

A Nonextensive Electrolyte UNIQUAC Model for Prediction of Mean Activity Coefficients of Binary Electrolyte Solutions

H. Rezaei^a, S. Abdolrahimi^b, G.R. Pazuki^{b,*} and A.A. Rohani^c

^aChemical Engineering Department, Islamic Azad University, Shahrood Branch, Iran

^bChemical Engineering Department, Amirkabir University of Technology, (Tehran Polytechnic), Tehran, Iran

^cRefining Technology Development Division, Research Institute of Petroleum Industry, National Iranian Oil Company, Tehran, Iran

(Received 22 June 2018, Accepted 10 September 2018)

In this work, an electrolyte-UNIQUAC model was developed by replacement of Boltzmann weight binary interaction parameters by the nonextensive Tsallis weight. A summation of the long-range electrostatic term (Debye-Huckel equation) and a short-range interaction term were considered in the calculation of thermodynamic properties. A framework proposed by Chen *et al.* was employed for the derivation of the local mole fractions. Application of the nonextensive theory increased the degree of freedom of the present model (T-E-UNIQUAC). Furthermore, the strength of the model lies in its ability to calculate individual activity coefficients of ions. The applicability of the T-E-UNIQUAC model were tested using aqueous electrolyte solutions, and subsequently, results were compared with Messnaoui, Chen and Pitzer models.

Keywords: Electrolyte solutions, Activity coefficient, Tsallis weight

INTRODUCTION

The Boltzmann-Gibbs statistical mechanics (BG) is not applicable to systems that are not in the thermodynamic limit. This is due to the finite size of the system, the existence of long-range interactions, and the presence of dissipative structures [1]. Nonextensive statistical thermodynamics proposes a new formalism for characterisation of the systems which are not properly described by Boltzmann-Gibbs statistical mechanics. Tsallis introduced the concept of nonextensive entropy as [2-7],

$$S_q = k \frac{1 - \sum_{i=1}^W p_i^q}{q-1}, \quad \sum_{i=1}^W p_i = 1 \quad (1)$$

where p_i is the probability of the microscopic state i , W is the total number of microstates, q is the entropic index,

and k is a positive constant. The entropic index q is a measure of the degree of nonextensivity in the system explained by the following pseudoadditivity rule:

$$S_q(A+B) = S_q(A) + S_q(B) + \frac{1-q}{k} S_q(A)S_q(B) \quad (2)$$

In this equation systems A and B are independent variables, and $S_q \geq 0$. Consequently, superextensivity, extensivity, and subextensivity are the cases related to $q < 1$, $q = 1$, and $q > 1$, respectively. In the limit $q \rightarrow 1$ of the Eqs. (1) and (2), the Boltzmann-Gibbs entropy and extensivity rule are respectively recovered as:

$$S_{BG} \equiv S_1 = -k_B \sum_{i=1}^W p_i \ln p_i, \quad (3)$$

$$S(A+B) = S(A) + S(B), \quad (4)$$

where k_B is Boltzmann's constant. It is worthwhile

*Corresponding author. E-mail: ghpazuki@aut.ac.ir

mentioning that the constant, k , in Eq. (1) differs from k_B , but in the limit $q = 1$, it reduces to $k_B = k$. In the microcanonical ensemble, the probability of all microstates are equal and, thus $p_i = 1/W$. This concept simplifies Tsallis' entropy to

$$S_q = k \ln_q W \quad (5)$$

where \ln_q is q-logarithm defined as $\ln_q x \equiv \frac{x^{1-q} - 1}{1-q}$ [8].

It is reasonable to introduce the inverse function of q-exponential as

$$\exp_q(x) = e_q^x \equiv \begin{cases} [1 + (1-q)x]^{1/(1-q)} & \text{if } [1 + (1-q)x] > 0 \\ 0 & \text{if } [1 + (1-q)x] \leq 0 \end{cases} \quad (6)$$

Boltzmann weight displays exponential tails while Tsallis weight presents power law tails which is long-lasting and vanishing for $q > 1$ and $q < 1$, respectively. A new concept of nondistributive q-deformed algebra has been introduced based on the q-exponential and q-logarithm functions [9, 10]. Furthermore, reading for comprehension of some properties of q-functions and q-algebra is recommended at [11-14], and references therein.

In other words, the extensivity (additivity) and intensivity concepts in thermodynamics are applied to the homogeneous systems with weak interactions, and the thermodynamic limit of $(N, V) \rightarrow \infty$ or $N/V = \text{finite}$. The notion of nonextensive statistical mechanics was introduced to overcome the limitations of Boltzmann-Gibbs statistical mechanics. This formalism is suitable for the study of the systems with long-range interactions as well as small systems, or systems with complex behavior, including nanosystems [15].

Some research studies have validated the application of Tsallis' entropy to complex systems. Cohen has successfully related the microscopic dynamics to the entropic index [16]. In another research, conducted by García-Morales and Pellicer [17], fractal phase space systems have been studied, and the entropic index has been referred to the fractal dimensions of the available phase space. Consequently,

Tsallis' entropy has found its platform in modern statistical mechanics.

Souza *et al.* replaced the ordinary product by a new nonquadratic mixing rule between species by means of the q-product of mole fractions [18]. They applied q-product for generalization of van der Waals mixing rules, and validated their proposal by evaluating vapor-liquid equilibrium at different temperatures.

In this study, the nonextensive Tsallis weight is applied rather than Boltzmann weight, and thus, nonextensive statistical mechanics propose a theoretical basis for derivation of the UNIQUAC model for electrolyte solutions. On this account, the Gibbs free energy of electrolyte solutions has been developed based on Tsallis entropy function.

