Modeling the Transport and Volumetric Properties of Solutions Containing Polymer and Electrolyte with New Model

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ABSTRACT: *A new theoritical model based on the local composition concept (TNRF-mNRTL model) was proposed to express the short-range contribution of the excess Gibbs energy for the solutions containing polymer and electrolyte. This contribution of interaction along with the long-range contribution of interaction (Pitzer-Debye-Hückel equation), configurational entropy of mixing (Flory-Huggins relation) and Eyring absolute rate theory were used to fit the viscosity values of ternary aqueous solutions of polymer + electrolyte with considering temperature dependency. The local composition models which are available for correlating the thermodynamic properties of ternary polymer + electrolyte solutions (ternary-Wilson, ternary-modified NRTL, and ternary-modified Wilson) with Eyring absolute rate theory were also used for fitting the viscosity values of ternary solutions for the first time. The fitting quality of Eyring-TNRF-mNRTL model was compared with these models. The equations of apparent molar volume were also derived from TNRF-mNRTL, ternary-Wilson, ternary-modified NRTL, and ternary-modified Wilson models. These equations were used for correlating the apparent molar volume and density values of ternary polymer + electrolyte solutions.*

KEYWORDS: *Modeling; Viscosity; Density; Solutions; TNRF-mNRTL model.*

INTRODUCTION

An aqueous two-phase system consisting of a polymer and one kosmotropic salt is a fast, cost-effective and ecofriendly method and has a great potential for development in biotechnology applications as separation media and purification of enzymes, drugs, macromolecules, metal ions and biomaterials [1-3]. This simple system can also be used in protein partitioning to obtain enriched products [1, 4]. The knowledge

of measurement, correlation, and prediction of the thermodynamic, transport and volumetric properties of polymer + electrolyte solutions is necessary for designing and operating the industrial processes. Measurement and modeling the transport and volumetric properties of solutions are a matter of interest for specifying the intermolecular interactions presented in the mixtures. The behavior of these quantities with increasing the temperature

and composition can be a powerful tool for using the polymer + electrolyte systems in the industry. While the density and viscosity data of aqueous polymer-salt systems are available in literature but the models based on the theories of thermodynamic are scarce. The experimentally determined values of viscosity for polymer-salt solutions have been correlated with the NRTL (non-random two-liquid) model [5], empirical Jonez-Dole equation [6] and other empirical equations [7]. A viscosity model, based on Eyring's absolute rate theory combined with a cubic PR equation of state and Wong-Sandler mixing rule has been used to correlate the viscosities of aqueous solutions of alkanolamine mixtures [8]. Excess molar volume and apparent molar volume are important physical properties which can be calculated from the density values of polymer-salt solutions. Apparent molar volumes of these solutions are usually fitted with the NRTL model [5], Pitzer equation [9], Redlich-Mayer type equation [6] and empirical equations [7].

Even though the several models are available in literature for modeling the transport and volumetric properties of the systems containing polymer and electrolyte but many of them are empirical or semi empirical equations, therefore, in this work we decided to develop a new excess Gibbs energy equation based on the local composition concept using Chen's local cell theory [10]. The three types of interactions (the short-range interaction, the long-range interaction and the configurational entropy of mixing) are considered in derivation the proposed model. The configurational entropy of mixing and the long-range contribution of interaction are represented by the Flory-Huggins relation [11] and Pitzer-Debye-Hückel model [12], respectively. The short-range contribution of interaction is expressed by the proposed local composition model (TNRF-mNRTL (ternary nonrandom factor-modified non-random two-liquid)). Proposed excess Gibbs energy equation along with the Eyring absolute rate theory [13] are used to fit the viscosity values of ternary aqueous solutions of polymer + electrolyte with considering temperature dependency. The local composition models which are available for correlating the thermodynamic properties of ternary polymer + electrolyte solutions (ternary-Wilson [14], ternary-modified NRTL (mNRTL) [15] and ternary-modified Wilson (mWilson) [16]) along with Eyring absolute rate theory have also been used for fitting the

viscosity values of ternary solutions. The fitting quality of Eyring-TNRF-mNRTL model is compared with these models. The equations for apparent molar volume have also been derived from TNRF-mNRTL, ternary-Wilson [14], ternary-mNRTL [15] and ternary-mWilson [16] models. These equations have been used for correlating the apparent molar volume and density values of ternary polymer + electrolyte solutions.

