

Correlation and prediction of thermodynamic properties for quaternary ammonium salt types by applying the modified nonelectrolyte UNIQUAC-NRF model

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Abstract

The osmotic and activity coefficients of quaternary ammonium salt types are correlated and predicted applying a modified nonelectrolyte UNIQUAC-NRF equation. The excess Gibbs energy of the model consists of the long-range term according to the Pitzer–Debye–Hückel equation and a short-range term expressed through the modified nonelectrolyte UNIQUAC-NRF model. The main difference between the equations of this model and the equations of its counterparts is that through these new equations, the ion or ion pair free electrolyte solutions model can be reduced to the basic nonelectrolyte UNIQUAC model, thus, useable in both nonelectrolyte and electrolyte solutions. The mean activity coefficients of more than 110 binary aqueous electrolyte systems (quaternary ammonium salts and strong aqueous electrolyte solutions) at 298.15 K at 1 bar is calculated through this new model, with two adjustable parameters per electrolyte. These adjustable parameters are applied in predicting osmotic coefficients for the quaternary ammonium salt types. The findings here are compared with that of the Pitzer, modified Wilson, E_NRTL, electrolyte Wilson, UNIQUAC-NRF, Wilson-NRF, NRTL-NRF and Extended UNIQUAC thermodynamic models where its outperformance in all aspects is revealed. It is notable that, by applying the adjustable parameters, the mean activity coefficient for methanol-water-salt systems is correlated at 298.15 K.

Keywords: Activity coefficient, osmotic coefficients, Modified UNIQUAC-NRF, quaternary ammonium salt, thermodynamic models

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1. Introduction

Low-melting organic salt types or ionic liquids (ILs) have been and are subject to serious studies. Due to their nature, they exhibit negligible vapor pressure, thus no harm to air quality. The ability of the solvents in reactions and the phase-transfer catalysts potential is the focus of many studies. High conductivity and appropriate heat transfer properties make these solvents essential. The solvents involved in chemical reactions and element separations are subject to their stability, wide liquid ranges and appropriate dissolution properties in polar and nonpolar compounds. By selecting the proper cation, anion, and substituents their physical properties can be tuned. An overview of these salt types' potential for synthesis, catalysis, and separation is given [1-5]. First, the primary thermodynamic properties of ILs and phase behavior with water and organic solvents need to be distinguished and then separated between organic phases and aqueous to consume ILs as the solvents. Since ILs are newly introduced salt types experimental measuring procedures of their activity coefficients and phase behavior, through which the thermodynamic models are assessed, are limited. Some infinite dilution activity coefficients of the chemicals in ILs [6-9]; some liquid-liquid equilibrium data, solid solubilities, some liquid and gas between ILs and alcohols constitute the only phase behavior data available [1,10-13]. The types of quaternary ammonium salt types that are commonly consumed in industry as phase-transfer catalysts, additives in animal feed, and preservatives and disinfectants in hair care and cosmetic products (choline salt types) are the subjects of focus in this study. Because these salt types are non-toxic, biodegradable and nonirritant, ILs are superior in comparison to other compound classes [14-15]. These salt types are limited in their relatively elevated melting points, unlike other classes of ionic liquids. This limitation can be overcome by consuming more complex anions and modifying the cation substituents, thus reducing the melting point [16]. Evaluating the efficacy of a conventional model on the local composition, where activity and osmotic coefficients of quaternary ammonium salt types in different concentrations of water are described, is sought in this study. The local composition models on aqueous electrolyte mixtures focusing on quaternary ammonium salt types are introduced in [17] where local composition models like Zhao et al [18] an electrolyte-NRTL model of Chen [19] and the modified Wilson models Xu and Macedo [20] are adopted to calculate the thermodynamic properties in water at 298.15 K for comparing these coefficients in aqueous electrolytes [17]. Researchers in [21] adopted the Extended UNIQUAC [22] model to correlate the activity coefficients of ammonium salt systems, applied four adjustable parameters, and found an acceptable agreement between the model result and the experiments. Researchers in [23] compared the results obtained by the results of Pitzer's model [24] and the Electrolyte NRTL [19] model. A new model is proposed here for the prediction and correlation of the quaternary ammonium salt types based on local composition theory. There exist different thermodynamic models developed based on the local composition model, like E-UNIQUAC-NRF [25], modified NRTL-NRF [26], Cruze and Renon [27], E-Wilson [19], E-NRTL-NRF [28], modified Wilson model [20], and Extended - UNIQUAC [22] These models are based on Chen et al [19]. Assumptions based on like-ion repulsion and local electro-neutrality. To date, Chen's model is one of the most cited researches in this field. Haghtalab and Vera followed Chen's assumption in developing the E-NRTL-NRF model by applying a random case reference; the experimental results and their introduced model are in good agreement [28]. The nonelectrolyte models like Wilson-NRF [29], UNIQUAC-NRF [30] and NRTL-NRF [31] are applied in electrolyte systems. An appropriate version of the Debye Hückel model should be considered for nonelectrolyte models. Although the mentioned models are being applied in correlating and predicting of osmotic and activity coefficients

of aqueous electrolytes systems, none of the nonelectrolyte models in the absence of an ion or ion pair in the solution are reduced to the basic nonelectrolyte Wilson, nonelectrolyte UNIQUAC, and nonelectrolyte NRTL models [26]. The basic nonelectrolyte Wilson and NRTL models cannot correlate the thermodynamic properties of aqueous electrolytes as well as the nonelectrolyte NRTL-NRF and Wilson-NRF models containing the exact count of adjustable parameters [32]. In this context, developing modified local composition model (nonelectrolyte UNIQUAC_NRF) which would predict and correlate the activity and osmotic coefficients of aqueous electrolytes and be reduced to nonelectrolyte models when there is no salt type or ions is necessary. Researchers developed and modified the nonelectrolytes NRTL-NRF (MNNN) and Wilson-NRF (MNWN) with the advantage of reducing the basic nonelectrolyte Wilson and NRTL, respectively. These models' prediction and correlation results are correspond with the available experimental.

This study aims to improve the modified nonelectrolyte UNIQUAC-NRF equation for electrolyte solutions to reduce it to the basic nonelectrolyte UNIQUAC in the absence of ionic species like the MNNN and MNWN models. This new model can be applied for the correlation and prediction of osmotic and activity coefficients of more than 110 quaternary ammonium salts types and strong aqueous electrolyte systems. Unlike the extended UNIQUAC [22] model, where four adjustable parameters are applied, in this model, only two adjustable parameters per electrolyte are applied for the correlation and prediction of thermodynamic properties. The results here are compared with the other thermodynamic models [17,21,23,29-31] reported to prove the model's ability to predict and correlate the thermodynamic properties. The new model is applied to correlated the mean activity coefficient of some ternary electrolytes systems(methanol-water-salts) at 298.15 K

2. The newly developed equation

This new model is based on the UNIQUAC model, where the internal energy is consumed as the interaction energy between different species in the mixtures. According to local two-liquid theory, a binary solution's internal energy is obtained through Eq. (1):

$$u^E = \frac{1}{2} Z x_1 q_1 (\theta_{11} U_{11} + \theta_{21} U_{21} - U_I^{Ref}) + \frac{1}{2} Z x_2 q_2 (\theta_{12} U_{12} + \theta_{22} U_{22} - U_{II}^{Ref}) \quad (1)$$

where Z , x , q , and θ are the coordination number, mole fraction, surface area parameter, and area fractions, respectively. U is the potential energy. Subscripts I and II represent the local cells with components 1 and 2 as central molecules expressed through Eqs. (2 and 3):

$$U_I^{Ref} = \theta_1 U_{11} + \theta_2 U_{21} \quad (2)$$

$$U_{II}^{Ref} = U_2 \quad (3)$$

In this study, the ion pair assumption is applied, so a binary aqueous electrolyte solution is assumed to be a binary solution with salt or electrolyte as component 1 and water as component 2. Eq. (2) and Eq. (3) show pure state adoption for reference state of water and random state adoption for electrolyte or salt. By inserting these equations in Eq. (1) and applying $\theta_{ij} + \theta_{jj} = 1$, Eq. (4) is yielded:

$$u^E = \frac{1}{2} Z N_A [x_1 q_1 (\theta_{21} - \theta_2) (U_{21} - U_{11}) + x_2 q_2 \theta_{12} (U_{12} - U_{22})] \quad (4)$$

By applying the local area fraction definition, θ_{ij} , the following equations are yielded:

$$u^E = x_1 q_1 \theta_2 \Delta u_{21} (\Gamma_{21} - 1) + x_2 q_2 \theta_1 \Delta u_{12} \Gamma_{12} \quad (5)$$

$$\theta_{ij} = \theta_i \Gamma_{ij} \quad (6)$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^m q_j x_j} \quad (7)$$

$$\Gamma_{ij} = \frac{\tau_{ij}}{\sum_{l=1}^n x_l \tau_{lj}} \quad (8)$$

$$\tau_{ij} = \exp \left[-\frac{\Delta u_{ij}}{RT} \right] = \exp \left[-\frac{\frac{1}{2} Z (U_{ii} - U_{jj}) N_A}{RT} \right] \quad (9)$$

where in Eq. (8), N_A is Avogadro's number. The molar excess Helmholtz energy, a^E , is obtained through Eq. (10):

$$\frac{a^E}{T} = \int_{1/T_0}^{1/T} u^E d\left(\frac{1}{T}\right) + C \quad (10)$$

where C is the integration constant, evaluated at $1/T_0 \rightarrow 0$ (i.e., very high temperatures); consequently, the following Guggenheim equation is applied for a thermal solution:

$$\left[\frac{a^E}{RT}\right]_{athermal} = -\left[\frac{S^E}{RT}\right]_{combinatorial} \quad (11)$$

$$= x_1 \ln \frac{\varphi_1}{x_1} + x_2 \ln \frac{\varphi_2}{x_2} + \frac{Z}{2} (x_1 q_1 \ln \frac{\varphi_1}{x_1} + x_2 q_2 \ln \frac{\varphi_2}{x_2})$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^m r_j x_j} \quad (12)$$

By referring to the temperature independence of Δu_{ij} and the similarity of g^E and a^E assumptions at low pressures, the new molar excess Gibbs energy for a binary system (solution) is calculated through (13-15):

$$\left(\frac{g^E}{RT}\right) = \left(\frac{g^E}{RT}\right)_c + \left(\frac{g^E}{RT}\right)_R \quad (13)$$

$$\left(\frac{g^E}{RT}\right)_c = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + \frac{Z}{2} (x_1 q_1 \ln \frac{\theta_1}{\Phi_1} + x_2 q_2 \ln \frac{\theta_2}{\Phi_2}) \quad (14)$$

$$\left(\frac{g^E}{RT}\right)_R = x_1 q_1 (\ln \Gamma_{11} + \theta_2 \ln \tau_{21}) + x_2 q_2 \ln \Gamma_{22} \quad (15)$$

where C and R are the combinatorial and residual parts, respectively, and the residual activity coefficients of components 1 and 2 are expressed as follows with correct differentiation:

$$(\ln y_1)_R = q_1 [\ln \Gamma_{11} + \theta_2 (\Gamma_{21} - \Gamma_{12}) + \theta_2^2 \ln \tau_{21}] \quad (16)$$

$$(\ln y_2)_R = q_2 [\ln \Gamma_{22} + \theta_1 (\Gamma_{12} - \Gamma_{21}) + \theta_1^2 \ln \tau_{21}] \quad (17)$$

Generalizations for the multi-component mixture yields:

$$\left(\frac{g^E}{RT}\right)_c = \sum_{i=1}^n x_i \ln \frac{\Phi_i}{x_i} + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \Gamma_{ii} \frac{\Phi_i}{x_i} \quad (18)$$

$$\left(\frac{g^E}{RT}\right)_R = \sum_{i=1}^n q_i x_i \ln \Gamma_{ii} + \sum_{i=\text{ion pair}}^n \theta_j \ln \tau_{ij} \quad (19)$$

$$(\ln y_i)_c = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} - \frac{Z}{2} q_i \left[\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right] \quad (20)$$

$$(\ln \gamma_{i=\text{ion pair}})_R \quad (21)$$

$$= q_i \left[1 + \ln \Gamma_{ii} - \sum_j \theta_j (\Gamma_{ij} - \ln \tau_{ji}) \right. \\ \left. - \sum_{p=\text{ion pair}} \theta_p \left(\ln \tau_{ip} - \sum_k x_k \ln \tau_{kp} \right) \right]$$

The newly modified nonelectrolyte UNIQUAC-NRF (MNUN) model is expressed through Eqs. (21).