Thermodynamic Model

The basis of the present thermodynamic model is the modification of the original UNIQUAC model [19] by addition of Debye-Huckel term and replacement of Boltzmann weight by the nonextensive Tsallis weight. Consequently, the proposed model has three fundamental terms: a combinatorial or entropic term, a residual or enthalpic term, and an electrostatic term. As a result, the excess Gibbs energy consists of a long-range electrostatic term along with a short-range interaction term. The electrostatic interaction between ions is regarded in long-range term while non-electrostatic interactions are accounted in the short-range term. Moreover, this paper deals with a single completely dissociated liquid electrolyte and a single solvent. It is evident that the procedure can be generalized for multicomponent electrolyte system. The UNIQUAC model is employed to describe the short-range term, while Debye-Huckel equation depicts the long-range term,

$$\frac{g^E}{RT} = \frac{g_{DH}^E}{RT} + \frac{g_c^E}{RT} + \frac{g_{res}^E}{RT} \quad (7)$$

Thus, γ_i can be derived as:

$$\ln \gamma_i = \ln \gamma_i^{DH} + \ln \gamma_i^c + \ln \gamma_i^{res} \quad (8)$$

The Long-range Contribution

The Debye-Huckel model [20] is the fundamental model in electrolyte solutions that accounts for the long-range ion-ion interactions. The excess Gibbs energy in this model can be written as:

$$\frac{g_{DH}^E}{RT} = -x_w M_w \frac{4A}{b^3} [\ln(1+b\sqrt{I}) - b\sqrt{I} + \frac{b^2 I}{2}], \quad (9)$$

where x_w and M_w are mole fraction and molar mass of water, respectively. A and b are the Debye-Huckel parameters, and I is the ionic strength defined as:

$$I = \frac{1}{2} \sum_i z_i^2 m_i. \quad (10)$$

Consequently, partial molar differentiation of g_{DH}^E leads to activity coefficient of water,

$$\ln \gamma_w^{DH} = M_w \frac{2A}{b^3} (1+b\sqrt{I} - \frac{1}{1+b\sqrt{I}} - 2\ln(1+b\sqrt{I})). \quad (11)$$

Moreover, the activity coefficients for the ions are:

$$\ln \gamma_i^{DH} = -z_i^2 \frac{A\sqrt{I}}{1+b\sqrt{I}}. \quad (12)$$

The Short-range Contribution

Combinatorial term. Although we are dealing with an electrolyte solution, the combinatorial term is identical to the one used in the traditional UNIQUAC thermodynamic model. The combinatorial or entropic term is defined as [1]:

$$\frac{g_c^E}{RT} = \sum_i X_i \ln\left(\frac{\beta_i}{x_i}\right) - \frac{z}{2} \sum_i q_i X_i \ln\left(\frac{\beta_i}{\theta_i}\right), \quad (13)$$

where $X_i = C_i x_i$, $C_i = Z_i$ for ions, and $C_i = 1$ for solvent, z is the coordination number and is equal to 10, β_i and θ_i are volume fraction and surface area fraction of component i , respectively,

$$\beta_i = \frac{X_i r_i}{\sum_j X_j r_j}, \quad \text{and} \quad \theta_i = \frac{X_i q_i}{\sum_j X_j q_j}, \quad (14)$$

where r_i and q_i are volume and surface area parameters for component i , respectively.

Therefore, by partial molar differentiation of combinatorial excess Gibbs energy, the activity coefficients are derived as [19]

$$\ln \gamma_i^c = \ln\left(\frac{\beta_i}{X_i}\right) + 1 - \left(\frac{\beta_i}{X_i}\right) - \frac{z}{2} q_i \left[\ln\left(\frac{\beta_i}{\theta_i}\right) + 1 - \left(\frac{\beta_i}{\theta_i}\right) \right]. \quad (15)$$

Residual term

Chen *et al.* [214,22] stated the existence of three types of cells. The first type has a solvent molecule (m) as its center, while other solvent molecules, anions (a) and cations (c) are in its immediate neighborhood. For this type of cell, the local electroneutrality assumption is valid. The other two types of cells either have a central cation or anion with solvent molecules and ions of opposite charge in the immediate neighborhood. For these two cells the like-ion repulsion assumption is valid; thus no ions of like charge exist near each other (*i.e.* $\theta_{cc} = \theta_{aa} = 0$). Thus, local mole fractions can be written as:

$$\begin{aligned} \theta_{cm} + \theta_{am} + \theta_{mm} &= 1 && \text{(central solvents cells),} \\ \theta_{ma} + \theta_{ca} &= 1 && \text{(central anions cells),} \\ \theta_{mc} + \theta_{ac} &= 1 && \text{(central cations cells),} \end{aligned} \quad (16)$$

where θ_{ij} is the local surface fraction of component i around the central j molecule.

The effective local surface areas with component i as the center are given by

$$\frac{\theta_{ji}}{\theta_{ki}} = \frac{\theta_j}{\theta_k} H_{ji,ki}, \quad (17)$$

where θ_{ji} and θ_{ki} are the effective local surface area of species j and k around the central component i , respectively. $H_{ji,ki}$ is defined as:

$$H_{ji,ki} = \exp_q\left(-\frac{u_{j,ki}}{RT}\right), \quad \text{and} \quad u_{j,ki} = h_{ji} - h_{ki}, \quad (18)$$

where h_{ji} and h_{ki} are the enthalpies of interaction between $j-i$ and $k-i$, respectively, and T is the absolute temperature. Besides, we assumed that $h_{ij} = h_{ji}$ which corresponds to the fact that interaction enthalpies are symmetrical. Combination of Eqs. (16) and (17) leads to:

$$\begin{aligned} \theta_{im} &= \frac{\theta_i H_{im,mm}}{\sum_{j=m}^c \theta_j H_{jm,mm}}, \\ \theta_{ca} &= \frac{\theta_c}{\theta_c + \theta_m H_{ma,ca}}, \\ \theta_{ac} &= \frac{\theta_a}{\theta_a + \theta_m H_{mc,ac}}. \end{aligned} \quad (19)$$

In order to obtain the residual molar Gibbs energy, g_{res}^E , we relate it to the residual molar excess enthalpy, h_{res}^E with the following expression:

$$\frac{g_{res}^E}{RT} = \frac{1}{R} \int_0^{1/T} h_{res}^E d\left(\frac{1}{T}\right). \quad (20)$$

Consequently, the analytical expression for g_{res}^E is obtained as (see Appendix)

$$\begin{aligned} \frac{g_{res}^E}{RT} &= q_m X_m \frac{\theta_a}{\theta_m} \frac{1}{q-2} \left[\tau_1^{2-q} \chi_q \left(\frac{\theta_a + \frac{q_a}{\theta_c} \theta_c}{\theta_m} \tau_1 \right) - \chi_q \left(\frac{\theta_a + \frac{q_a}{\theta_c} \theta_c}{\theta_m} \right) \right] \\ &+ q_m X_m \frac{\theta_c}{\theta_m} \frac{1}{q-2} \left[\tau_2^{2-q} \chi_q \left(\frac{\theta_c + \frac{q_c}{\theta_a} \theta_a}{\theta_m} \tau_2 \right) - \chi_q \left(\frac{\theta_c + \frac{q_c}{\theta_a} \theta_a}{\theta_m} \right) \right] \\ &+ q_a Z_a X_a \frac{\theta_m}{\theta_c} \frac{1}{q-2} \left[\tau_3^{2-q} \chi_q \left(\frac{\theta_m}{\theta_c} \tau_3 \right) - \chi_q \left(\frac{\theta_m}{\theta_c} \right) \right] \\ &+ q_c Z_c X_c \frac{\theta_m}{\theta_a} \frac{1}{q-2} \left[\tau_4^{2-q} \chi_q \left(\frac{\theta_m}{\theta_a} \tau_4 \right) - \chi_q \left(\frac{\theta_m}{\theta_a} \right) \right], \end{aligned} \quad (21)$$

where $\tau_i = \exp_q \left(\frac{-c_i}{T} \right)$. Thus, it can be inferred that:

$$\tau_1 = H_{am,mm}; \quad \tau_2 = H_{cm,mm}; \quad \tau_3 = H_{ma,ca}; \quad \tau_4 = H_{mc,ac}. \quad (22)$$