THEORETICAL SECTION
New excess Gibbs energy

Following the *Chen et al.*'s approach, we assume the existence of four types of cell; one of the cells has a polymer segment as a central molecule with solvent, polymer segment, anion and cation molecules in the surrounding and the second cell has a solvent as a central molecule with solvent, polymer segment, anion and cation molecules in the surrounding and the third cell has an anion as a central molecule with solvent, polymer segment, and cation molecules in the surrounding and the fourth cell has a cation as a central molecule with solvent, polymer segment, and anion molecules in the surrounding. Thus the excess Gibbs energy (g^{ex}) can be obtained with considering the contributions of the excess Gibbs energy of each cell (g_m^{ex}, g_a^{ex}, g_c^{ex} and g_s^{ex}) as follow

$$\frac{g^{ex,TNRF-mNRTL}}{RT} = x_m \frac{g_m^{ex}}{RT} + x_a \frac{g_a^{ex}}{RT} + \tag{1}$$

$$x_c \frac{g_c^{ex}}{RT} + r_p x_p \frac{g_s^{ex}}{RT}$$

where x_m, x_a, x_c, and x_p are the mole fraction of solvent, anion, cation, and polymer. The number of polymer segments, r_p, approximates the ratio of the molar volume of the polymer and that of the solvent molecules. T is temperature and R is the universal constant of gases. Subscripts *m, a, c* and *s* represent the solvent, anion, cation, and segment of the polymer chain, respectively. The contributions of the excess Gibbs energy for the four cells are defined as [10, 17]

$$g_m^{ex} = \left(X_{mm} g_{mm} + X_{cm} g_{cm} + \tag{2a}\right.$$

$$\left. X_{am} g_{am} + X_{sm} g_{sm} \right) - g_m^0$$

$$g_a^{ex} = (X_{ma} g_{ma} + X_{ca} g_{ca} + X_{sa} g_{sa}) - g_a^0 \tag{2b}$$

$$g_c^{ex} = (X_{mc}g_{mc} + X_{ac}g_{ac} + X_{sc}g_{sc}) - g_c^0 \tag{2c}$$

$$g_s^{ex} = (X_{ms}g_{ms} + X_{as}g_{as} + X_{cs}g_{cs} + X_{ss}g_{ss}) - g_s^0 \tag{2d}$$

where g_m^0, g_a^0, g_c^0 and g_s^0 are the reference states Gibbs energy for cells with central solvent, anion, cation, and segment, respectively. g_{ij} and g_{ii} are the energies of interaction between j-i and i-i pairs of species, respectively. X_{ji} and X_{ii} are the effective local mole fractions of species j and i.

In this work, the new relations as follow are used for the reference states of the four types of cell

$$g_m^0 = X_m g_{mm} + X_a g_{am} + X_c g_{cm} + X_s g_{sm} \tag{3a}$$

$$g_a^0 = \frac{X_c g_{ca} + X_m g_{ma} + X_s g_{sa}}{X_c + X_m + X_s} \tag{3b}$$

$$g_c^0 = \frac{X_a g_{ac} + X_m g_{mc} + X_s g_{sc}}{X_a + X_m + X_s} \tag{3c}$$

$$g_s^0 = \frac{X_m g_{ms} + X_a g_{as} + X_c g_{cs} + X_s g_{ss}}{X_m + X_a + X_c + X_s} \tag{3d}$$

where

$$X_a = z_a x_a = X_E = z_a z_c x_h \tag{4a}$$

$$X_c = z_c x_c = X_E = z_a z_c x_h \tag{4b}$$

$$X_m = x_m \tag{4c}$$

$$X_s = \frac{x_p}{r_p x_p + x_m + 2z_a z_c x_h} \tag{4d}$$

where z_a and z_c are the charge number of anion and cation, respectively. From Eqs. (4a) and (4b) we have the relation $X_a = X_c$ which shows the electroneutrality.

Using the nonrandom factor the same as that defined by Haghtalab and Vera. [18] and considering the above assumptions, we propose the TNRF-mNRTL equation for the unsymmetrical convention ($g^{ex*,\text{TNRF-mNRTL}}$) by following the same procedure as our previous works [19-21] used in obtaining the excess Gibbs energy expression for electrolyte solutions and polymer solutions, as follow

$$\frac{g^{ex*,\text{TNRF-mNRTL}}}{RT} = x_m[\lambda_{Em}(x_m\Gamma_m - x_m) + \tag{5a}$$

$$\lambda_{sm}(X_s\Gamma_m - X_s)] + \frac{z_a z_c x_h}{z_a + z_c} \times$$

$$\left[\frac{z_a z_c x_h \lambda_{mE}(-1 + z_a z_c x_h \Gamma_E + x_m \Gamma_E + X_s \Gamma_E)}{X_E + x_m + X_s} + \right.$$

$$\left. \frac{X_s \lambda_{Es}(z_a z_c x_h \Gamma_s + X_s \Gamma_s + X_m \Gamma_s - 1)}{X_E + x_m + X_s} \right] +$$