3. The new equation for strong electrolytes

The assumption of ion pair is adopted to apply this new electrolyte solutions equation. An electrolyte's molar excess Gibbs energy is calculated by adding its short- and long-range interaction energies, Eq. (22):

$$\frac{g^{E*}}{RT} = \frac{g_{SR}^{E*}}{RT} + \frac{g_{LR}^{E*}}{RT} \quad (22)$$

where superscript SR, LR, E, and * are the short-range, long-range, excess property, and unsymmetrical normalization, respectively. After normalization, Eqs. (18 and 19) provide the short-range contribution to the excess Gibbs energy. In a binary electrolyte solutions, salt or electrolyte is considered as component 1 and water as component 2. Component 1 of salt's unsymmetrical short-range activity coefficient is expressed as follows:

$$\ln \gamma_{1,SR}^* = \ln \gamma_{\pm,SR}^* = \ln \left(\frac{\gamma_{1,SR}}{\gamma_{1,SR}^\infty} \right)_C + \ln \left(\frac{\gamma_{1,SR}}{\gamma_{1,SR}^\infty} \right)_R \quad (23)$$

$$\ln \left(\frac{\gamma_{1,SR}}{\gamma_{1,SR}^\infty} \right)_C = \ln \frac{\varphi_1}{x_1} + 1 - \frac{\varphi_1}{x_1} - \frac{10}{2} q_1 \left[\ln \frac{\varphi_1}{\theta_1} + 1 - \frac{\varphi_1}{\theta_1} \right] \\ - \left(\ln \frac{r_1}{r_2} + 1 - \frac{r_1}{r_2} - \frac{10}{2} q_1 \left[\ln \frac{r_1 q_2}{r_2 q_1} + 1 - \frac{r_1 q_2}{r_2 q_1} \right] \right) \quad (24)$$

$$\ln\left(\frac{\gamma_{1,SR}}{\gamma_{1,SR}^{\infty}}\right)_R = q_1[\ln\Gamma_{11} + \theta_2(\Gamma_{21} - \Gamma_{12}) + \theta_2^2 \ln(\tau_{21}) + \tau_{12} - 1]$$

(25)

where, ∞ is the infinite dilution (i.e., x_{ion} approaches zero and x_w is the unity). The Pitzer-Debye-Hückel equation provides the long-range contributions to the activity coefficients of ion and water through Eq. (26):

$$\ln\gamma_{ion}^* = -A_{\phi}\left(\frac{1000}{M_w}\right)^{0.5}\left(\frac{z_{ion}^2}{\rho}\ln(1 + \rho I_x^{0.5}) + \frac{z_{ion}^2 I_x^{0.5} - 2I_x^{1.5}}{1 + \rho I_x^{0.5}}\right)$$

(26)

$$I_x = \frac{1}{2}\sum_{ion} x_{ion} z_{ion}^2$$

(27)

$$\ln\gamma_{1,LR}^* = \ln\gamma_{\pm,LR}^* = \frac{v_a(\ln\gamma_a)_{LR}^* + v_c(\ln\gamma_c)_{LR}^*}{v_a + v_c}$$

(28)

$$\ln\gamma_{2,LR} = \ln\gamma_{water,LR} = -A_{\phi}\left(\frac{1000}{M_w}\right)^{0.5}\left(-\frac{2I_x^{1.5}}{1 + \rho I_x^{0.5}}\right)$$

(29)

where z is the charge number of ionic species, A_{ϕ} is the Debye-Hückel constant, M_w is the molecular weight of water, and ρ is the closest approach parameter. These stoichiometric coefficients of a cation and an anion are symbolized as v_c and v_a respectively. The electrolyte's unsymmetrical mean activity coefficient (with salt as component 1) is obtained as follows:

$$\ln\gamma_{\pm}^* = \ln\gamma_1^* = \ln\gamma_{SR}^* + \ln\gamma_{LR}^*$$

(30)

The osmotic coefficient is determined through Eq. (32):

$$\Phi = -1000\frac{\ln(x_w\gamma_{2,SR}\gamma_{2,LR})}{(\sum_{ion} m_{ion})M_w}$$

(31)

$$\ln\gamma_{2,SR} = \ln(\gamma_{2,SR})_C + \ln(\gamma_{2,SR})_R$$

(32)

where, $\ln\gamma_{2,LR}$, $\ln(\gamma_{2,SR})_R$ and $\ln(\gamma_{2,SR})_C$ are calculated through Eqs. (17, 20, and 30), respectively.

4. RESULTS AND DISCUSSION

4.1 Parameter estimation

This new model is evaluated through the many aqueous strong electrolytes' mean activity and osmotic coefficients at 298.15 K and 1 bar. This new model's binary adjustable parameters for each electrolyte are a_{12}/T and a_{21}/T ,

which appear in its short-range contribution, which is obtained for each electrolyte by correlating the experimental mean activity coefficients of the quaternary ammonium salt types. As the objective function, the absolute average relative deviation (AARD) of the mean activity coefficient data is applied to obtain the electrolyte binary adjustable parameters through Eq. (33):

$$\% \text{AARD} = \frac{100}{N} \sum \frac{|(\gamma_{\pm m}^{*exp})_i - (\gamma_{\pm m}^{*cal})_i|}{(\gamma_{\pm m}^{*exp})_i} \quad (33)$$

where N is the number of experimental data points, and the superscripts exp and cal are the computed and experimental data, respectively. The constants of $A\phi$ and ρ in the long-range equation are set to 14.9 and 0.3909 in the Pitzer-Debye-Hückel equations, respectively. Because this system is apparent binary, the mole fraction of salt and water is calculated as $x_1 = \nu m / (\nu m + 55.51)$ and $x_2 = 1 - x_1$, respectively. The ions', q and r, surface and volume parameters for the anions ion consumed in the combinatorial part of the UNIQUAC-NRF model, are borrowed from [25], where these two are calculated based on the their radius, and values which for electrolytes have a positive effect on the results of the correlation and prediction of the subject salt types. Eqs. (35 and 36) are applied to calculate these parameters:

$$r_{salt} = (r_a^3 + r_c^3)^{\frac{1}{3}} \quad (34)$$

$$q_{salt} = (q_a^2 + q_c^2)^{\frac{1}{2}} \quad (35)$$

where a is an anion and c is a cation. The CHEM DRAW software is applied to calculate some cations parameters like $(C_2H_5)_4N$, $(C_3H_7)_4N$, $(C_4H_9)_4N$, $SO_3-C_6H_4-CH_2-CH_2-C_6H_4SO_3$, and $SO-C_6H_4-SO_3$ radius, because they do not exist in the related literature. The remaining cation parameters are obtained through references [21,33-34]. The r and q parameters for the quaternary ammonium salt types for the modified nonelectrolyte UNIQUAC-NRF model applied in this assessment are tabulated in Table 1.

Table 1. The modified nonelectrolyte UNIQUAC-NRF and nonelectrolyte UNIQUAC-NRF models structural parameters r and q for different cations

<i>Component</i>	<i>R</i>	<i>q</i>
<i>CH₃SO₃</i>	<i>2.092</i>	<i>1.655</i>
<i>C₂H₅SO₃</i>	<i>1.525</i>	<i>1.341</i>
<i>SO-C₆H₄-SO₃</i>	<i>4.878</i>	<i>2.911</i>
<i>SO₃-C₆H₄-CH₂-CH₂-C₆H₄-SO₃</i>	<i>8.74</i>	<i>4.3</i>
<i>CH₃NH₃</i>	<i>1.104</i>	<i>1.081</i>
<i>(CH₃)₂NH₂</i>	<i>2.926</i>	<i>2.071</i>
<i>(CH₃)₃NH</i>	<i>3.422</i>	<i>2.298</i>
<i>(CH₃)₄N</i>	<i>2.952</i>	<i>2.083</i>
<i>(C₂H₅)₄N</i>	<i>4.504</i>	<i>2.76</i>
<i>(C₃H₇)₄N</i>	<i>6.263</i>	<i>3.439</i>
<i>(C₄H₉)₄N</i>	<i>1.61</i>	<i>1.39</i>
<i>(CH₃)₄(C₂H₄OH)N</i>	<i>1.78</i>	<i>1.49</i>
<i>(CH₃)₂(C₂H₄OH)(C₆H₅)N</i>	<i>5.477</i>	<i>3.145</i>
<i>(CH₃)₃(C₆H₅)N</i>	<i>3.163</i>	<i>2.181</i>
<i>(C₂H₄OH)₄N</i>	<i>5.02</i>	<i>2.97</i>
<i>(t-C₄H₉)NH₃</i>	<i>3.654</i>	<i>2.401</i>
<i>(CH₃)₃N-CH₂-CH₂-(CH₃)₃N</i>	<i>1.638</i>	<i>1.407</i>
<i>Water</i>	<i>0.92</i>	<i>1.40</i>

4.2 Quaternary ammonium salt types

The activity coefficients of many aqueous strong electrolytes, including more than 70 quaternary ammonium salt types, are calculated through this new model at 298.15 K and 1 bar.

The osmotic coefficient is predicted by applying the binary parameters of the activity coefficients' correlation, and the deviation of prediction is calculated through Eq. (26):

$$\% \text{AARD} = \frac{100}{N} \sum \frac{|\Phi^{\text{exp}} - \Phi^{\text{cal}}|}{(\Phi^{\text{exp}})} \quad (36)$$

Details of the calculation of thermodynamic properties of the modified nonelectrolyte UNIQUAC-NRF model for quaternary ammonium salt types at 298.15 K are tabulated in Table 2.

Table 2. The binary adjustable parameters and results of the new model in correlation and prediction mean activity and osmotic coefficients of quaternary ammonium salt types in water at 298.15 K

<i>Aq.sys.</i>	<i>Max.m</i>	<i>a12/T</i>	<i>a21/T</i>	γ_{\pm}	ϕ	<i>Source</i>
<i>NH₄Cl</i>	7.4	-0.884	1.214	0.15	0.13	[45]
<i>NH₄NO₃</i>	26	0.166	1.013	1.04	0.91	[45]
<i>NH₄CLO₃</i>	2.1	-0.943	1.674	0.64	0.69	[45]
<i>NH₄HCO₃</i>	1	-1.207	2.612	0.34	0.44	[46]
<i>NH₄I</i>	7.5	-0.888	0.925	0.44	0.38	[47]
<i>NH₄Br</i>	7.5	-0.857	1.011	0.21	0.18	[48]
<i>NH₄SCN</i>	23	-0.85	-1.546	1.94	1.68	[49]
<i>NH₄CH₃SO₃</i>	4	-0.984	1.265	0.13		[50]
<i>NH₄C₂H₅SO₃</i>	4	-1.013	1.052	0.37		[50]
<i>CH₃NH₃ Cl</i>	7.5	-0.919	1.548	1.06	0.84	[51]
<i>CH₃NH₃ ClO₄</i>	4	-0.621	1.21	0.82	0.97	[52]
<i>CH₃NH₃ NO₃</i>	9.5	-0.274	0.98	0.41	0.54	[53]
<i>(CH₃)₂NH₃ Cl</i>	6.5	-0.979	1.317	0.49	0.39	[51]
<i>(CH₃)₂NH₃ ClO₄</i>	7.5	-0.43	-0.523	1.93	1.82	[52]
<i>(CH₃)₂NH₃ NO₃</i>	6	-0.76	0.723	0.32	0.39	[53]
<i>(CH₃)₃NH₃ Cl</i>	15	-1.076	1.531	1.65	1.56	[54]
<i>(CH₃)₃NH₃ ClO₄</i>	1.8	-0.667	1.2	0.71	0.95	[52]
<i>(CH₃)₃NH₃ NO₃</i>	8.5	-0.876	1.003	0.84	0.78	[53]
<i>(CH₃)₄NCl</i>	19	-1.106	1.784	4.63	3.27	[55]
<i>(CH₃)₄NBr</i>	5.5	-0.85	1.404	1.12	1.03	[55]
<i>(CH₃)₄NI</i>	0.25	31.217	-0.389	0.6	0.39	[55]
<i>(CH₃)₄NF</i>	7	-1.613	2.555	9.19	4.96	[56]
<i>(CH₃)₄N NO₃</i>	7	-0.892	1.404	1.48	1.37	[47]
<i>(CH₃)₄NCH₃SO₃</i>	4	-1.06	1.429	0.96		[50]
<i>(CH₃)₄NC₂H₅SO₃</i>	4	-1.11	1.42	1.33		[50]
<i>(C₂H₅)₄NCl</i>	9	-1.29	1.85	6.02	8.32	[55]
<i>(C₂H₅)₄NBr</i>	12	-1.12	1.63	2.97	8.3	[55]
<i>(C₂H₅)₄NI</i>	1.9	-0.95	1.62	1.35	1.88	[55]
<i>(C₂H₅)₄NF</i>	5.5	-1.69	2.62	16.12	6.82	[56]
<i>(C₂H₅)₄N NO₃</i>	8	-1.02	1.34	2.96	3.2	[47]
<i>C₂H₅)₄NCH₃SO₃</i>	4	-1.2	1.54	1.13		[50]
<i>(C₂H₅)₄NC₂H₅SO₃</i>	4	-1.29	1.71	1.65		[50]
<i>(C₃H₇)₄N Cl</i>	18	-1.46	1.97	3.39	3.92	[55]
<i>(C₃H₇)₄NF</i>	5	-1.78	2.81	17.96	7.11	[56]
<i>(C₃H₇)₄N Br</i>	9	-1.31	1.63	4.14	3.87	[55]
<i>(C₃H₇)₄N I</i>	0.5	-1.2	1.75	0.47	0.34	[55]