It should be noted that τ_1 and τ_2 , τ_3 and τ_4 can be related to each other. It is performed by the following analysis. Local

electroneutrality assumption around solvent molecules' cell leads to

$$Z_a \theta_{am} = Z_c \theta_{cm}. \quad (23)$$

Division by θ_{mm} and replacement of Eq. (17), it results in

$$Z_a \theta_a H_{am} = Z_c \theta_c H_{cm}. \quad (24)$$

Moreover, surface area fractions, θ_a and θ_c ; can be substituted using Eq. (14). Therefore, it can be simplified to

$$Z_a n_a q_a H_{am} = Z_c n_c q_c H_{cm}. \quad (25)$$

Since, $n_a Z_a = n_c Z_c$, the above equation can be written as

$$q_a H_{am} = q_c H_{cm}. \quad (26)$$

Thus, it can be generalized to

$$H_{am,mm} = \frac{q_c}{q_a} H_{cm,mm} \Rightarrow \tau_1 = \frac{q_c}{q_a} \tau_2. \quad (27)$$

As the interaction enthalpies are symmetric, the same expression can be concluded for $H_{ma,ca}$ and $H_{mc,ac}$

$$H_{ma,ca} = \frac{q_c}{q_a} H_{mc,ac} \Rightarrow \tau_3 = \frac{q_c}{q_a} \tau_4. \quad (28)$$

Substitution of the above expressions in the excess Gibbs energy and partial differentiation can result in the activity coefficients of the species in the solutions. The result for the cation is:

$$\begin{aligned} \ln \gamma_c^{res} &= \frac{\theta_a}{\theta_m} \frac{q_a}{3-q} \left[\tau_1^{3-q} \phi_q \left(\frac{\theta_a + \frac{q_a}{\theta_c} \theta_c}{\theta_m} \tau_1 \right) - \phi_q \left(\frac{\theta_a + \frac{q_a}{\theta_c} \theta_c}{\theta_m} \right) \right] - \frac{q_c}{2-q} \left[\tau_2^{2-q} \chi_q \left(\frac{\theta_c + \frac{q_c}{\theta_a} \theta_a}{\theta_m} \tau_2 \right) - \chi_q \left(\frac{\theta_c + \frac{q_c}{\theta_a} \theta_a}{\theta_m} \right) \right] \\ &+ \frac{\theta_c}{\theta_m} \frac{q_m}{3-q} \left[\tau_3^{3-q} \phi_q \left(\frac{\theta_m}{\theta_c} \tau_3 \right) - \phi_q \left(\frac{\theta_m}{\theta_c} \right) \right] + Z_c^2 \frac{\theta_m}{\theta_c^2} \frac{q_c}{2-q} \left[\tau_3^{2-q} \chi_q \left(\frac{\theta_m}{\theta_c} \tau_3 \right) - \chi_q \left(\frac{\theta_m}{\theta_c} \right) \right] \\ &- Z_c^2 \frac{\theta_m}{\theta_c^2} \frac{q_c}{3-q} \left[\tau_3^{3-q} \phi_q \left(\frac{\theta_m}{\theta_c} \tau_3 \right) - \phi_q \left(\frac{\theta_m}{\theta_c} \right) \right] - Z_c^2 \frac{\theta_m}{\theta_a} \frac{q_c}{2-q} \left[\tau_4^{2-q} \chi_q \left(\frac{\theta_m}{\theta_a} \tau_4 \right) - \chi_q \left(\frac{\theta_m}{\theta_a} \right) \right], \end{aligned} \quad (29)$$

and for the anion:

$$\begin{aligned} \ln \gamma_a^{res} = & \frac{\theta_c}{\theta_m} \frac{q_c}{3-q} [\tau_1^{3-q} \phi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_c}{\tau_1}) - \phi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_c}{\tau_1})] - \frac{q_a}{2-q} [\tau_1^{2-q} \chi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_c}{\tau_1}) - \chi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_c}{\tau_1})] \\ & + \frac{\theta_a}{\theta_m} \frac{q_a}{3-q} [\tau_1^{3-q} \phi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1}) - \phi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1})] + Z_c^2 \frac{\theta_c \theta_a}{\theta_m^2} \frac{q_a}{2-q} [\tau_1^{2-q} \chi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1}) - \chi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1})] \\ & - Z_c^2 \frac{\theta_c \theta_a}{\theta_m^2} \frac{q_a}{3-q} [\tau_1^{3-q} \phi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1}) - \phi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1})] - Z_c^2 \frac{\theta_c}{\theta_m} \frac{q_a}{2-q} [\tau_1^{2-q} \chi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1}) - \chi_q (\frac{\theta_c + \theta_a}{\theta_m} \frac{q_a}{\tau_1})], \end{aligned} \quad (30)$$

and for the solution:

$$\begin{aligned} \ln \gamma_m^{res} = & \frac{n_a + n_c}{n_m \theta_m} \frac{1}{3-q} [-\theta_a q_a (\tau_1^{3-q} \phi_q (\frac{\lambda}{q_c} \tau_1) - \phi_q (\frac{\lambda}{q_c} \tau_1)) - \theta_c q_c (\tau_1^{3-q} \phi_q (\frac{\lambda}{q_a} \tau_1) - \phi_q (\frac{\lambda}{q_a} \tau_1))] \\ & - \frac{\theta_a}{\theta_m} Z_c^2 \frac{q_m}{2-q} [\tau_3^{2-q} \chi_q (\frac{\theta_m}{\theta_c} \tau_3) - \chi_q (\frac{\theta_m}{\theta_c} \tau_3)] + \frac{\theta_m}{\theta_c} \frac{2-q}{3-q} (\tau_3^{2-q} \phi_q (\frac{\theta_m}{\theta_c} \tau_3) - \phi_q (\frac{\theta_m}{\theta_c} \tau_3)) \\ & - \frac{\theta_c}{\theta_a} Z_c^2 \frac{q_m}{2-q} [\tau_4^{2-q} \chi_q (\frac{\theta_m}{\theta_a} \tau_4) - \chi_q (\frac{\theta_m}{\theta_a} \tau_4)] + \frac{\theta_m}{\theta_a} \frac{2-q}{3-q} (\tau_4^{2-q} \phi_q (\frac{\theta_m}{\theta_a} \tau_4) - \phi_q (\frac{\theta_m}{\theta_a} \tau_4)). \end{aligned} \quad (31)$$