$$r_p x_p \left[\frac{2z_a z_c x_h \lambda_{sE}(\Gamma_E - 1) + X_s \lambda_{ms}(\Gamma_s - 1)}{x_m + X_s + 2z_a z_c x_h} \right] -$$

$$\nu x_h \lambda_{Em}(1 - \Gamma_m)$$

where

$$\frac{g_{ca} - g_{ma}}{RT} \equiv \lambda_{mE} \quad , \quad \frac{g_{mm} - g_{Em}}{RT} \equiv \lambda_{Em} \tag{5b}$$

$$\frac{g_{sa} - g_{ma}}{RT} \equiv \lambda_{Es} \quad , \quad \frac{g_{Es} - g_{ms}}{RT} \equiv \lambda_{sE} \tag{5c}$$

$$\frac{g_{sm} - g_{Em}}{RT} \equiv \lambda_{sm} \quad , \quad \frac{g_{ss} - g_{ms}}{RT} \equiv \lambda_{ms} \tag{5d}$$

$$\Gamma_s = \frac{1}{2z_a z_c x_h \beta_{Es} + x_m \beta_{ms} + X_s} \quad , \tag{5e}$$

$$\beta_{Es} = \exp\left(-\frac{\lambda_{Es}}{Z}\right) \quad , \quad \beta_{ms} = \exp\left(-\frac{\lambda_{ms}}{Z}\right)$$

$$\Gamma_m = \frac{1}{2z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm}} \tag{5f}$$

$$\beta_{Em} = \exp\left(-\frac{\lambda_{Em}}{Z}\right) \quad , \quad \beta_{sm} = \exp\left(-\frac{\lambda_{sm}}{Z}\right)$$

$$\Gamma_E = \frac{\beta_{mE}}{z_a z_c x_h \beta_{mE} + x_m + X_s \beta_{sE}} \tag{5g}$$

$$\beta_{mE} = \exp\left(-\frac{\lambda_{mE}}{Z}\right) \quad , \quad \beta_{sE} = \exp\left(-\frac{\lambda_{sE}}{Z}\right)$$

Where $x_h = 1 - x_m - x_p$; and λ_{mE}, λ_{Em}, λ_{sE}, λ_{Es}, λ_{sm} and λ_{ms} are the adjustable parameters of TNRF-mNRTL model; Z is the nonrandom factor which is set to 8 for obtaining the better quality of fitting in this work; $\nu = \nu_c + \nu_a$, where ν_c and ν_a are the stochiometric coefficients of cation and anion, respectively.

Viscosity

The model proposed by *Esteves et al.* [22-24] has been utilized for correlating the viscosity values (η) of ternary aqueous solutions of polymer + electrolyte as follow

$$\ln(\eta - \eta_0) = \ln(A\eta_m \left(\sum_{N=i}^{N_{solu}} c_i \right)) + \left(\frac{g^{ex}}{RT} \right) \tag{6}$$

here A (L/mol) is used as $(A = A_0 + A_1(T-298.15))$, where A_0 and A_1 are the temperature-dependence parameters. η_m and c_i are the solvent viscosity and molar concentration of the solute species i. T is the absolute temperature and R is the universal constant of gases. Excess Gibbs energy of solutions ($_g^{ex}$) can be used as the summation of three contributions, Flory-Huggins relation (F-H) [11] (the configurational entropy of mixing), Pitzer-Debye-Hückel expression (PDH) (the long-range interaction) and the proposed model (TNRF-mNRTL), as follow

$$\frac{g^{ex}}{RT} = \frac{g^{ex,F-H}}{RT} + \frac{g^{ex,PDH}}{RT} + \frac{g^{ex,TNRF-mNRTL}}{RT} \tag{7}$$

The Flory-Huggins relation [11] and the Pitzer-Debye-Hückel equation [12] for g^{ex} are as Eqs. (8) and (9), respectively

$$\frac{g^{ex,F-H}}{RT} = \sum_i x_i \ln\left(\frac{X_i}{x_i} \right) \tag{8}$$

$$\frac{g^{ex,PDH}}{RT} = -\left(\sum_i x_i \right) \frac{4A_\varphi I_x}{M_m^{0.5}\rho} \ln\left(1 + \rho I_x^{0.5}\right) \tag{9}$$

Where the Debye-Hückel constant for osmotic coefficient (A_ϕ) is represented as

$$A_\varphi = \frac{1}{3}(2\pi N_A d_m)^{1/2}(\frac{e^2}{4\pi\varepsilon D_m kT})^{3/2} \tag{10}$$

A_ϕ at 298.15 K is equal to 0.390947 for water as solvent. M_m and d_m are the molar mass and density of the solvent, respectively. N_A, k, ε, D_m and e are Avogadro's number, Boltzmann constant, the permittivity of vacuum, the dielectric constant of pure solvent and electronic charge, respectively. ρ is the closest distance parameter and

the value of 14.9 is commonly applied for the aqueous electrolyte solutions [25]. Therefore, we use this value for ρ in our work. I_x is the ionic strength in mole fraction basis, $I_x = 0.5\sum_i x_i z_i^2$; z_i is the charge number of ion i. When we replace the excess molar Gibbs energy of Eq. (6) with that represented in Eq. (7) by Flory–Huggins (Eq. (8)), PDH (Eq. (9)) and TNRF-mNRTL (Eq. (5)) models, the Eyring-TNRF-mNRTL equation can be obtained for viscosity.