$(C_4H_9)_4N Br$	27	0	1.518	3.01	3.73	[55]
$(C_4H_9)_4N Cl$	15	-0.758	0.93	4.31	4.19	[55]
$(C_4H_9)_4N F$	1.6	-1.97	2.811	1.72	8.78	[56]
$(C_4H_9)_4N CH_3SO_3$	4	-1.156	-2.767	1.8		[50]
$(C_4H_9)_4N C_2H_5SO_3$	4	-1.31	-4.22	1.65		[50]
$(CH_3)_2(C_2H_4OH)(C_6H_5)NCl$	9	-1.11	1.01	0.71	0.92	[57]
$(CH_3)_2(C_2H_4OH)(C_6H_5)NBr$	13	-0.94	0.63	1.95	3.37	[57]
$(CH_3)_3(C_2H_4OH)NCl$	6	-0.95	1.84	1.17	1.12	[57]
$(CH_3)_3(C_2H_4OH)NBr$	7	-0.7	1.67	1.95	1.96	[57]
$(C_2H_4OH)_4NF$	6.5	-1.36	1.65	0.49	0.68	[58]
$(C_2H_4OH)_4NBr$	6.5	-1.05	1.03	1.75	1.9	[58]
$(t-C_4H_9)NH_3Cl$	7	-0.98	0.9	1.28	1.09	[59]
$(CH_3)_3(C_6H_5)NBr$	12	-0.55	1.43	1.75	2.92	[57]
$(CH_3)_3(C_6H_5)NCl$	8	-0.86	1.52	0.66	0.82	[57]
$[NH_4^+]_2[SO_4]_2$	4	-0.82	1.539	1.4	1.38	[60]
$[NH_4^+]_2[B_{10}H_{10}O_2^-]$	3.5	-1.312	1.171	0.94	0.86	[61]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N I_2$	4	-0.578	2.023	4.22	7.41	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N (SO_2)_2$	3.5	-1.436	1.39	7.39	6.12	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N SO_3-C_6H_4-SO_3$	1.2	-1.855	-9.681	16.45	19.13	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N SO_3-C_6H_4-CH_2-CH_2-C_6H_4-SO_3$	0.2	-1.69	2.95	6.39		[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N Cl_2$	4.4	-1.119	2.231	1.51	1.35	[62]
Bu_2Et_2NBr	0.97	-0.62205	1.7503	0.39	0.52	[63]
$HexEt_3NI$	2.24	-0.66506	1.6634	1.03	2.5	[64]
Me_3BuNI	2.65	-0.94294	2.499	1.76	3.5	[65]

<i>Me₂Bu₂NI</i>	4.22	-0.63499	2.7706	2.97	6.84	[65]
<i>HepEt₃NI</i>	3	-0.76001	3.1177	3.31	5.78	[64]
<i>MeBu₃NI</i>	3.96	0.19804	2.4059	2.22		[65]
<i>Iso-Bu₄NBr</i>	1.05	-0.91456	1.9471	0.87	0.7	[63]
<i>Overall</i>				2.59	2.87	

At $\tau_{\text{salt-salt}}=0$ in this modified nonelectrolyte UNIQUAC-NRF model, it is possible to correlate and predict the mean activity and osmotic coefficient in mixed salt systems by only the binary adjustable parameters, something evident in this article. The accuracy of the correlation of the activity coefficient of this model is compared with the findings in [17, 21, 23, 29-31], Tables 3-6, respectively.

Table 3. The deviation comparison of mean activity coefficients of quaternary ammonium salts types applying the modified nonelectrolyte UNIQUAC-NRF (MNUN), PITZER and E-NRTL [23] in water at 298.15 K.

<i>Aq.sys.</i>	<i>Max.m</i>	<i>MNUN</i> γ_{\pm}	<i>E-NRTL</i> γ_{\pm}	<i>PITZER</i> γ_{\pm}	<i>Source</i>
<i>NH₄Cl</i>	7.4	0.15	0.12	0.13	[45]
<i>NH₄NO₃</i>	26	1.04	0.94	0.43	[45]
<i>NH₄ClO₃</i>	2.1	0.64	0.7	0.04	[45]
<i>NH₄HCO₃</i>	1	0.34	0.37	0.06	[46]
<i>NH₄I</i>	7.5	0.44	0.54	0.12	[47]
<i>NH₄Br</i>	7.5	0.21	0.1	0.14	[48]
<i>NH₄SCN</i>	23	1.94	2.1	0.05	[49]
<i>NH₄CH₃SO₃</i>	4	0.13	0.13	0.13	[50]
<i>NH₄C₂H₅SO₃</i>	4	0.37	0.4	0.36	[50]
<i>CH₃NH₃ Cl</i>	7.5	1.06	0.94	0.12	[51]
<i>CH₃NH₃ ClO₄</i>	4	0.82	0.88	0.16	[52]
<i>CH₃NH₃ NO₃</i>	9.5	0.41	0.37	0.34	[53]
<i>(CH₃)₂NH₃ Cl</i>	6.5	0.49	0.62	0.11	[51]
<i>(CH₃)₂NH₃ ClO₄</i>	7.5	1.93	2	0.52	[52]
<i>(CH₃)₂NH₃ NO₃</i>	6	0.32	0.35	0.31	[53]
<i>(CH₃)₃NH₃ Cl</i>	15	1.65	1.46	0.3	[54]

$(\text{CH}_3)_3\text{NH}_3 \text{ClO}_4$	1.8	0.71	0.78	0.11	[52]
$(\text{CH}_3)_3\text{NH}_3 \text{NO}_3$	8.5	0.84	0.93	0.61	[53]
$(\text{CH}_3)_4\text{NCl}$	19	4.63	5.39	0.8	[55]
$(\text{CH}_3)_4\text{NBr}$	5.5	1.12	1.45	1.05	[55]
$(\text{CH}_3)_4\text{NI}$	0.25	0.6	0.68	0.03	[55]
$(\text{CH}_3)_4\text{NF}$	7	9.19	5.38	0.47	[56]
$(\text{CH}_3)_4\text{N NO}_3$	7	1.48	1.8	0.37	[47]
$(\text{CH}_3)_4\text{NCH}_3\text{SO}_3$	4	0.96	0.81	0.47	[50]
$(\text{CH}_3)_4\text{NC}_2\text{H}_5\text{SO}_3$	4	1.33	0.55	0.58	[50]
$(\text{C}_2\text{H}_5)_4\text{NCl}$	9	6.02	4.83	2.05	[55]
$(\text{C}_2\text{H}_5)_4\text{NBr}$	12	2.97	1.91	2.64	[55]
$(\text{C}_2\text{H}_5)_4\text{NI}$	1.9	1.35	1.69	0.43	[55]
$(\text{C}_2\text{H}_5)_4\text{NF}$	5.5	16.12	9.64	1.42	[56]
$(\text{C}_2\text{H}_5)_4\text{N NO}_3$	8	2.96	4	0.75	[47]
$\text{C}_2\text{H}_5)_4\text{NCH}_3\text{SO}_3$	4	1.13	0.72	0.6	[50]
$(\text{C}_2\text{H}_5)_4\text{NC}_2\text{H}_5\text{SO}_3$	4	1.65	0.99	0.82	[50]
$(\text{C}_3\text{H}_7)_4\text{NI}$	0.5	0.47	0.57	1.85	[55]
$(\text{C}_3\text{H}_7)_4\text{NCl}$	18	3.39	6.53	5.29	[55]
$(\text{C}_3\text{H}_7)_4\text{NBr}$	9	4.14	5.99	0.25	[55]
$(\text{C}_3\text{H}_7)_4\text{NF}$	5	17.96	5.22	2.84	[56]
$(\text{C}_4\text{H}_9)_4\text{NBr}$	27	3.01	3.29	4.84	[55]
$(\text{C}_4\text{H}_9)_4\text{NF}$	1.6	1.72	1.4	0.49	[56]
$(\text{C}_4\text{H}_9)_4\text{NCl}$	15	4.31	4.57	4.03	[55]
$(\text{C}_4\text{H}_9)_4\text{N C}_2\text{H}_5\text{SO}_3$	4	1.65	5.59	1.24	[50]
$(\text{C}_4\text{H}_9)_4\text{N CH}_3\text{SO}_3$	4	1.8	3.91	1.08	[50]
$(\text{CH}_3)_2(\text{C}_2\text{H}_4\text{OH})(\text{C}_6\text{H}_5)\text{NBr}$	13	1.95	3.98	4.1	[57]
$(\text{CH}_3)_2(\text{C}_2\text{H}_4\text{OH})(\text{C}_6\text{H}_5)\text{NCl}$	9	0.71	1.15	2.07	[57]
$(\text{CH}_3)_3(\text{C}_6\text{H}_5)\text{NBr}$	12	1.75	2.86	3.81	[57]
$(\text{CH}_3)_3(\text{C}_6\text{H}_5)\text{NCl}$	8	0.66	0.62	1.57	[57]
$(\text{CH}_3)_3(\text{C}_2\text{H}_4\text{OH})\text{NBr}$	7	1.95	2.28	0.33	[57]
$(\text{CH}_3)_3(\text{C}_2\text{H}_4\text{OH})\text{NCl}$	6	1.17	1.57	0.2	[57]
$(\text{C}_2\text{H}_4\text{OH})_4\text{NF}$	6.5	0.49	0.58	0.37	[58]
$(\text{C}_2\text{H}_4\text{OH})_4\text{NBr}$	6.5	1.75	2.1	0.69	[58]
$(t\text{-C}_4\text{H}_9)\text{NH}_3\text{Cl}$	7	1.28	1.14	0.08	[59]
$[\text{NH}_4^+]_2[\text{SO}_4]_2$	4	1.4	1.17	1.43	[60]
$[\text{NH}_4^+]_2[\text{B}_{10}\text{H}_{10}^{2-}]$	3.5	0.94	0.48	10.48	[61]
$(\text{CH}_3)_3\text{N}^+\text{-CH}_2\text{-CH}_2\text{-(CH}_3)_3\text{N I}_2$	4	4.22	4.55	5.34	[62]

$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N$ $(SO_4)^2$	3.5	7.39	7.82	8.45	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N$ $SO_3-C_6H_4-SO_3$	1.2	16.45	30.53	2.13	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N$ $SO_3-C_6H_4-CH_2-CH_2-C_6H_4-SO_3$	0.2	6.39	1.81	6.21	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N$ Cl_2	4.4	1.51	6.72	6.03	[62]
Overall		2.59	2.81	1.61	

Table 4. The deviation comparison of the mean activity coefficients of quaternary ammonium salts types applying the modified nonelectrolyte UNIQUAC-NRF (MNUN) with Extended UNIQUAC [21] in water at 298.15 K.

