CH_3OH Interaction Parameters of the Modified Pitzer Equations for NaCl in Different Mass Fractions (x) of CH_3OH in Water, at 298.15 K

CH_3OH (x)	$\chi^{(0)}_{\text{AMX}}$	$\chi^{(1,0)}_{\text{AMX}}$	$\chi^{(1,1)}_{\text{AMX}}$	ξ_{MXA}	ω_{MXA}	σ
0.10	−0.0037	−0.1000	0.0485	0.0004	−0.0003	$6.88 \cdot 10^{-3}$
0.20	0.0067	−0.1950	0.0289	0.0096	−0.0047	$3.03 \cdot 10^{-3}$
0.30	0.0071	−0.1730	0.0228	0.0039	−0.0049	$4.54 \cdot 10^{-3}$
0.40	−0.0056	−0.1779	0.0144	0.0051	−0.0018	$2.36 \cdot 10^{-3}$
0.50	0.0045	−0.1810	0.0063	−0.0014	−0.0007	$1.44 \cdot 10^{-3}$

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