Excess molar volume

The excess molar volume equation can be derived from the differentiation of g^{ex} respect to the pressure (p) at constant temperature (T) and composition (n) [26]

$$V^{ex} = \left(\frac{\partial g^{ex}}{\partial p} \right)_{T,n} \tag{11}$$

$\left(\frac{\partial g^{ex}}{\partial p} \right)_{T,n}$ for Flory-Huggins relation is equal to zero, therefore, for the local composition models considered here, the excess molar volume is written as the sum of two contributions

$$V^{ex} = V^{ex,PDH} + V^{ex,LC} \tag{12}$$

The excess molar volume of PDH equation developed by Pitzer is as following equation [26],

$$V^{ex,PDH} = \sqrt{\frac{1}{M_m}}A_v \frac{I_x}{\rho} \ln\left(1 + \rho\sqrt{I_x}\right) \tag{13}$$

A_v is the limiting Debye-Hückel slope for apparent molar volume and in this work, the A_v values have been taken from the literature [27]. The necessary relations for the excess molar volume of TNRF-mNRTL, ternary-Wilson, ternary-mNRTL, and ternary-mWilson models are not available in the literature. In this work, the equations for the excess volume of the aforementioned models have been derived. Using the Eqs. (5) and (11), the following relation is obtained for the excess molar volume of TNRF-mNRTL model for the ternary polymer + electrolyte solutions:

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$$V^{ex,TNRF-mNRTL} = x_m \big[\lambda_{Em}^v x_m (Q_1 - 1) - \tag{14a}$$

$$\lambda_{Em}^v x_m (Q_1^2 (-\frac{2z_a z_c x_h \lambda_{Em}^v \beta_{Em}}{ZRT} - \frac{X_s \lambda_{sm}^v \beta_{sm}}{ZRT})) +$$

$$\lambda_{sm}^v (Q_1 - 1) -$$

$$\lambda_{sm}^v X_s (Q_1^2 (-\frac{2z_a z_c x_h \lambda_{Em}^v \beta_{Em}}{ZRT} - \frac{X_s \lambda_{sm}^v \beta_{sm}}{ZRT})) \big] +$$

$$\frac{z_a z_c x_h}{(z_a + z_c)(z_a z_c x_h + X_s + x_m)} \times$$

$$\big[\lambda_{mE}^v z_a z_c x_h (-1 + z_a z_c x_h \beta_{mE} Q_2 + x_m \beta_{mE} Q_2 + X_s \beta_{mE} Q_2) +$$

$$\lambda_{mE} z_a z_c x_h (-z_a z_c x_h \lambda_{mE}^v \beta_{me} \frac{Q_2}{ZRT} - z_a z_c x_h \beta_{mE} (Q_2 Q_3) -$$

$$x_m \lambda_{mE}^v \beta_{mE} (\frac{Q_2}{ZRT}) - x_m \beta_{mE} (Q_2^2 Q_3) - X_s \lambda_{mE}^v (Q_2^2 Q_3)) +$$

$$\lambda_{Es}^v X_s (z_a z_c x_h Q_4 + X_s Q_4 + x_m Q_4 - 1) +$$

$$\lambda_{Es} X_s Q_4^2 (-\frac{2z_a z_c x_h \lambda_{Es}^v \beta_{Es}}{ZRT} - \frac{X_s \lambda_{ms}^v \beta_{ms}}{ZRT}) \times$$

$$(-z_a z_c x_h - X_s - x_m) \big] +$$

$$\frac{r_p x_p}{2z_a z_c x_h + x_m + X_s} \times$$

$$\big[2z_a z_c x_h (\frac{1}{(2z_a z_c x_h \beta_{mE} + x_m + X_s \beta_{sE})ZRT}) \times$$

$$(-\lambda_{mE}^v + \lambda_{mE} (-\frac{z_a z_c x_h \lambda_{mE}^v \beta_{mE}}{ZRT} - \frac{X_s \lambda_{ms}^v \beta_{ms}}{ZRT})) -$$

$$\lambda_{mE} X_s ((\frac{1}{(2z_a z_c x_h \beta_{mE} + x_m + X_s \beta_{sE})ZRT})^2 \times$$