<i>Aq.sys.</i>	<i>Max.m</i>	<i>MNUN</i> γ_{\pm}	<i>E-UNIQUAC</i> γ_{\pm}	<i>Source</i>
$CH_3NH_3 ClO_4$	4	0.82	0.97	[52]
$CH_3NH_3 NO_3$	9.5	0.41	4.78	[53]
$(CH_3)_2NH_3 Cl$	6.5	0.49	1.33	[51]
$(CH_3)_2NH_3 ClO_4$	7.5	1.93	2.75	[52]
$(CH_3)_2NH_3 NO_3$	6	0.32	3.63	[53]
$(CH_3)_3NH_3 Cl$	15	1.65	5.25	[54]
$(CH_3)_3NH_3 ClO_4$	1.8	0.71	3.30	[52]
$(CH_3)_3NH_3 NO_3$	8.5	0.84	3.98	[53]
$(CH_3)_4NCl$	19	4.63	1.16	[55]
$(CH_3)_4NBr$	5.5	1.12	1.23	[55]
$(CH_3)_4NI$	0.25	0.6	5.15	[55]

$(CH_3)_4NF$	7	9.19	0.81	[56]
$(CH_3)_4NCH_3SO_3$	4	0.96	4.18	[50]
$(CH_3)_4NC_2H_5SO_3$	4	1.33	3.93	[50]
$(C_2H_5)_4NCl$	9	6.02	9.23	[55]
$(C_2H_5)_4NBr$	12	2.97	3.96	[55]
$(C_2H_5)_4NI$	1.9	1.35	4.77	[55]
$(C_2H_5)_4NF$	5.5	16.12	2.75	[56]
$(C_2H_5)_4NCH_3SO_3$	4	1.13	1.27	[50]
$(C_3H_7)_4N Cl$	18	3.39	3.53	[55]
$(C_3H_7)_4N I$	0.5	0.47	0.87	[55]
$(C_4H_9)_4N Br$	27	3.01	0.19	[55]
$(C_4H_9)_4N Cl$	15	4.31	1.35	[55]
$(C_4H_9)_4N F$	1.6	1.72	4.57	[56]
$(C_4H_9)_4N C_2H_5SO_3$	4	1.65	1.83	[50]
$(CH_3)_3(C_2H_4OH)NBr$	7	1.95	3.30	[57]
$(CH_3)_3(C_6H_5)NCl$	8	0.66	1.98	[57]
$(C_2H_4OH)_4NBr$	6.5	1.75	1.74	[58]
<i>HexEt</i> ₃ <i>NI</i>	2.24	1.03	1.88	[64]
<i>Me</i> ₃ <i>BuNI</i>	2.65	1.76	1.31	[65]
<i>Me</i> ₂ <i>Bu</i> ₂ <i>NI</i>	4.22	2.97	3.65	[65]
<i>HepEt</i> ₃ <i>NI</i>	3	3.31	3	[64]
<i>MeBu</i> ₃ <i>NI</i>	3.96	2.22	2.21	[65]
<i>Iso-Bu</i> ₄ <i>NBr</i>	1.05	0.87	0.97	[63]
<i>Overall</i>		2.41	2.79	

Table 5. The deviation comparison of the mean activity coefficients of quaternary ammonium salts types applying the modified nonelectrolyte UNIQUAC-NRF (MNUN) with E_ Wilson and modified Wilson [17] in water at 298.15 K.

<i>Aq.sys.</i>	<i>Max.m</i>	<i>MNUN</i> γ_{\pm}	<i>E_ Wilson</i> γ_{\pm}	<i>modified Wilson</i> γ_{\pm}	<i>Source</i>
NH_4I	7.5	0.44	0.5	0.5	[47]
$NH_4CH_3SO_3$	4	0.13	0.1	0.2	[50]
$NH_4C_2H_5SO_3$	4	0.37	0.6	0.4	[50]
$(CH_3)_4NCl$	19	4.63	2.9	6.5	[55]
$(CH_3)_4NBr$	5.5	1.12	1.5	0.4	[55]
$(CH_3)_4NI$	0.25	0.6	0.7	0.7	[55]
$(CH_3)_4NCH_3SO_3$	4	0.96	0.5	0.5	[50]
$(CH_3)_4NC_2H_5SO_3$	4	1.33	0.5	0.6	[50]
$(C_2H_5)_4NI$	1.9	1.35	1.6	1.5	[55]
$(C_2H_5)_4NNO_3$	8	2.96	4	2.2	[47]
$(C_2H_5)_4NCH_3SO_3$	4	1.13	0.7	0.8	[50]
$(C_2H_5)_4NC_2H_5SO_3$	4	1.65	0.9	1.2	[50]
$(C_3H_7)_4NCl$	18	3.39	8.1	5.2	[55]
$(C_3H_7)_4NBr$	9	4.14	6.1	2.1	[55]
$(C_3H_7)_4NI$	0.5	0.47	0.6	0.6	[55]
$(C_4H_9)_4NCl$	15	4.31	4.3	4.2	[55]
$(C_4H_9)_4NCH_3SO_3$	4	1.8	5.9	2.9	[50]
$(C_4H_9)_4NC_2H_5SO_3$	4	1.65	7.4	4.6	[50]
$(CH_3)_3(C_2H_4OH)NCl$	6	1.17	1.6	1	[57]
$(CH_3)_3(C_2H_4OH)NBr$	7	1.95	2.3	1.2	[57]
$(CH_3)_2(C_2H_4OH)(C_6H_5)NCl$	9	0.71	1.2	2	[57]
$(CH_3)_2(C_2H_4OH)(C_6H_5)NBr$	13	1.95	3.8	2.8	[57]
$(C_2H_4OH)_4NBr$	6.5	1.75	2.1	0.9	[58]
$(CH_3)_3(C_6H_5)NCl$	8	0.66	0.6	2.5	[57]
$(CH_3)_3(C_6H_5)NBr$	12	1.75	2.7	3	[57]

$[NH_4^+]_2[B_{10}H_{10}]_2$	3.5	0.94	0.5	0.5	[61]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N I_2$	4	4.22	4.2	2.5	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N (SO_2)_2$	3.5	7.39	8.1	7.9	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N SO_3-C_6H_4-SO_3$	1.2	16.45	30.3	29.7	[62]
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N Cl_2$	4.4	1.51	2	4	[62]
Overall		2.43	3.51	3.1	

Table6 .The binary adjustable parameters and deviation comparison of the mean activity coefficients of quaternary ammonium salts types applying M-N-UNIQUAC-NRF(MNUN), N-UNIQUAC-NRF(NUN), N-Wilson-NRF(NWN), N-NRTL-NRF(NNN) in water at 298.15 K.

<i>Aq.sys.</i>	<i>Max.m</i>	NUN		NWN		NNN		γ^\pm	γ^\pm	γ^\pm	γ^\pm
		<i>a12/T</i>	<i>a21/T</i>	<i>h12/T</i>	<i>h21/T</i>	λ_{12}/T	λ_{21}/T	<i>MU</i>	<i>NUN</i>	<i>NWN</i>	<i>NNN</i>
<i>NH₄Cl</i>	7.4	5.759	-	6.605	-6.822	-0.886	1.224	0.15	0.2	0.19	0.15
<i>NH₄NO₃</i>	26	7.064	-	0	-4.729	0.116	1.021	1.04	1.91	1.9	1.04
<i>NH₄ClO₃</i>	2.1	2.6	1.479	9.318	9.609	-0.929	1.644	0.64	0.69	0.75	0.65
<i>NH₄HCO₃</i>	1	5.336	2.604	13.849	11.591	1.14	2.53	0.34	0.37	0.39	0.36
<i>NH₄I</i>	7.5	2.224	0	-4.051	3.998	-0.868	0.823	0.44	1.1	0.48	0.54
<i>NH₄Br</i>	7.5	2.017	-	4.824	-3.1	-0.84	0.937	0.21	0.21	0.2	0.24
<i>NH₄SCN</i>	23	1.691	0	-3.152	-3.359	-0.677	-0.41	1.94	2.62	1.96	1.94
<i>NH₄CH₃SO₃</i>	4	2.499	-	8.229	-8.51	-0.983	1.262	0.13	0.14	0.16	0.13
<i>NH₄C₂H₅SO₃</i>	4	2.8	0.016	-4.712	-4.89	-0.998	0.75	0.37	1.03	0.39	0.38
<i>CH₃NH₃Cl</i>	7.5	2.377	1.272	-3.73	5.42	12.315	-	1.06	1.29	1.37	1.95
<i>CH₃NH₃ClO₄</i>	4	1.538	1.13	5.288	7.669	-3.152	5.991	0.82	0.85	1.02	1.01
<i>CH₃NH₃NO₃</i>	9.5	0.791	0.999	2.318	4.379	1.623	3.067	0.41	0.39	0.5	0.5
<i>(CH₃)₂NH₃Cl</i>	6.5	2.603	-	89.631	-	5.022	4.387	0.49	0.8	1.45	1.08
<i>(CH₃)₂NH₃ClO₄</i>	7.5	1.1	0.46	2.969	7.113	2.079	4.986	1.93	1.75	2.37	2.39
<i>(CH₃)₂NH₃NO₃</i>	6	1.871	-	3.893	5.179	2.753	3.618	0.32	0.93	0.44	0.44
<i>(CH₃)₃NH₃Cl</i>	15	2.97	-	-4.034	6.217	5.274	4.776	1.65	1.12	1.92	2.5
<i>(CH₃)₃NH₃ClO₄</i>	1.8	1.609	1.065	9.547	11.221	7.386	7.97	0.71	0.73	0.83	0.85
<i>(CH₃)₃NH₃NO₃</i>	8.5	2.097	0.001	-4.252	7.687	12.84	-	0.84	0.9	1.48	3.9
<i>(CH₃)₄NCl</i>	19	11.11	-	7.228	-7.922	6.183	5.386	4.63	3.11	2.61	2.61