RESULTS AND DISCUSSION

Combining the residual activity coefficients (Eqs. (29), (30) and (31)) with the Debye-Huckel (Eq. (11) for solvent and Eqs. (12) for ions) and combinatorial term (Eqs. (15)) leads to the derivation of the activity coefficients of ions and solvent. Furthermore, the Debye-Huckel parameter for aqueous electrolyte system in Eq. (11) is calculated by the following expression:

$$\begin{aligned} A = & -61.44534 \exp\left(\frac{T-273.15}{273.15}\right) + 2.864468 \left(\exp\left(\frac{T-273.15}{273.15}\right)\right)^2 + 183.5379 \ln\left(\frac{T}{273.15}\right) \\ & - 0.6820223(T-273.15) + 0.0007875695(T^2 - (273.15)^2) + 58.95788\left(\frac{273.15}{T}\right). \end{aligned} \quad (32)$$

For evaluation of the applicability of the proposed model, the sum of squares of the deviations between calculated and experimental molal mean ionic activity coefficient γ_{\pm}^m was minimized,

$$\sigma = \sum_i (\ln \gamma_{\pm_i}^{m,cal} - \ln \gamma_{\pm_i}^{m,exp})^2. \quad (33)$$

In this equation, γ_{\pm}^m is calculated using the following equations:

$$\ln \gamma_{\pm}^* = \frac{v_c \ln \gamma_c + v_a \ln \gamma_a}{\nu}, \quad (34)$$

$$\ln \gamma_{\pm}^m = \ln \gamma_{\pm}^* - \ln\left(1 + \frac{M_s m \nu}{1000}\right), \quad (35)$$

where γ_{\pm}^* is the mean ionic activity coefficient of an electrolyte, ν_c and ν_a are the stoichiometric numbers of the cation and the anion of the electrolyte, respectively, $\nu = \nu_c + \nu_a$, M_s is the molecular weight of the solvent, and m is the molality of the electrolyte solution.

Using this scenario, the adjustable parameters in T-E-UNIQUAC model are surface area parameters r and q_i for species i , the binary interaction energy parameter $u_{am,mm}$, $u_{ma,ca}$ and q . Treating r and q_i as adjustable parameters are reasonable as their effective dimensions in the solution are hardly associated with their crystal structure. Having in mind the Eq. (18), $u_{am,mm}$ is the difference of the interaction enthalpies of the ion-molecule pair and the molecule-molecule pair, and $u_{ma,ca}$ is defined as the difference of the interaction enthalpies of the molecule-ion and the cation-anion pair. Moreover, q is the entropic index in the nonextensive Tsallis weight. The experimental data available in the literature [23] were employed for evaluation of these adjustable parameters.

Table 1 demonstrates the evaluated adjustable parameters along with σ obtained from the T-E-UNIQUAC model, the modified electrolyte-UNIQUAC model developed by Messnaoui *et al.* [24], E-NRTL model reported by Chen *et al.* [21,22], and the Pitzer model [25, 26]. It can be interpreted that the results are comparable and in some cases with better accuracy. Indeed, the results of the proposed model are satisfactory leading to the accurate calculation of molal mean ionic activity coefficients.

Figures 1-6 are the visual indication of the accuracy of the present model in the calculation of the individual activity coefficient in the binary mixture in comparison with experimental data.

CONCLUSIONS

Boltzmann weight and Boltzmann distribution are the fundamental bases for the current electrolyte models. However, the introduction of nonextensivity to the UNIQUAC model proposes a new theoretical basis for describing the behavior of electrolyte systems. Accordingly,

Table 1. Calculated Interaction Parameters for the Developed T-E-UNIQUAC Model, and a Comparison with Results Obtained with the Chen *et al.*, Messnaoui *et al.* and Pitzer Models for Mean Ionic Activity Coefficients

Electrolyte	m_{\max}	$u_{ma,ca}$	$u_{am,mm}$	q	σ			
					T-E-UNIQUAC	Messnaoui	Chen	Pitzer
CsI	3.0	-990.7529	838.71	0.50	0.0333	0.0104	0.0075	0.0101
HBr	6.0	694.9412	28.47	0.50	0.0982	0.0452	0.1532	0.0164
HCl	6.0	-1204.69	-333.54	0.70	0.0878	0.012	0.0331	0.0033
HI	6.0	-1088.13	655.05	0.67	0.0505	0.0381	0.167	0.0255
KCl	5.0	-1545.03	4388.13	0.70	0.0346	0.0088	0.0127	0.0115
LiBr	6.0	-3133.83	3079.81	0.72	0.1195	0.0221	0.043	0.0078
LiClO ₄	4.5	605.9063	-528.36	0.43	0.1272	0.014	0.0261	0.0074
LiI	3.0	-4537.24	3845.31	0.78	0.0291	0.0181	0.0221	0.0191
LiNO ₃	6.0	-746.18	1230.95	0.51	0.0679	0.0042	0.0113	0.0036
LiOH	5.0	-781.461	1938.36	0.57	0.0377	0.021	0.0202	0.0499
NaCl	6.0	-3551.44	2064.38	0.42	0.0522	0.0035	0.018	0.0036
NaClO ₃	3.0	-530.294	1187.75	0.46	0.0403	0.0008	0.0051	0.0081
NaClO ₄	6.0	-1238.29	2648.60	0.65	0.0364	0.0017	0.0096	0.0041
NaF	1.0	-473.133	484.243	0.43	0.0136	0.0069	0.0077	0.0082
NaOH	6.0	-271.66	-1727.07	0.47	0.1113	0.01	0.0228	0.0099
CaCl ₂	6.0	-918.788	571.60	0.62	0.4192	0.0318	0.1753	0.0360
MgBr ₂	3.0	646.5172	-1378.58	0.61	0.9305	0.0327	0.1196	0.0063
MgI ₂	3.5	-890.744	2209.36	0.43	0.2367	0.0680	0.1999	0.0076
Zn(ClO ₄) ₂	4.0	404.4911	-964.63	0.50	0.6017	0.2280	0.2892	0.0093 ^a
Li ₂ SO ₄	3.0	-831.7793	-115.49	0.31	0.0377	0.0233	0.0198	0.0075
Na ₂ CrO ₄	4.0	-169.09	-80.36	0.73	0.0495	-	0.057	-
Na ₂ SO ₄	4.0	-1593.353	-155.28	0.50	0.3635	0.0560	0.0308	0.0109
AlCl ₃	1.8	-172.087	4249.84	0.72	0.1551	-	0.115	-
Cr ₂ (SO ₄) ₃	1.2	-692.416	3993.97	0.42	0.1153	-	0.129	-