$$(-\frac{z_a z_c x_h \lambda_{mE}^v \beta_{mE}}{ZRT} - \frac{X_s \lambda_{ms}^v \beta_{ms}}{ZRT})) \big] -$$

$$v z_a z_c x_h \lambda_{Em}^v (\frac{1}{2z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm}}) +$$

$$v z_a z_c x_h \lambda_{Em} ((\frac{1}{2z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm}})^2 \times$$

$$(-\frac{2z_a z_c x_h \lambda_{Em}^v \beta_{Em}}{ZRT} - \frac{X_s \lambda_{sm}^v \beta_{sm}}{ZRT}))$$

where

$$Q_1 = \frac{1}{2z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm}} \tag{14b}$$

$$Q_2 = \frac{1}{z_a z_c x_h \beta_{mE} + x_m + X_s \beta_{sE}} \tag{14c}$$

$$Q_3 = -\frac{z_a z_c x_h \lambda_{mE}^v \beta_{mE}}{ZRT} - \frac{X_s \lambda_{sE}^v \beta_{sE}}{ZRT} \tag{14d}$$

$$Q_4 = \frac{1}{2z_a z_c x_h \beta_{Es} + x_m \beta_{ms} + X_s} \tag{14e}$$

$$\beta_{Es} = \exp\left(-\frac{\lambda_{Es}}{Z}\right) \quad , \quad \beta_{sE} = \exp\left(-\frac{\lambda_{sE}}{Z}\right) \tag{14f}$$

$$\beta_{Em} = \exp\left(-\frac{\lambda_{Em}}{Z}\right) \quad , \quad \beta_{mE} = \exp\left(-\frac{\lambda_{mE}}{Z}\right) \tag{14g}$$

$$\beta_{ms} = \exp\left(-\frac{\lambda_{ms}}{Z}\right) \quad , \quad \beta_{sm} = \exp\left(-\frac{\lambda_{sm}}{Z}\right) \tag{14h}$$

In these equations. λ_{Es}, λ_{sE}, λ_{Em}, λ_{mE}, λ_{ms} and λ_{sm} are the excess Gibbs energy parameters which can be determined from fitting the thermodynamic properties of the considered ternary solutions. λ_{Es}^v, λ_{sE}^v, λ_{Em}^v, λ_{mE}^v, λ_{ms}^v and λ_{sm}^v are the adjustable parameters of the proposed model which are obtained from pressure derivative of λ_{Es}, λ_{sE}, λ_{Em}, λ_{mE}, λ_{ms} and λ_{sm}, respectively. The derived excess molar volume equations for ternary-Wilson, ternary-mNRTL, and ternary-mWilson models are reported in Appendix A.

RESULTS AND DISCUSSION

Viscosity values of the ternary aqueous solutions of polymer + electrolyte have been correlated by Eyring-TNRF-mNRTL model with the results reported in Table 1.

For two systems the viscosity values are available at different temperatures, therefore, for these systems, the correlation has been performed considering temperature dependency; in general, the ternary systems with enough data points are scarce thereby, we check the fitting quality of Eyring-TNRF-mNRTL model with only six systems. In the PDH equation, the molar volumes of pure water at different temperatures have been determined from the density data. The density (d_m), viscosity (η_m) and the dielectric constant (D_m) values for water are determined from the Eqs (15-18), respectively [28-31]

Table 1: Parameters of the Eyring-TNRF-mNRTL model along with absolute average relative deviation (100.AARD)ᵃ obtained from correlating the viscosity values (η) of the ternary aqueous solutions of polymer + electrolyte at different temperatures