$(CH_3)_4NBr$	5.5	2.115	1.132	-5.771	10.151	-4.054	7.119	1.12	1.37	1.8	1.87
$(CH_3)_4NI$	0.25	-0.991	-	-4.928	-	91.435	-	0.6	0.58	0.59	0.59
$(CH_3)_4NF$	7	6.321	1.458	14.423	6.239	14.424	6.239	9.19	2.39	0.75	0.75
$(CH_3)_4N NO_3$	7	6.204	-	7.002	8.243	5.02	5.748	1.48	2.91	2.56	2.61
$(CH_3)_4NCH_3SO_3$	4	3.247	-	52.015	-	13.874	-	0.96	0.68	0.6	0.56
$(CH_3)_4NC_2H_5SO_3$	4	3.151	-	13.554	-	9.746	-7.471	0.63	0.54	0.55	0.55
$(C_2H_5)_4NCl$	9	7.97	2.57	13.038	10.264	9.663	7.066	5.41	1.91	1.31	1.33
$(C_2H_5)_4NBr$	12	4.164	2.537	9.272	10.15	-4.565	8.261	2.37	1.05	4.33	3.18
$(C_2H_5)_4NI$	1.9	-1.139	2.704	-7.765	15.278	12.659	10.219	1.2	1.07	1.72	1.97
$(C_2H_5)_4NF$	5.5	50	2.864	21.507	7.432	21.508	7.433	14.39	4.16	3.7	3.7
$(C_2H_5)_4N NO_3$	8	-1.13	2.954	7.292	10.455	-3.825	7.929	2.78	1.91	5.56	5.33
$(C_2H_5)_4NCH_3SO_3$	4	5.033	1.303	99.846	-	8.672	4.98	1.12	0.52	1.25	0.49
$(C_2H_5)_4NC_2H_5SO_3$	4	6.606	1.538	-7.968	11.275	9.363	4.972	1.46	0.72	0.77	0.71
$(C_3H_7)_4N Cl$	18	4.568	0.816	9.393	4.861	6.763	3.178	6.41	12.0	11.4	11.5
$(C_3H_7)_4N NF$	5	31.47	2.611	29.861	10.707	25.292	7.362	14.85	2.21	2.21	2.31
$(C_3H_7)_4N Br$	9	-1.055	2.859	29.873	18.065	29.743	13.095	4.23	0.46	0.56	0.58
$(C_3H_7)_4N I$	0.5	-1.378	2.784	-6.952	12.518	-4.739	8.486	0.45	2.36	7.84	8.24
$(C_4H_9)_4N F$	1.6	12.89	-	-8.401	1.294	79.077	-	1.72	1.81	1.66	1.9
$(C_4H_9)_4N Cl$	15	2.352	-1.55	6.298	-6.168	42.424	-	4.31	4.2	4.14	4.06
$(C_4H_9)_4N Br$	27	-0.014	1.516	0	7.464	0	5.267	3.01	3.01	3.87	4.03
$(C_4H_9)_4N CH_3SO_3$	4	-1.095	-0.81	-5.408	-	-5.431	-	1.8	1.8	1.45	1.38
$(C_4H_9)_4N C_2H_5SO_3$	4	-1.271	-	-5.878	-	-5.74	-14.51	1.88	1.79	1.14	1.3
$(CH_3)_3(C_6H_5)NCl$	8	2.196	1.301	7.788	9.988	5.621	6.977	0.66	0.58	1.69	1.83
$(CH_3)_3(C_6H_5)NBr$	12	1.37	1.4	-3.846	10.761	-2.66	7.519	1.75	1.69	5.15	5.43
$(CH_3)_2(C_2H_4OH)(C_6H_5)NBr$	13	-1.475	2.04	-4.881	10.358	4.425	6.743	1.95	2.51	2.28	2.75
$(CH_3)_3(C_2H_4OH)NBr$	7	2.572	1.629	9.256	8.974	6.625	6.163	1.95	1.64	2.42	2.48
$(CH_3)_2(C_2H_4OH)(C_6H_5)NCl$	9	2.467	0	3.509	10.344	-2.059	7.316	0.71	12.7	6.75	6.87
$(CH_3)_3(C_2H_4OH)NCl$	6	-1.023	1.88	7.422	9	-3.92	7.12	1.17	1.32	3.18	3.02
$(C_2H_4OH)_4NF$	6.5	-1.64	2.388	5.954	4.016	14.255	-	0.49	5.03	0.53	0.94
$(C_2H_4OH)_4NBr$	6.5	2.875	0.001	-3.634	7.086	-3.635	7.063	1.75	8.37	2.72	2.72
$(t-C_4H_9)NH_3Cl$	7	-1.357	1.84	4.491	4.013	4.476	-5.071	1.28	0.21	1.27	1.35
$[NH_4^+]_2[SO_4]_2$	4	3.331	1.983	-5.019	8.973	-3.522	6.294	1.4	1.56	1.87	1.91
$[NH_4^+]_2[B_{10}H_{10}]_2$	3.5	-1.639	2.273	-6.25	-11.75	-4.32	-8.14	1.97	2.45	1.52	1.54
$(CH_3)_3N+-CH_2-CH_2-(CH_3)_3N I_2$	4	-0.895	2.121	-6.209	12.86	-4.358	9.003	4.22	3.71	5.97	6.24

$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N (SO_2)_2$	3.5	-1.835	-	-8.985	-	-6.4	-9.53	7.39	16.4	7.95	8
			7.252		12.291				3		
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N SO_3^-C_6H_4-$ SO_3	1.2	12.23	2.82	-13.887	-	-	-133.4	16.45	7.31	21.6	18.2
					80.061	11.365				9	8
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N SO_3^-C_6H_4-$ $CH_2-CH_2-C_6H_4-SO_3$	0.2	2.106	1.384	197.41	21.757	196.02	21.72	6.39	1.58	7.04	7.08
				3							
$(CH_3)_3N^+-CH_2-CH_2-(CH_3)_3N Cl_2$	4.4	-1.403	0	11.67	10.4	8.644	7.234	1.51	16.1	3.01	3.18
									7		
<i>Overall</i>								2.66	2.68	2.72	2.72

As observed in Table 3, the comparison among the results of the correlations of the mean activity coefficient of 57 quaternary ammonium salt types through this and available models, including E-NRTL [19] and Pitzer [24] indicates that the present model outperforms the E-NRTL [19] model. The Pitzer [24] and E-NRTL [19] models are more complicated than the modified nonelectrolyte UNIQUAC-NRF model. The Pitzer [24] and E-NRTL [19] models have three adjusted parameters, while the proposed model has two. Note that, parameters of new model were determined here applying the same data sets, as were applied for the Pitzer and E-NRTL models. There are also parameter values for the E-NRTL [19] and Pitzer [24] models available in the literature [19,24]. In these context for the 57 salt types, Table3, the total parameter fitted through models E-NRTL [19], Pitzer [24] and nonelectrolyte UNIQUAC-NRF are 171,171 and 114, respectively. As observed in table 4, the %AARD of this new model with two adjustable parameters for 34 salt types is 2.44, while the same for the Extended UNIQUAC model [21] with four adjustable parameters is 2.79. For Extended UNIQUAC model [22] the structural parameters(r and q)parameters are among the adjustable parameters, while in this newly proposed model, they are constant, indicating that for the 34 salt types, table 4, the fitted parameters through model nonelectrolyte UNIQUAC-NRF is 67 and through model Extended UNIQUAC is more than 100.The mean activity correlation coefficients for 32 electrolytes through modified nonelectrolyte UNIQUAC-NRF and compared with models like modified Wilson and E-Wilson [17] are tabulated in Table 5, where, as it was observed this proposed model is more reliable. Note that the fitted parameters count in the three models is the same. This model's advantage is that applying only two adjustable parameters without applying any additional parameters or mixing rules, so no extra parameters are needed to predict the osmotic coefficient of aqueous electrolytes. This model is particular in estimating salt solubility when there is insufficient experimental data to calculate the solubility of two salt types

with high accuracy by applying only binary adjustable parameters. The binary adjustable parameters due to the mean ionic activity coefficient regression of N-Wilson-NRF, N-UNIQUAC-NRF and N-NRTL-NRF are tabulated in Table 6. As can be observed in this table, accuracy of the mean activity coefficient of the M-N-UNIQUAC-NRF model is better than NRF models for the systems. Note that the fitted parameters count in the three models is the same. Table 7 shows standard deviation and the binary adjustable parameters for the new model correspond with the experiments [66-67] for each electrolyte systems.

Table 7. The deviation comparison and binary adjustable parameters of mean activity coefficients of several aqueous strong electrolyte solutions applying the N-UNIQUAC-NRF(NUN) [30] and M-N-UNIQUAC-NRF(MNUN).

<i>Aq.sys</i>	<i>Max.m</i>	<i>a12/T</i>	<i>a12/T</i>	<i>MNUN</i>		<i>NUN</i>	
				γ_{\pm}	γ_{\pm}	ϕ	ϕ
<i>NaCl</i>	6.144	-1.454	2.212	1.263	0.807	0.950	0.536
<i>NaNO₃</i>	1083	-0.694	1.333	3.262	3.926	3.133	3.452
<i>NaAc</i>	3.5	-1.3	1.61	0.517	0.854	0.393	0.598
<i>NaI</i>	3.5	-1.35	1.812	0.837	0.671	0.628	0.487
<i>Na₂SO₄</i>	4	-0.922	1.481	1.4308	2.162	1.779	2.674
<i>NaF</i>	1	-0.607	-0.9	0.0651	0.066	0.065	0.066
<i>LiOH</i>	5	-1.73	3.411	1.369	1.669	1.415	1.673
<i>LiAc</i>	4	-1.28	1.701	0.392	0.573	0.307	0.321
<i>LiI</i>	3	-1.538	1.994	1.928	1.937	1.399	1.293
<i>Li₂SO₄</i>	3	-1.175	1.463	1.498	1.405	1.643	1.488
<i>KCl</i>	5	-1.04	1.563	0.209	0.604	0.198	0.445
<i>KBr</i>	55	-1.022	1.445	0.608	0.596	0.213	0.211
<i>KNO₃</i>	3.5	0.695	1.796	0.477	0.599	0.477	0.700
<i>Kac</i>	3.5	-1.293	1.648	0.573	1.063	0.442	0.597
<i>Ki</i>	4.5	-1.009	1.186	0.373	1.281	0.244	0.791
<i>K₂SO₄</i>	0.7	-1.035	1.833	0.517	0.627	0.940	1.174
<i>KF</i>	6	-1.646	2.595	0.838	0.700	0.677	0.465
<i>Ca(NO₃)₂</i>	5	-1.518	1.991	3.419	3.623	2.831	2.050
<i>MgAc₂</i>	4	-1.374	2.007	0.744	0.661	0.814	0.698
<i>Mg₂(SO₄)₂</i>	3	-1.581	2.747	3.076	3.375	9.441	9.534
<i>RbCl</i>	7.8	-0.983	1.616	0.249	1.817	0.201	1.021
<i>RbBr</i>	5	-0.888	1.43	0.247	1.050	0.208	0.594
<i>RbNO₃</i>	4.5	0.439	1.859	0.611	0.818	0.716	1.182
<i>Rbac</i>	3.5	-1.287	1.662	0.551	0.930	0.435	0.508
<i>Rbi</i>	5	-0.915	1.381	0.247	0.924	0.225	0.461
<i>Rb₂SO₄</i>	1.8	-0.727	0.864	0.602	0.695	0.729	0.934
<i>CsCl</i>	11	-0.872	1.656	0.641	0.744	0.504	0.507
<i>CsBr</i>	5	-0.842	1.618	0.381	2.653	0.370	1.805
<i>CsNO₃</i>	1.5	-0.565	2.09	0.137	0.142	0.154	0.167
<i>Csac</i>	3.5	-1.22	1.546	0.494	1.082	0.335	0.597
<i>Csi</i>	3	-0.757	1.353	0.554	1.129	0.550	0.728
<i>Cs₂SO₄</i>	1.8	-0.666	0.516	0.621	0.642	0.669	0.838
<i>NH₄Cl</i>	7.405	-0.883	1.214	0.145	0.227	0.135	0.176

NH_4NO_3	25.954	0.161	1.02	1.025	1.880	0.880	1.649
NH_4SO_4	4	-0.82	1.538	1.398	1.699	1.941	2.499
HNO_3	28	-1.616	2.386	2.409	5.490	1.454	2.480
$BaCl_2$	1.8	-1.503	-3.228	1.5	1.544	1.567	1.573
$BaBr_2$	2	-1.525	1.715	1.873	3.345	1.765	2.352
$Ba(NO_3)_2$	4	0.139	1.949	0.558	0.580	0.857	0.914
$BaAc_2$	3.5	-1.264	-2.973	1.222	1.626	1.425	1.856
BaI_2	2	-1.656	2.237	2.725	3.004	2.396	2.203
$Al_2(SO_4)_3$	1	-1.712	2.167	5.19	5.813	11.256	13.134
$CrCl_3$	1.2	-2.009	1.81	3.639	3.828	3.627	3.813
$Cr(NO_3)_3$	1.4	-1.908	-0.417	3.78	3.972	3.454	3.699
$Cr_2(SO_4)_3$	1.2	-1.694	-2.935	9.663	9.705	19.395	19.515
Overall				1.419	1.834	1.850	2.099

As one can observe, the newly modified model results of these systems are better than that of the nonelectrolyte UNIQUAC-NRF model [30]. The results of simple ammonium salt types are tabulated in Table 3 and diagrammed in Fig. (1).