 m_{\max} : Maximum molality of the electrolyte. ^a m_{\max} : 2.0.

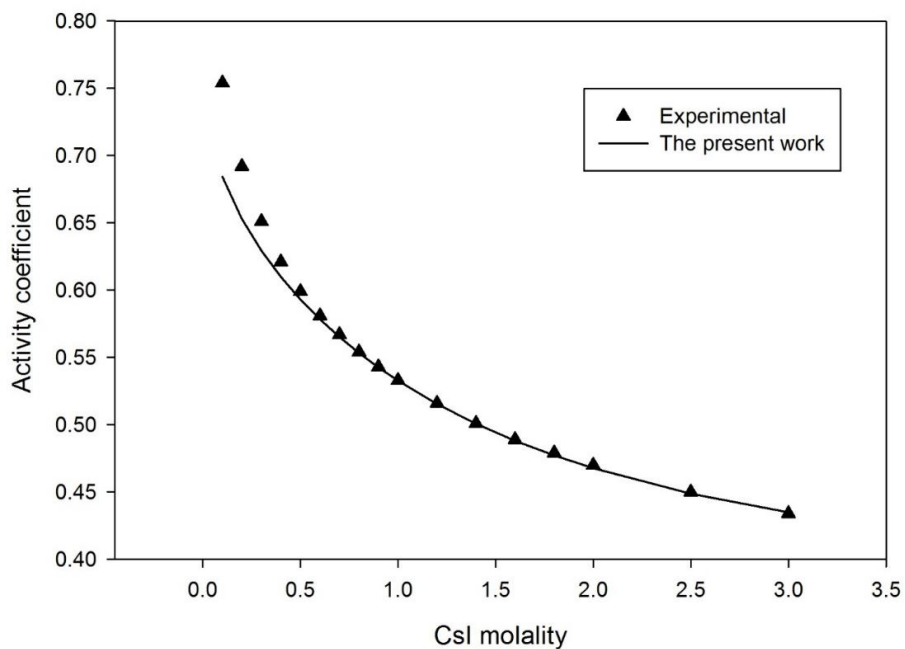


Fig. 1. A comparison of the mean ionic activity coefficients of CsI electrolyte with experimental data at 298.15 °K [23].

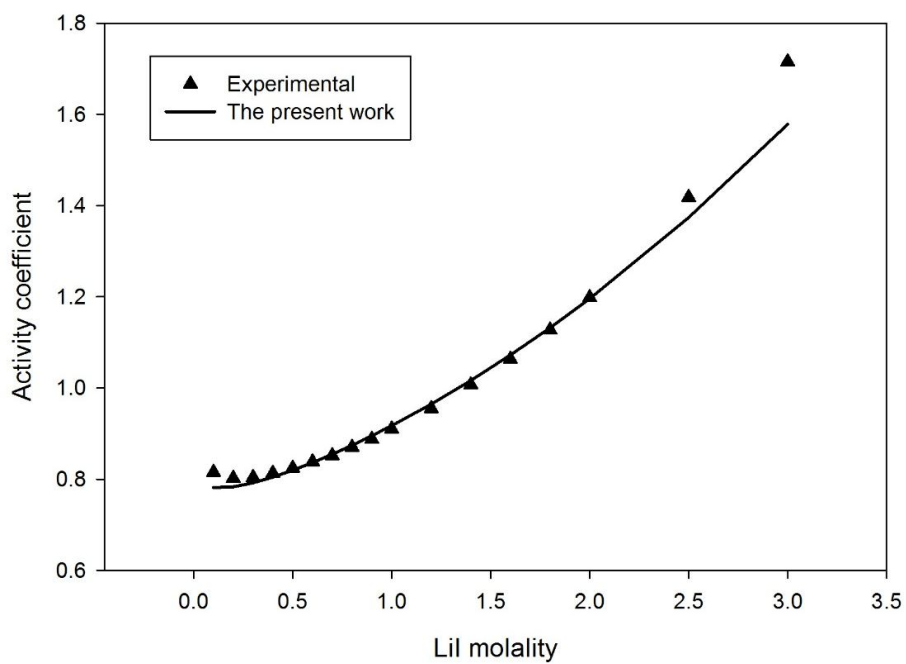


Fig. 2. Comparison of the experimental and calculated mean ionic activity coefficients of LiI electrolyte at 298.15 °K [23].

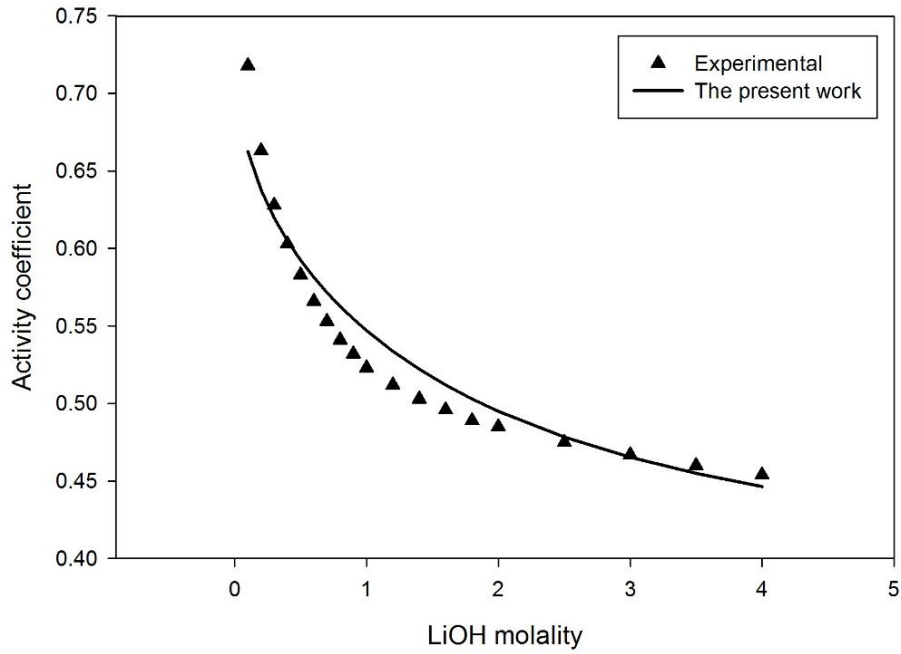


Fig. 3. Comparison of the experimental and calculated mean ionic activity coefficients of LiOH electrolyte at 298.15 °K [23].