System	M_n (g.mol⁻¹)	Temperature range (°C)	N_P	Concentration range (w/w)	λ_{sm}	λ_{ms}	λ_{Em}	λ_{mE}	λ_{sE}	λ_{Es}	$10^3.A_0$	$10^3.A_1$	100.AARD	Source data
PEG + NaClO₄	4000	15-35	36	0.250-0.350 0.002-0.339	-58.93± 0.233	-677.30± 0.005	-10.180± 0.493	-41.660± 0.769	-0.1895± 0.001	0.000429± 0.631	7.425± 1.757	-0.02824± 0.0005	2.92 (1.83)ᵇ	[5]
PEG + Triammonium Citrate	6000	25-45	145	0.050-0.500 0.020-0.100	-53.03± 0.600	-0.4148± 0.047	-7.843± 0.439	-225.80± 2.854	1.200± 0.001	939800± 0.045	1750.00± 0.135	-36.190± 0.003	6.56 (2.85)	[32]
PEG + K₃PO₄	1000	20	7	0.130-0.220 0.105-110	0.00398± 0.001	-1054± 0.0001	-9.295± 0.212	0.00011± 0.001	0.1848± 0.0001	-0.7819± 0.0005	2.513± 0.401	0.1205± 0.252	4.44 (0.45)	[33]
PPG + MgSO₄	404	25	22	0.010-0.850 0.000-0.250	-39.440± 0.034	-12.340± 0.527	-5.2750± 0.651	-26.720± 0.012	-46.970± 0.003	3798± 0.192	64.760± 2.005	500± 1.002	3.40 (1.56)	[7]
PPG + (NH₄)₂SO₄	404	25	8	0.605-0.772 0.100-0.500	0.0093± 0.008	19.320± 0.011	494.200± 0.0004	0.600± 0.001	0.4950± 0.0001	0.2160± 0.0005	4467± 30.092	500± 0.0001	3.82 (1.99)	[34]
PPG + Na₂SO₄	404	25	8	0.550-0.780 0.100-0.500	-1.9180± 0.218	0.844± 0.0005	1462± 20.822	0.1510± 0.0004	0.2460± 0.0001	0.0620± 0.0002	25550± 11.882	250± 0.0001	1.91 (1.04)	[34]

a) $= \dfrac{1}{N_p}\sum\limits_{i=1}^{N}\dfrac{\left|\eta_i^{exp}-\eta_i^{cal}\right|}{\eta_i^{exp}}$, where N_P is the total number of data points

b) The standard deviations of viscosity ($10^3\sigma(\eta)/(Pa\,s)$) are reported in the parenthesis; where, $\sigma=\sqrt{\sum\limits_{i=1}^{N}\dfrac{(\eta_i^{exp}-\eta_i^{cal})^2}{N_p}}$.

$$d_m = \frac{999.83952+16.945176t-7.9870401\times10^{-3}t^2}{1+16.879850\times10^{-3}t}+ \quad (15)$$

$$\frac{-46.170461\times10^{-6}t^3+105.56302\times10^{-9}t^4}{1+16.879850\times10^{-3}t}$$

$$\frac{-280.54253\times10^{-12}t^5}{1+16.879850\times10^{-3}t}$$

$$\eta_m / (mPa.s) = \frac{t+246}{(0.05594t+5.2842)t+137.37} \quad (16)$$

At low temperatures:

$$D_m = 10^{(1.94404-1.991\times10^{-3}t)} \quad (17)$$

At high temperatures:

$$D_m = \frac{5321}{T}+233.76-0.9297T+ \quad (18)$$

$$0.001417T^2-0.0000008292T^3$$

t is the temperature in the centigrade Celsius unit. As can be seen from Table 1, the performance of Eyring-

Table 2: Comparison of the absolute average relative deviation (100.AARD) of the different local composition models in the correlation of viscosity (η) of the ternary aqueous solutions of polymer + electrolyte at different temperatures.

System	M_n (g/mol)	Temperature range (°C)	N_P	Concentration range (w/w)	100.AARD Eyring-ternary-Wilson	100.AARD Eyring-ternary-mNRTL	100.AARD Eyring- ternary-mWilson	100.AARD Eyring- TNRF-mNRTL	Source data
PEG + NaClO$_4$	4000	15-35	36	0.250-0.350 0.002-0.339	12.47(4.88)[a]	7.06 (2.89)	12.47(4.88)	2.92(1.83)	[5]
PEG + Triammonium Citrate	6000	25-45	145	0.050-0.500 0.020-0.100	48.66(12.41)	30.57(7.54)	50.47(12.5)	6.56 (2.85)	[32]
PEG + K$_3$PO$_4$	1000	20	7	0.130-0.220 0.105-110	3.91 (0.40)	17.27(1.38)	4.18 (0.38)	4.44 (0.45)	[33]
PPG + MgSO$_4$	404	25	22	0.010-0.850 0.000-0.250	21.75 (5.60)	11.57(2.96)	21.73(5.61)	3.40(1.56)	[7]
PPG + (NH$_4$)$_2$SO$_4$	404	25	8	0.605-0.772 0.100-0.500	4.43 (2.17)	5.59 (2.97)	4.43 (2.17)	3.82 (1.99)	[34]
PPG + Na$_2$SO$_4$	404	25	8	0.550-0.780 0.100-0.500	6.63 (2.92)	7.71 (3.42)	6.63 (2.92)	1.91 (1.04)	[34]
overall					16.31 (4.73)	13.30(3.53)	16.65(4.74)	3.84 (1.62)	

a) The standard deviations of viscosity ($10^3\sigma(\eta)/(Pa\ s)$) are reported in the parenthesis.