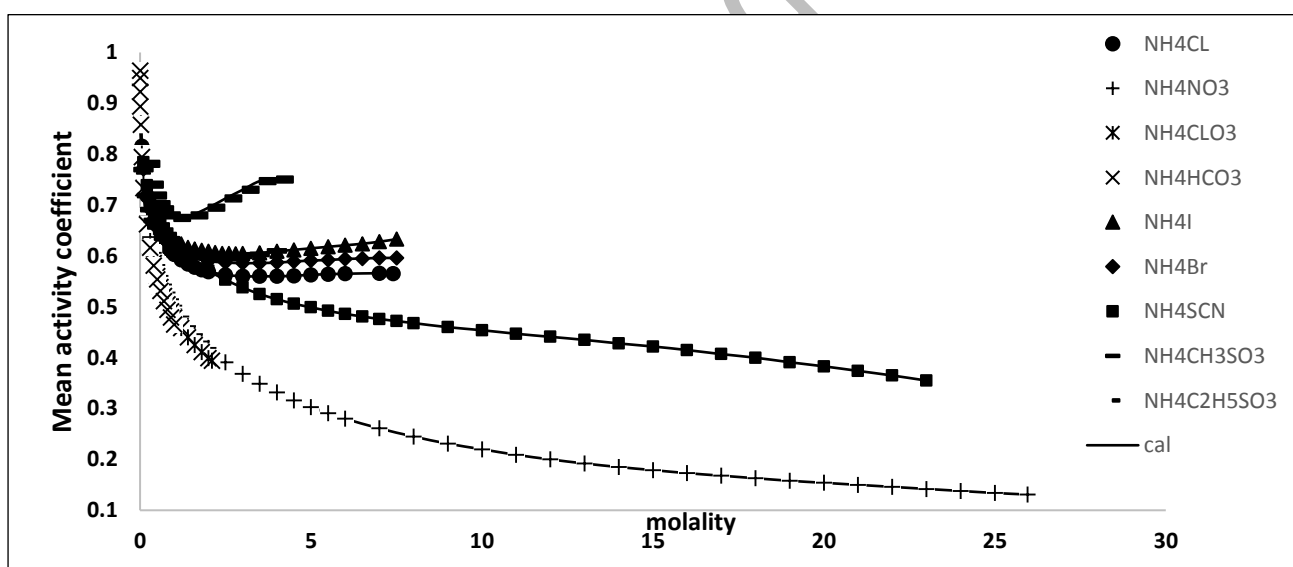


Fig. 1. The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

The modified nonelectrolyte UNIQUAC-NRF model is practical in correlating the experiment. The newly introduced model with two adjustable parameters provides a correlation almost as well as the three-parameter Pitzer and the E_NRTL models. The data are available at concentrations up to 26 molal at the most and the modified nonelectrolyte UNIQUAC-NRF model can be practically adopted in the experimental data over the entire composition range. The details of Methylammonium salt types are shown in Fig. (2), and are tabulated in Table 3.

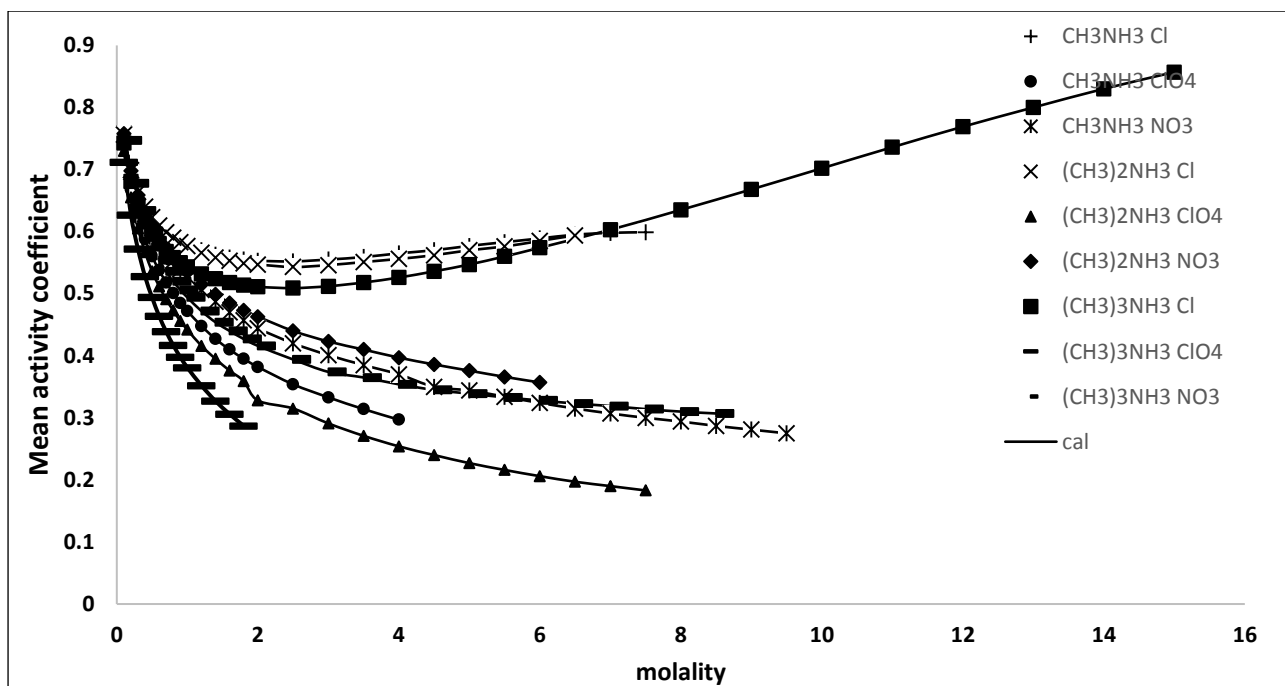


Fig. 2. The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K .

The tetramethyl, tetraethyl, tetrapropyl and tetrabutyl ammonium salt types are shown in Figs. (3-5), and tabulated in Table 3, respectively.

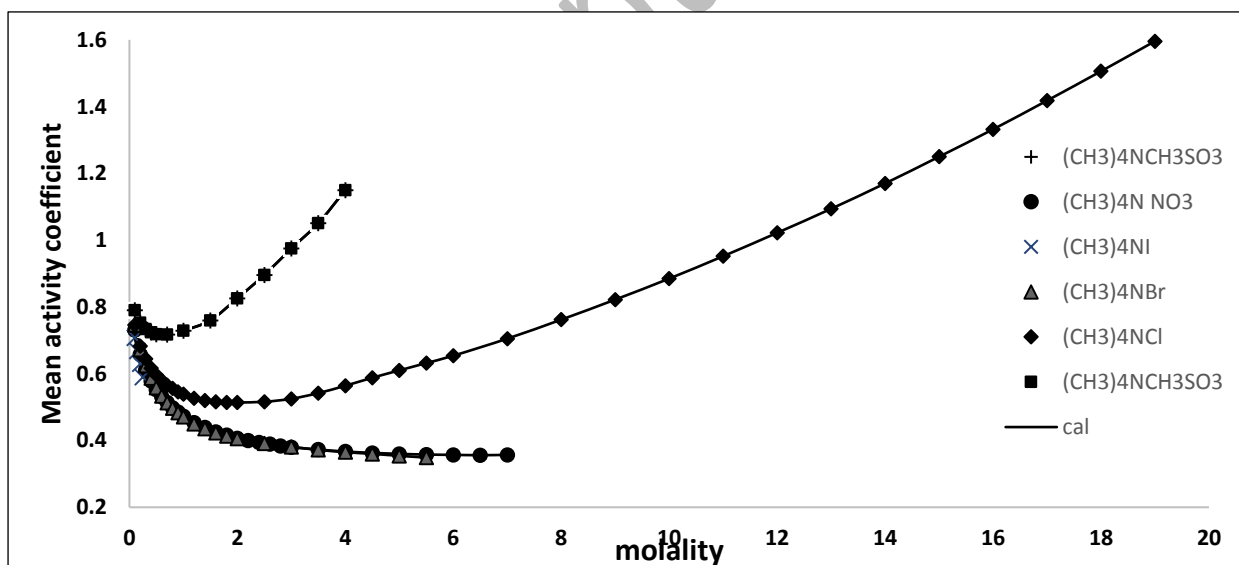


Fig. 3. The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

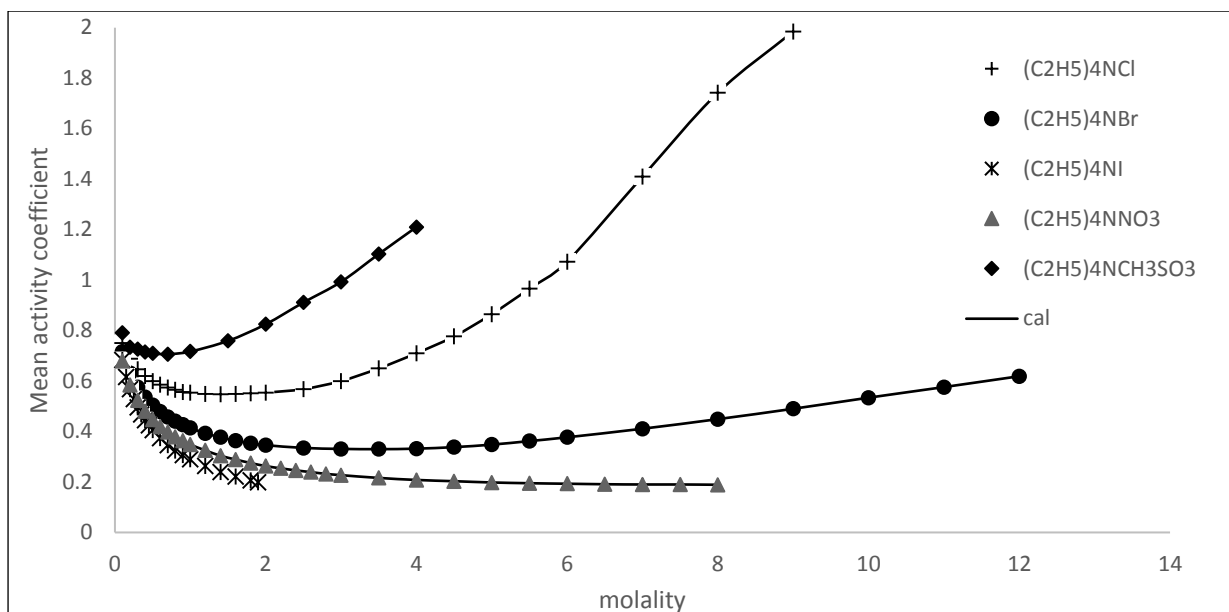


Fig. 4 The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

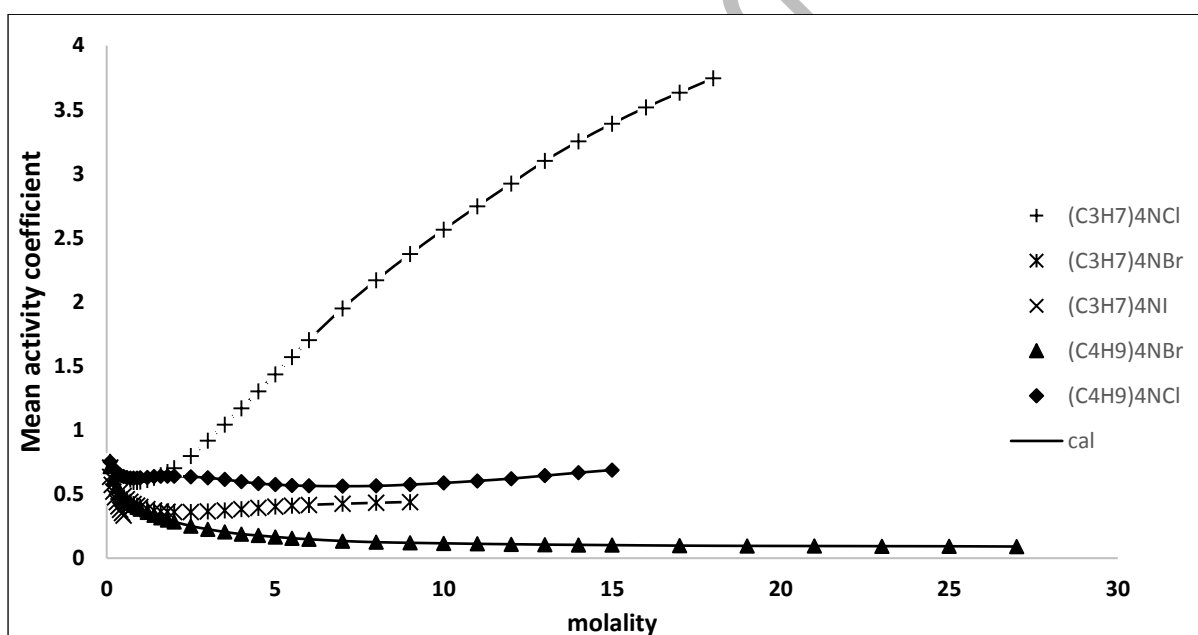


Fig. 5. The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

The highest concentration for which data is available for each salt type is tabulated in Table 3. For common ammonium salt types, their mean activity coefficients in water are produced by the modified nonelectrolyte UNIQUAC-NRF model. Some of the quaternary ammonium salt types like tetramethyl and tetraethyl ammonium fluoride have activity coefficients higher than unity, one can determine the considerable difference between the model and the experimental data at higher molality. The same holds for tetramethyl ammonium chloride ($[(\text{CH}_3)_4\text{N}^+][\text{Cl}^-]$). Some of the many quaternary ammonium salt types containing ethoxy and benzyl substituents are shown in Figs. (6 and 7), are tabulated in Table 3.