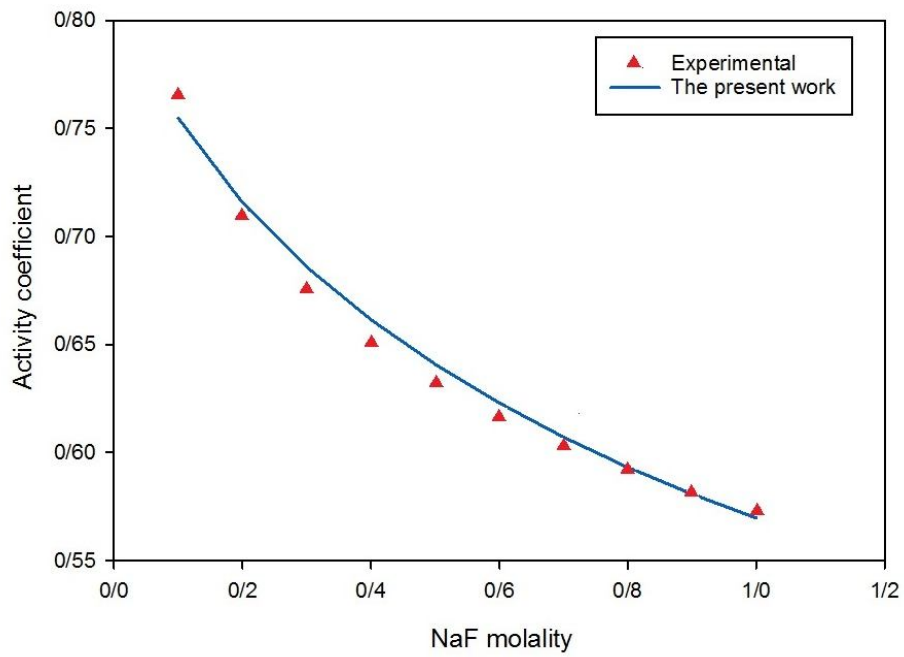


Fig. 4. Comparison of the experimental and calculated mean ionic activity coefficients of NaF electrolyte at 298.15 °K [23].

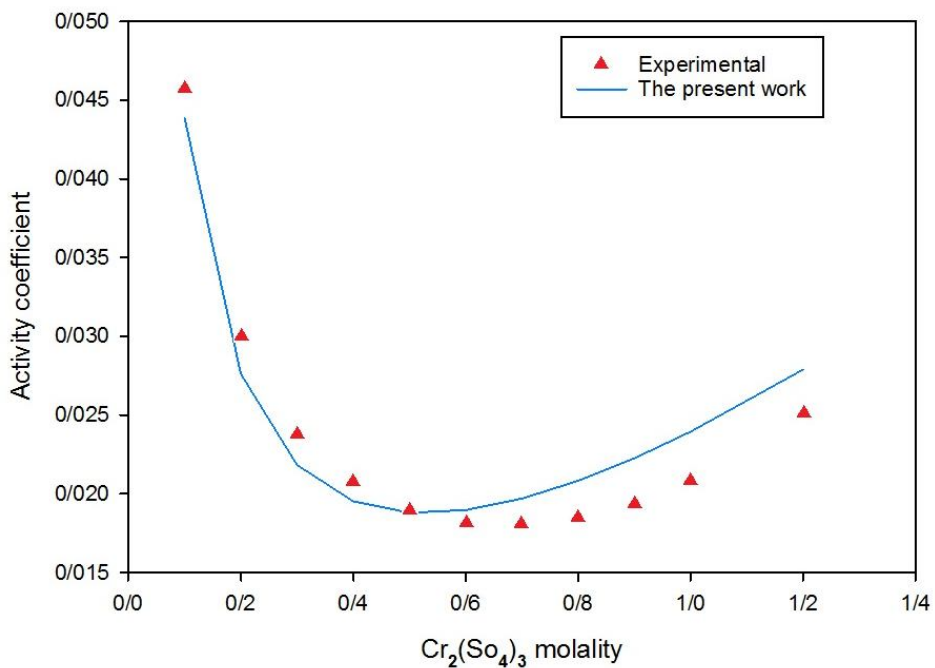


Fig. 5. Comparison of the experimental and calculated mean ionic activity coefficients of $\text{Cr}_2(\text{SO}_4)_3$ electrolyte at 298.15 °K [23].

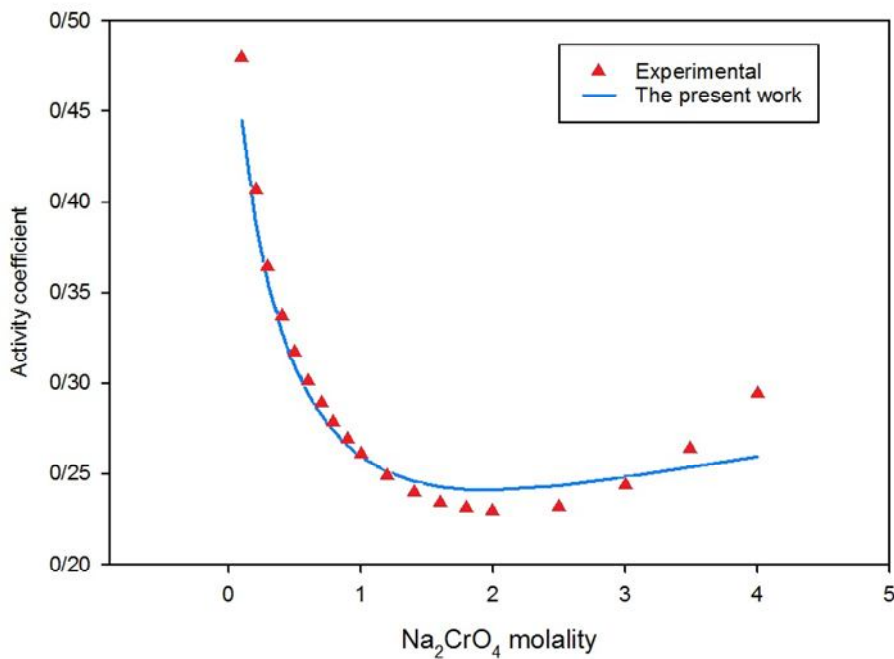


Fig. 6. Comparison of the experimental and calculated mean ionic activity coefficients of Na_2CrO_4 electrolyte at 298.15 °K [23].