TNRF-mNRTL model in fitting the viscosity values of ternary solutions is good especially with considering temperature dependency. The local composition models which are available for correlating the thermodynamic properties of ternary polymer + electrolyte solutions (ternary-Wilson [14], ternary-mNRTL [15] and ternary-mWilson [16]) along with Eyring absolute rate theory have also been used for fitting the viscosity values of ternary solutions. Performance of the Eyring-TNRF-mNRTL

model in fitting the viscosity values of the ternary aqueous solutions of polymer + electrolyte is compared with these models. In Table 2 the obtained Absolute Average Relative Deviations (AARD) and also the standard deviations (σ) of the aforementioned models in correlating the viscosity values are given. In this Table, total AARD and σ values have also been reported for the systems investigated.

From Table 2, one can conclude that the reliability of Eyring-TNRF-mNRTL model in the correlation of
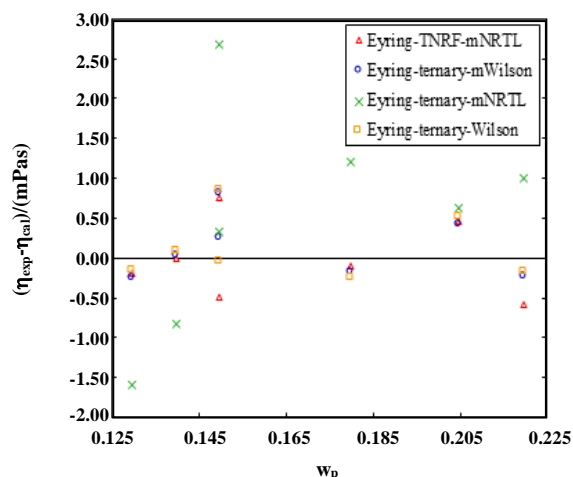
Fig. 1: Difference between experimental and calculated viscosity values (η) plotted against weight fraction of polymer (wₚ) for PEG1000 + K₃PO₄+H₂O system at 293.15 K with different models.

Fig. 2: Difference between experimental and calculated viscosity values (η) plotted against weight fraction of polymer (wₚ) for PPG + Na₂SO₄ + H₂O system at 298.15 K with different models.

viscosity values of ternary polymer + electrolyte solutions are better than other local composition models investigated in this work especially with considering temperature dependency. To see the performance of the investigated models in a better manner, the differences between experimental and calculated viscosity values for the systems of PEG1000 + K₃PO₄+H₂O at 293.15K and PPG + Na₂SO₄ + H₂O at 308.15 K have been shown respectively in Figs. 1 and 2 as examples.

From Fig. 1 it is obvious that for PEG1000 + K₃PO₄+H₂O system the performance of Eyring-ternary-Wilson, Eyring-ternary-mWilson, and Eyring-TNRF-mNRTL models is similar to each other in correlating the viscosity values; however, the fitting quality of Eyring-ternary-mNRTL model is not satisfactory. Fig. 2 shows that the fitting quality of Eyring-TNRF-mNRTL model is better than other models.

The apparent molar volumes of the polymer + electrolyte solutions (V_ϕ) are determined from the density data using the following equation [26]

$$V_\varphi = \frac{M_m}{d} - \frac{d - d_m}{mdd_m} \qquad (19)$$

where d and m are the density and molality of the solution, respectively. The apparent molar volume is related to the excess molar volume by following equation [26]
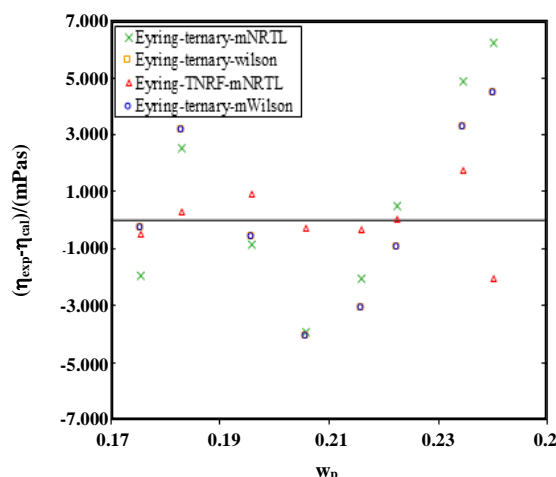
$$V_\varphi = V_\varphi^0 + (\frac{1}{mM_m} + \nu)V^{ex} \qquad (20)$$

where V_ϕ^0 is the limiting apparent molar volume of the solution? The calculated apparent molar volume values are fitted with the TNRF-mNRTL model using Eqs. (12-14 and 20). The evaluated parameters of the TNRF-mNRTL model have been reported in Table 3.