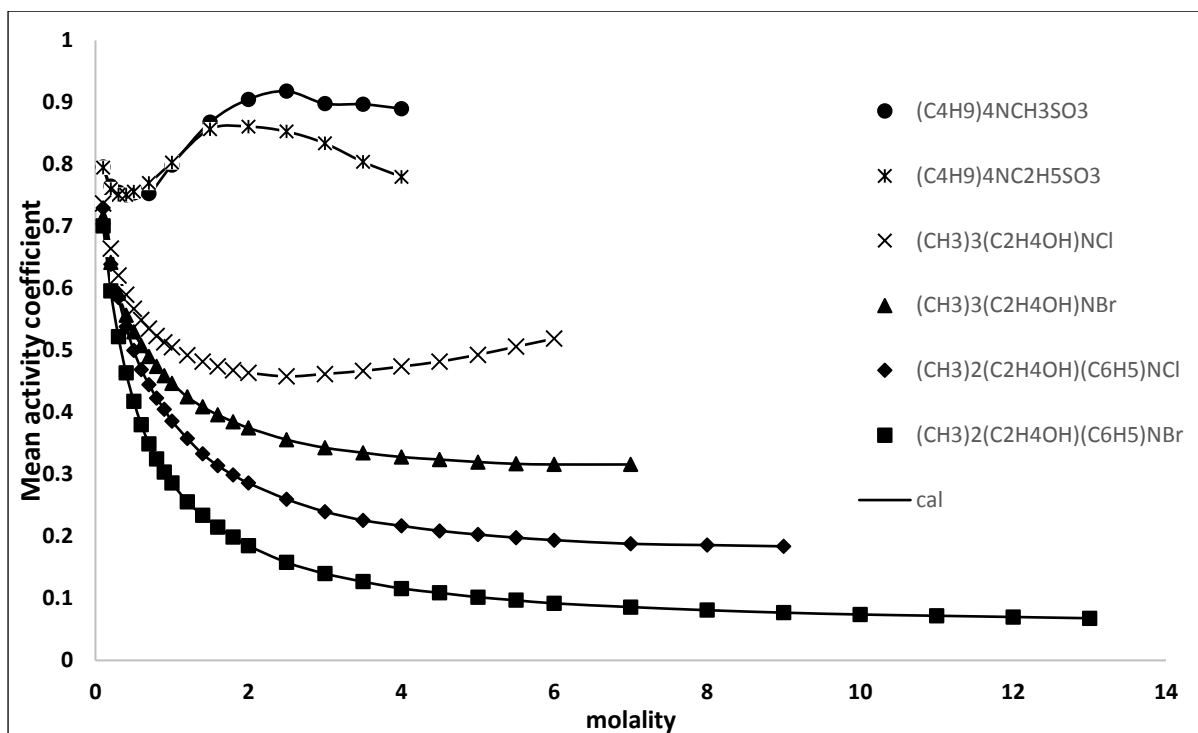


Fig. 6. The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

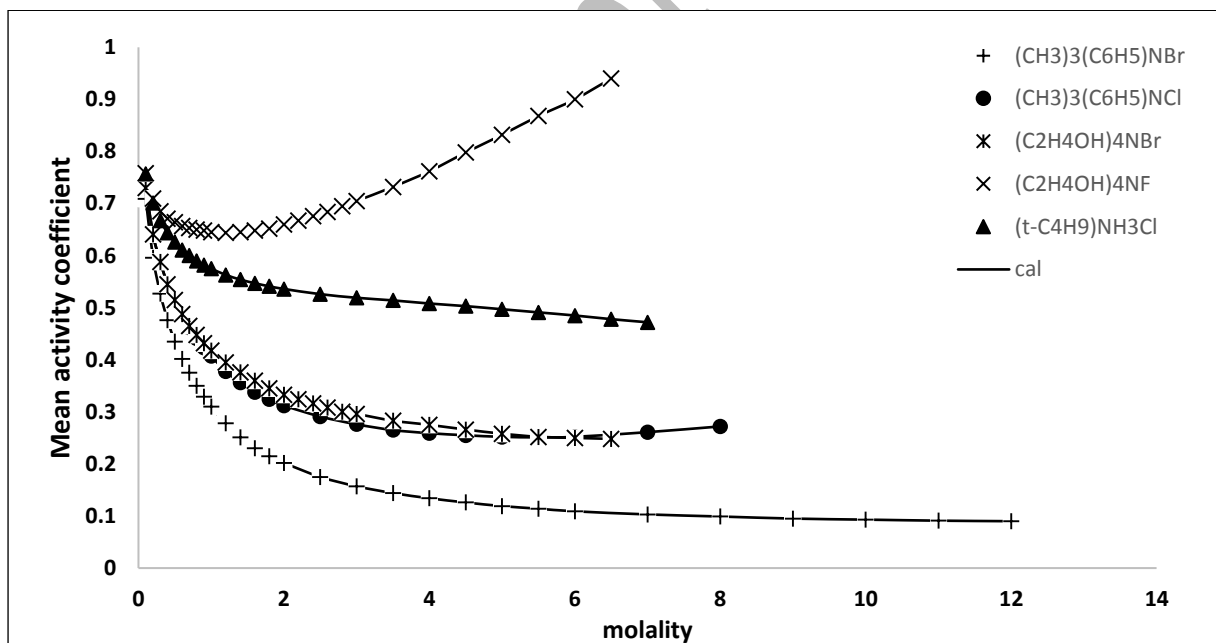


Fig. 7. The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

Just like the case of the common quaternary ammonium salt types, the modified nonelectrolyte UNIQUAC-NRF model is appropriate for modeling these systems. Some ammonium salt types containing divalent anions and divalent cations are shown in Fig. (8) and tabulated in Table 3, where many of the divalent cations are dimers, where two singly charged quaternary ammonium cations share an alkyl chain.

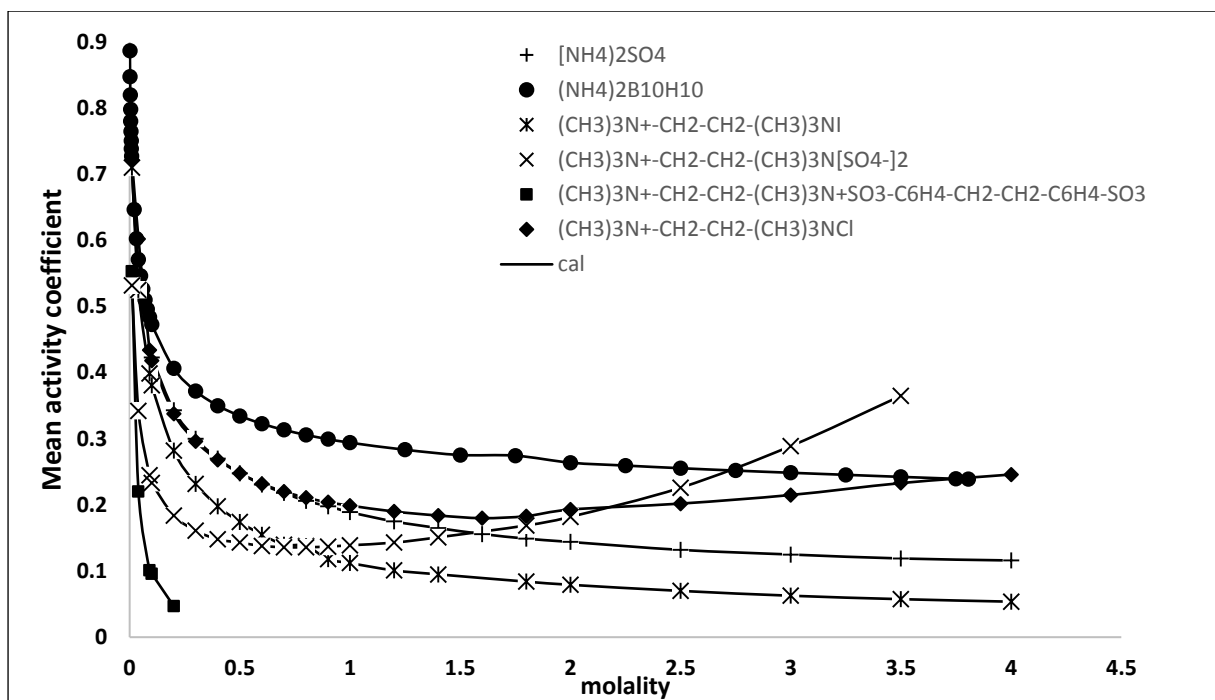


Fig. 8. The new model's correlation results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

Though the modified nonelectrolyte UNIQUAC-NRF model is proper for the common ammonium salt types with fluoride anions ($(\text{CH}_3)_4\text{NF}$, $(\text{C}_2\text{H}_5)_4\text{NF}$ and $(\text{C}_3\text{H}_7)_4\text{NF}$), it cannot represent the thermodynamic behavior for the salt types with divalent cations and is weak in the case of benzyldisulfonate anion. These data are shown in solid squares, Fig. (8), and the weak model is shown in a solid line with a sharp minimum and termination at molality of 1.2. The creation of $(\text{CH}_3)_3\text{-N}^+\text{-CH}_2\text{-CH}_2\text{-N}^+\text{-(CH}_3)_3$ micelles in solution, which is not consistent with this model, could be the explanation of this event. The two negative charges of the aromatic sulfonate anions are directly related to their potentially unique behavior, as they are far more separated than those of a smaller divalent anion such as SO_4 . The osmotic coefficient of salt types at different molalities is predicted at 298.15K. There exist agreements between new model predictions (applying only the binary parameters, Table 1) and experimental data, Figs. (9 and 10).