replacement of the Boltzmann's weight by the Tsallis' weight leads to an increase in the degree of freedom of the T-E-UNIQUAC model. The entropic index q is the extra parameter that increases the degree of freedom of the proposed model that also describes the degree of nonextensivity observed in the system. Furthermore, the introduction of q can make the fitting procedure more accurate.

In order to achieve an overall conclusion regarding the applicability of the proposed T-E-UNIQUAC model, the following closures can be stated: (i) our proposed model has a notable complexity in comparison to current models. Higher complexity means an extended runtime in order to achieve the optimal results. (ii) A remarkable strength of this model lies in its ability to predict the individual activity coefficients of the ion. As a result, the physical significance of the proposed T-E-UNIQUAC model introduces a unique platform for future research studies.

Appendix A

h_{res}^E can be calculated by considering the excess enthalpies of all cells,

$$h_{res}^E = q_m X_m (h_m - h_m^{ref}) + q_c X_c (h_c - h_c^{ref}) + q_a X_a (h_a - h_a^{ref}), \tag{A1}$$

where h_i and h_i^{ref} are the residual molar and reference enthalpies of cells with i as a central species, respectively. The following equations relate h_i to the local area fractions:

$$\begin{aligned} h_m &= \theta_{mm} h_{mm} + \theta_{cm} h_{cm} + \theta_{am} h_{am}, \\ h_c &= Z_c (\theta_{mc} h_{mc} + \theta_{ac} h_{ac}), \\ h_a &= Z_a (\theta_{ma} h_{ma} + \theta_{ca} h_{ca}). \end{aligned} \tag{A2}$$

Chen *et al.* [21,22] considered the reference states as a pure solvent and a pure completely ionized electrolyte. Thus, h_i^{ref} are defined as

$$\begin{aligned} h_m^{ref} &= h_{mm}, \\ h_c^{ref} &= Z_c h_{ac}, \\ h_a^{ref} &= Z_a h_{ca}. \end{aligned} \tag{A3}$$

With the substitution of Eqs. (A2) and (A3) in Eq.

(A1), h_{res}^E can be calculated as:

$$h_{res}^E = q_m X_m (\theta_{am} u_{am,mm} + \theta_{cm} u_{cm,mm}) + q_c X_c (Z_c \theta_{mc} u_{mc,ac}) + q_a X_a (Z_a \theta_{ma} u_{ma,ca}). \tag{A4}$$

Furthermore, local area fractions can be substituted in the above equation and thus:

$$\begin{aligned} h_{res}^E &= q_m X_m \left(\frac{\theta_a H_{am,mm} u_{am,mm} + \theta_c H_{cm,mm} u_{cm,mm}}{\theta_m + \theta_a H_{am,mm} + \theta_c H_{cm,mm}} \right) + q_c X_c Z_c \left(\frac{\theta_m H_{mc,ac} u_{mc,ac}}{\theta_a + \theta_m H_{mc,ac}} \right) \\ &+ q_a X_a Z_a \left(\frac{\theta_m H_{ma,ca} u_{ma,ca}}{\theta_c + \theta_m H_{ma,ca}} \right). \end{aligned} \tag{A5}$$

The residual excess molar Gibbs energy, g_{res}^E , can be derived by the substitution of Eq. (18) in Eq. (A5) and the use of Eq.(20),

$$\begin{aligned} g_{res}^E &= q_m X_m \theta_a \int_0^x \frac{c_1 \exp_q(-c_1 x)}{\theta_m + (\theta_a + \theta_c \frac{q_a}{q_c}) \exp_q(-c_1 x)} dx + q_m X_m \theta_c \int_0^x \frac{c_2 \exp_q(-c_2 x)}{\theta_m + (\theta_a + \theta_c \frac{q_c}{q_a}) \exp_q(-c_2 x)} dx \\ &+ q_a X_a Z_a \theta_m \int_0^x \frac{c_3 \exp_q(-c_3 x)}{\theta_c + \theta_m \exp_q(-c_3 x)} dx + q_c X_c Z_c \theta_a \int_0^x \frac{c_4 \exp_q(-c_4 x)}{\theta_a + \theta_m \exp_q(-c_4 x)} dx \end{aligned} \tag{A6}$$

where we have used the change of variables $c_1 = u_{am,mm} / R$, $c_2 = u_{cm,mm} / R$, $c_3 = u_{ma,ca} / R$, $c_4 = u_{mc,ac} / R$ and $x = 1/T$.

Integration of the above equation requires the use of the following equations (Eq. 3.194 5 and 3.194 1 of [27]):

$$\begin{aligned} \int_0^x \frac{c \exp_q(-cx)}{a + b \exp_q(-cx)} dx &= -\frac{1}{a} \int_1^{\tau} \frac{\tau'}{1 + \frac{b}{a} \tau'} d\tau' \\ &= -\frac{1}{a(2-q)} \left[\tau^{2-q} \chi_q \left(\frac{b}{a} \tau \right) - \chi_q \left(\frac{b}{a} \right) \right], \end{aligned} \tag{A7}$$

$$\chi_q(x) = {}_2F_1(1, 2-q; 3-q; -x), \tag{A8}$$

where $q < 2$, $\tau = \exp_q(-cx)$ and ${}_2F_1(\alpha, \beta; \gamma; x)$ is the hypergeometric function.

The analytical expression for g_{res}^E is obtained as (see Appendix):

$$\begin{aligned} \frac{g_{res}^E}{RT} = & q_m X_m \frac{\theta_a}{\theta_m} \frac{1}{q-2} \left[\tau_1^{2-q} \chi_q \left(\frac{\theta_a + q_a \theta_c}{\theta_m} \tau_1 \right) - \chi_q \left(\frac{\theta_a + q_a \theta_c}{\theta_m} \right) \right] \\ & + q_m X_m \frac{\theta_c}{\theta_m} \frac{1}{q-2} \left[\tau_2^{2-q} \chi_q \left(\frac{\theta_c + q_c \theta_a}{\theta_m} \tau_2 \right) - \chi_q \left(\frac{\theta_c + q_c \theta_a}{\theta_m} \right) \right] \\ & + q_a X_a X_c \frac{\theta_m}{\theta_c} \frac{1}{q-2} \left[\tau_3^{2-q} \chi_q \left(\frac{\theta_m}{\theta_c} \tau_3 \right) - \chi_q \left(\frac{\theta_m}{\theta_c} \right) \right] \\ & + q_c X_c X_a \frac{\theta_m}{\theta_a} \frac{1}{q-2} \left[\tau_4^{2-q} \chi_q \left(\frac{\theta_m}{\theta_a} \tau_4 \right) - \chi_q \left(\frac{\theta_m}{\theta_a} \right) \right], \end{aligned} \tag{A9}$$

REFERENCES

- [1] Sattler, K. D., Handbook of Nanophysics, Principles and Methods. CRC Press, 2011.
- [2] Tsallis, C., Possible generalization of Boltzmann-Gibbs statistics. *J. Stat. Phys.* **1998**, *52*, 479-487, DOI: 10.1007/BF01016429.
- [3] Curado, E. M. F.; Tsallis, C., Generalized statistical mechanics: connection with thermodynamics. *J. Phys. A: Math. Gen.* **1991**, *24*, L69-L72, DOI: 10.1088/0305-4470/25/4/038.
- [4] Tsallis, C.; Cirto, L. J. L., Thermodynamics is more powerful than the role to it reserved by Boltzmann-Gibbs statistical mechanics, *Eur. Phys. J. Special Topics*, **2014**, *223*, 2161-2175, DOI: 10.1140/epjst/e2014-02256-1.
- [5] Gell-Mann, M.; Tsallis, C., Nonadditive Entropy-Interdisciplinary Applications. Oxford University Press, 2004.
- [6] Borges, E. P., On a q-generalization of circular and hyperbolic functions, *J. Phys. A: Math. Gen.* **1998**, *31*, 5281-5288, DOI: 10.1088/0305-4470/31/23/011.
- [7] Tsallis, C., Nonextensive physics: a possible connection between generalized statistical mechanics and quantum groups, *Phys. Lett. A*, **1994**, *195*, 329-334, DOI: 10.1016/0375-9601(94)90037-X.
- [8] Tsallis, C., What are the numbers that experiments provide, *Quimica Nova*. **1994**, *17*, 468-471.
- [9] Nivanen, L.; Mehaute, A. L.; Wang, Q. A., Generalized algebra within a nonextensive statistics. *Rep. Math. Phys.* **2003**, *52*, 437-448, DOI: 10.1016/S0034-4877(03)80040-X.
- [10] Borges, E. P., A possible deformed algebra and calculus inspired in nonextensive thermostatistics, *Physica A*. **2004**, *340*, 95-101, DOI: 10.1016/j.physa.2004.03.082.
- [11] Yamano, T., Some properties of q-logarithm and q-exponential functions in Tsallis statistics, *Physica A*. **2002**, *305*, 486-496, DOI: 10.1016/S0378-4371(01)00567-2.
- [12] Naudts, J., Deformed exponentials and logarithms in generalized thermostatistics, *Physica A*. **2002**, *316*, 323-334, DOI: 10.1016/S0378-4371(02)01018-X.
- [13] Cardoso, P. G. S.; Borges, E. P.; Lobao, T. C. P.; Pinho, S. T. R., Nondistributive algebraic structures derived from nonextensive statistical mechanics, *J. Math. Phys.* **2008**, *49*, 093509, 1-10, DOI: 10.1063/1.2982233.
- [14] Tsallis, C., Introduction to Nonextensive Statistical Mechanics-Approaching a Complex World, Springer-Verlag: 2009.
- [15] Mansoori, G. A., Principles of Nanotechnology: Molecular-Based Study of Condensed Matter in Small Systems. World Scientific, New Jersey, 2005.
- [16] Cohen, E. G. D., Statistics and dynamics, *Physica A*. **2002**, *305*, 19-26, DOI: 10.1016/S0378-4371(01)00634-3.
- [17] Garcia-Morales, V.; Pellicer, J., Microcanonical foundation of nonextensivity and generalized thermostatistics based on the fractality of the phase space, *Physica A*. **2006**, *361*, 161-175, DOI: 10.1016/j.physa.2005.07.006.
- [18] Souza, L. S.; Borges, E. P.; Pessoa, L. P., q-Quadratic mixing rule for cubic equations of state, *Chem. Eng. Sci.* **2015**, *132*, 150-158, DOI: 10.1016/j.ces.2015.04.022.
- [19] Abrams, D. S.; Prausnitz, J. M., Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems, *AIChE J.* **1975**, *21*, 116-128, DOI: 10.1002/aic.690210115.
- [20] Debye, P.; Hückel, E., De la theorie des electrolytes. I. Abaissement du point de congelation et phenomenes associes. *Phys. Z.* **1923**, *24*, 185-206.
- [21] Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B.,

- Local composition model for excess Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated electrolyte systems, *AIChE. J.* **1982**, *28*, 588-596, DOI: 10.1002/aic.690280410.
- [22] Chen, C. C.; Evans, L. B., A local composition model for the excess Gibbs energy of aqueous electrolyte system, *AIChE. J.* **1986**, *32*, 444-454, DOI: 10.1002/aic.690320311.
- [23] Robinson, R. A.; Stokes, R. H., *Electrolyte Solutions*. Courier Corporation, 1970.
- [24] Messnaoui, B.; Ouiazzane, S.; Bouhaouss, A.; Bounahmidi, T., A modified electrolyte-UNIQUAC model for computing the activity coefficient and phase diagrams of electrolyte systems, *Calphad.* **2008**, *32*, 566-576, DOI: 10.1016/j.calphad.2008.04.003.
- [25] Pitzer, K. S., Thermodynamics of electrolytes. I. Theoretical basis and general equations, *J. Phys. Chem.* **1973**, *77*, 268-277, DOI: 10.1021/j100621a026.
- [26] Pitzer, K. S.; Mayorga, G., Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, *J. Phys. Chem.* **1973**, *77*, 2300-2308, DOI: 10.1021/j100638a009.
- [27] Gradshteyn, I. S.; Ryzhik, I. M., *Table of Integrals, Series, and Products*. Academic Press, 1996.