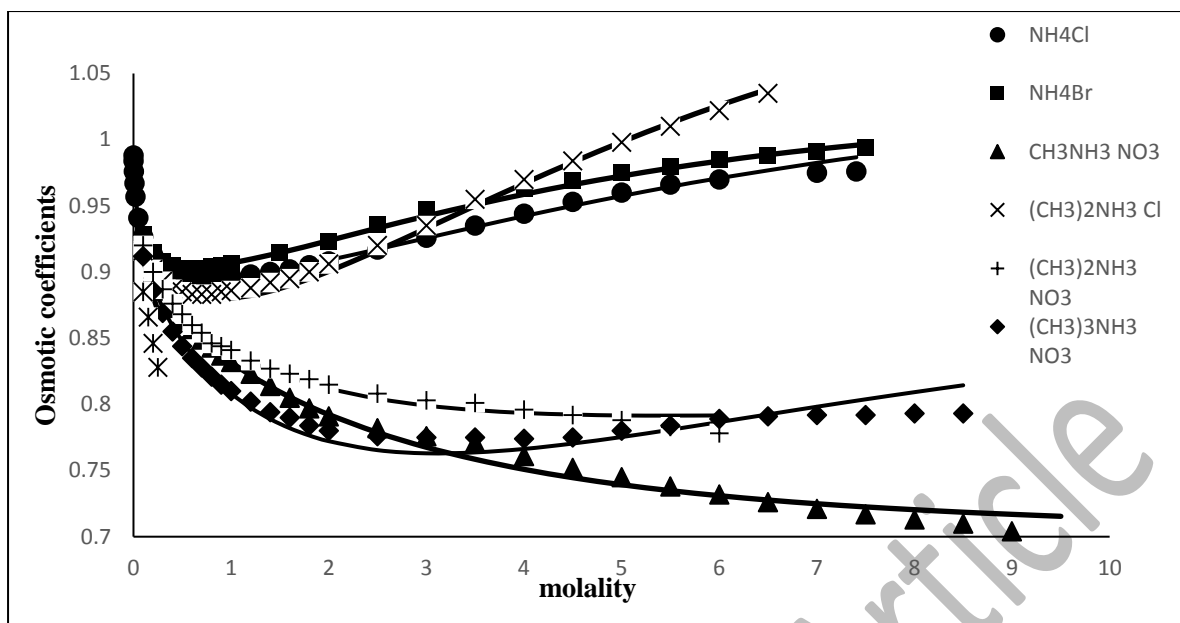


Fig. 9. The new model's prediction results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

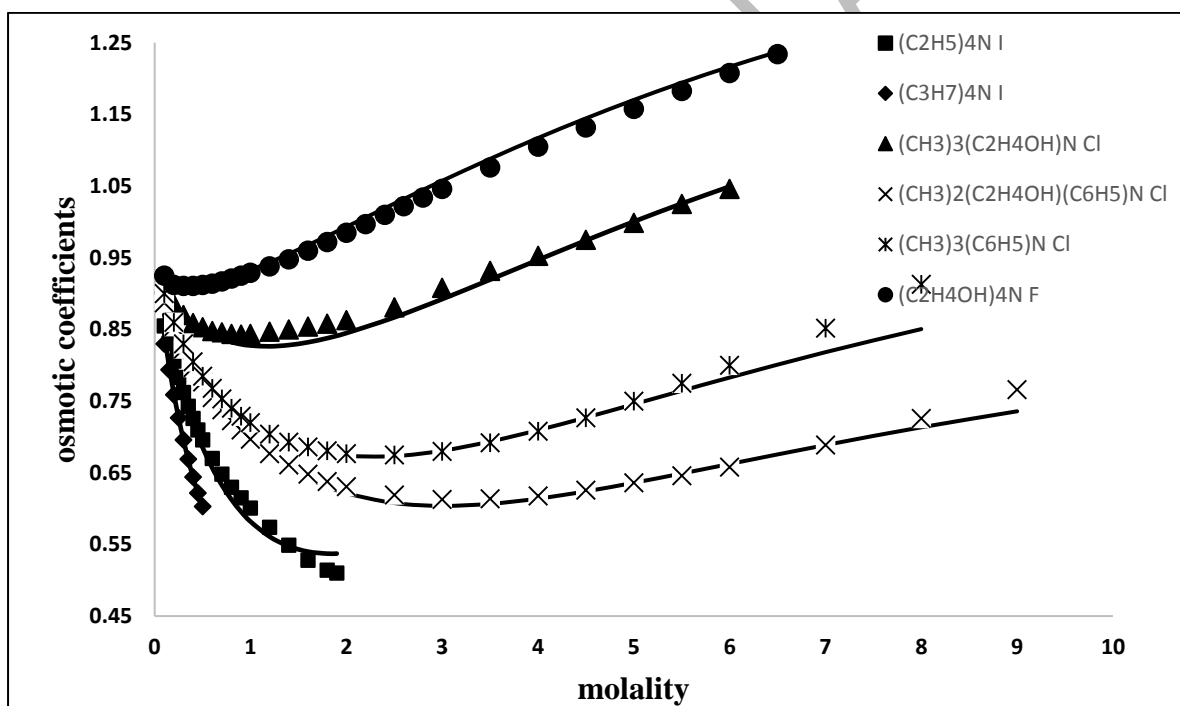


Fig. 10. The new model's prediction results and experimental mean activity coefficients for some quaternary ammonium salts types in water at 298.15 K.

This modified nonelectrolyte UNIQUAC-NRF model with volume and surface area fractions yields more acceptable results than E-Wilson and modified Wilson, Extended UNIQUAC, and NRTL models. This M-N-UNIQUAC-NRF model can be reduced to a basic UNIQUAC model without electrolytes, indicating that the mixed solvent systems apply UNIQUAC parameters. The mean activity coefficient for the ternary aqueous system (RbCl - H₂O - CH₃OH and NaCl - H₂O - CH₃OH) is correlated. The binary adjustable parameters of salt-water are tabulated in Table 7, while, the binary adjustable parameters of Metanol-Salt (RbCl-Metanol(-256.12), Metanol - RbCl(1111.75), NaCl-Metanol(-500.68) and Metanol -NaCl(728.58)) and Metanol -Water (-72.58), Water-Metanol (5.46) are correlated through the fitting of available mean activity coefficients [68-69]. The mean activity

coefficients of the ternary aqueous system RbCl - H₂O- CH₃OH and NaCl - H₂O-Ch₃OH are compared with the literature data and shown in Figs. (11-12). The obtained results correspond to the experimental data at 298.15 K.

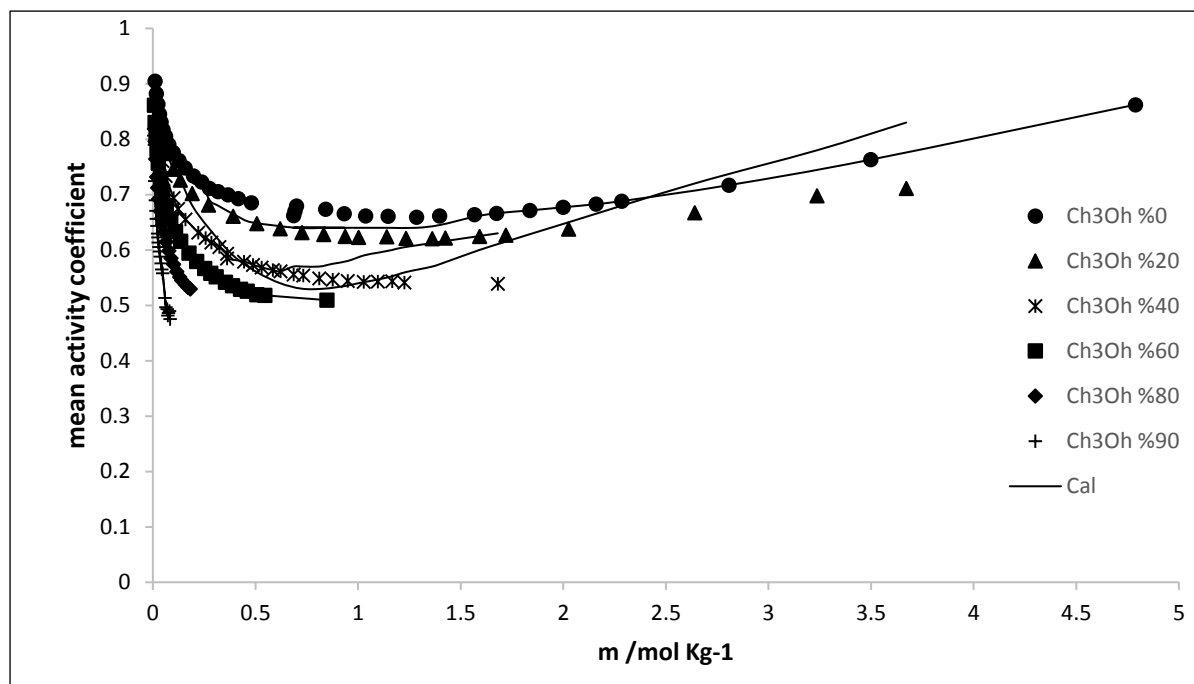


Fig. 11. The new model's correlation results and experimental mean activity coefficients for methanol-water-NaCl system at 298.15K.

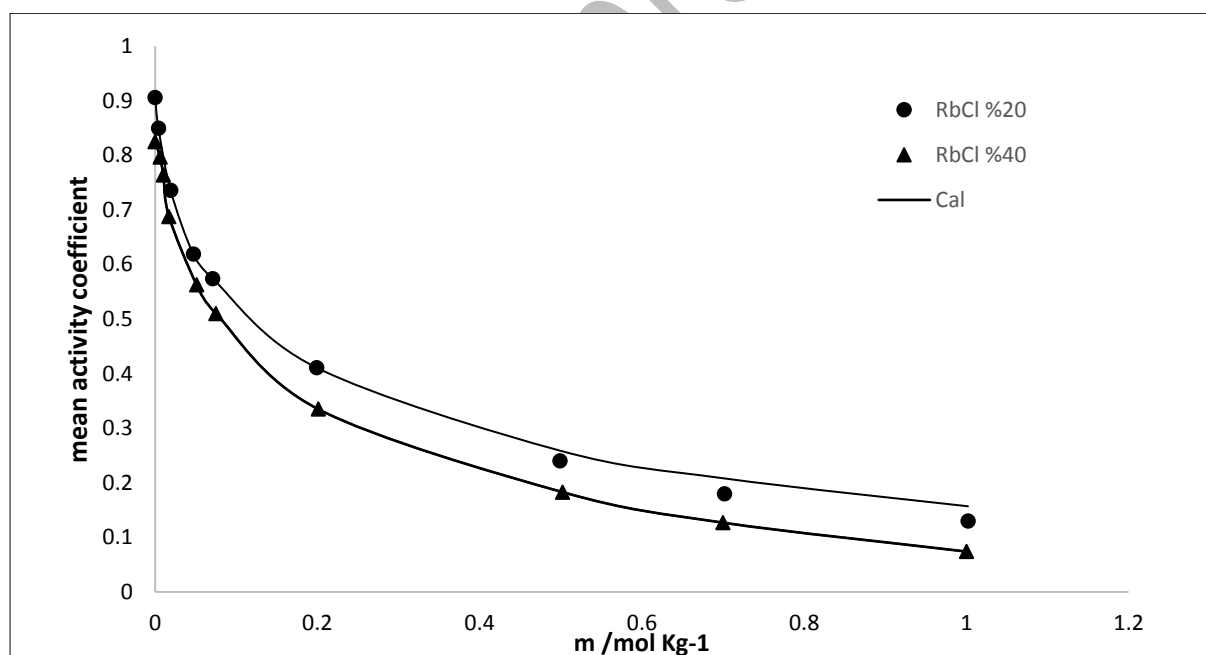


Fig. 12. The new model's correlation results and experimental mean activity coefficients for methanol-water-RbCl system at 298.15K.

5-Conclusion

The nonelectrolyte local composition UNIQUAC-NRF model is modified and developed for aqueous quaternary ammonium salt types in this study. The activity and osmotic coefficients of aqueous strong electrolyte solutions at 298.15 K and 1bar are represented by the summation of Pitzer-Debye-Hückel as the long-range and modified

nonelectrolyte- UNIQUAC-NRF as the short-range contributions. The mean activity coefficients for each binary aqueous quaternary ammonium salt are correlated to provide the two binary adjustable parameters for the current model. The modified nonelectrolyte UNIQUAC-NRF model with volume and surface area fractions yields more accurate results than E-Wilson, modified Wilson, and E-NRTL. The %AARD of the mean activity coefficients for 30 quaternary ammonium salt types of 3.1 and 3.54 (are obtained) through the E-Wilson and modified Wilson models, respectively, while in this study, the same is 2.43. The %AARD percentage is 2.81 for 52 quaternary ammonium salt types by applying the E-NRTL model, while in this study, the same is 2.59. The %AARD of the modified nonelectrolyte- UNIQUAC-NRF model with two adjustable parameters for 34 salt types is 1.41, while the same for the Extended UNIQUAC model with four adjustable parameters is 2.79. The three nonelectrolyte models of NRTL-NRF, Wilson-NRF, and UNIQUAC-NRF are used to correlate the aqueous quaternary ammonium salt mean activity coefficient. That the M-N-UNIQUAC-NRF model with volume and surface area fractions is more accurate than the mentioned models is evident. The comparison between the findings of this model and the nonelectrolyte- UNIQUAC-NRF model reveals that this newly proposed model is applicable for strong aqueous electrolyte solutions at 298.15K and 1 bar with high accuracy. It is found that by using only binary parameters and without any fitting parameters, the modified nonelectrolyte-UNIQUAC-NRF model can predict the osmotic coefficient of the aqueous quaternary ammonium salt types. The mean activity coefficient for methanol-water-salt systems is highly correlated at 298.15 K when the binary adjustable parameters are applied. The main advantage of this model is that, in the absence of salt or ions, it may be reduced to the original UNIQUAC model.

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