The values of the excess Gibbs energy parameters (λ_{Es}, λ_{sE}, λ_{Em}, λ_{mE}, λ_{ms} and λ_{sm}) can be determined by fitting the experimental solvent activity data with the model considered. However, the experimental osmotic coefficient data or solvent activities are scarce for ternary polymer + electrolyte solutions. Therefore, in this work, we use the values obtained from correlating the viscosity data with TNRF-mNRTL model reported in Table 1 for these parameters. As can be seen from Table 3 the performance of TNRF-mNRTL model is satisfactory in fitting the apparent molar volumes. Ternary-Wilson, ternary-mNRTL, and ternary-mWilson models have also been extended for fitting the apparent molar volume of ternary polymer + electrolyte solutions. These models are also used for correlating the apparent molar volumes of ternary solutions. AARD and the standard deviation values of these three models have been compared with those of TNRF-mNRTL model in Table 4.

Table 3: Parameters of the TNRF-mNRTL model along with absolute average relative deviation (100.AARD) and standard deviation (σ) obtained from correlating the apparent molar volume values (V_ϕ) of the ternary aqueous solutions of polymer + electrolyte at different temperatures.

System	M_n (g.mol⁻¹)	Temperature range (°C)	N_P	Concentration range (w/w)	$10^3 . \lambda^v_{sm}$	$10^3 . \lambda^v_{ms}$	$10^3 . \lambda^v_{Em}$	$10^3 . \lambda^v_{mE}$	$10^3 . \lambda^v_{sE}$	$10^3 . \lambda^v_{Es}$	$10^3 . V^0_\phi$	100. AARD (V_ϕ)	$10^6 . \sigma(V_\phi)$ (m³ mol⁻¹)	Source data
PEG + NaClO₄	4000	15	12	0.002-0.339 0.256-0.370	-1.486± 0.041	0.313± 0.002	0.007597± 0.00002	0.110± 0.012	0.4997± 0.061	0.1883± 0.002	0.02632±0.00 03	0.54 (0.09) [a]	0.22 (1.38) [b]	[5]
PEG + NaClO₄	4000	25	12	0.002-0.339 0.256-0.370	-1.511± 0.056	0.3305±0.003	0.007227± 0.00003	0.1054± 0.002	0.4996± 0.092	0.190± 0.002	0.02382±0.00 04	0.57 (0.09)	0.22 (1.37)	[5]
PEG + NaClO₄	4000	35	12	0.002-0.339 0.256-0.370	-1.511±0.051	0.3305±0.024	0.007085± 0.00003	0.1054± 0.017	0.4996± 0.090	0.190± 0.001	0.02382±0.00 04	0.65 (0.10)	0.28 (1.76)	[5]
PEG +Triammoniu m Citrate	6000	25	29	0.050-0.500 0.020-0.100	14.550±0.022	1.635± 0.004	0.0000176±0. 000	1.454±0.0010	250.400±0.377	60.220± 3.422	-0.1262± 0.0002	8.04 (0.39)	15.40 (5.4)	[32]
PEG +Triammoniu m Citrate	6000	30	29	0.050-0.500 0.020-0.100	67.630± 0.025	9.907± 0.004	-0.000679± 0.000001	2.965± 0.001	246200± 401.915	1448.00± 3.586	-0.2961± 0.0002	7.30 (0.38)	16.16 (5.17)	[32]
PEG +Triammoniu m Citrate	6000	35	29	0.050-0.500 0.020-0.100	67.220± 0.017	9.978± 0.003	-0.0006902 ±0.000001	2.964± 0.001	245900± 268.501	1449.00±2.35 3	-0.2961± 0.0001	4.63 (0.23)	10.65 (3.02)	[32]
PEG +Triammoniu m Citrate	6000	40	29	0.050-0.500 0.020-0.100	66.790± 0.013	10.050±0.002	-0.0006741 ±0.000001	2.963± 0.001	245600± 205.382	1450.00±1.768	-0.296± 0.0001	3.98 (0.17)	8.02 (2.15)	[32]
PEG +Triammoniu m Citrate	6000	45	29	0.050-0.500 0.020-0.100	66.400± 0.011	10.120±0.002	-0.0006635 ±0.000001	2.962± 0.001	245300± 181.427	1451.00±1.53 2	-0.2959± 0.0001	3.57 (0.15)	7.01 (1.99)	[32]
PEG + K₃PO₄	1000	20	7	0.130-0.220 0.105-0.122	-2.258±0.004	-4.371±0.032	0.006559± 0.00001	54.940±0.094	250.000±2.045	63.180±0.027	1.122±0.0010	1.73 (0.14)	1.54 (1.67)	[33]

Table 3:

System	M_n (g/mol)	Temperature range (°C)	N_P	Concentration range (w/w)	$10^3 \cdot \lambda_{sm}^v$	$10^3 \cdot \lambda_{ms}^v$	$10^3 \cdot \lambda_{Em}^v$	$10^3 \cdot \lambda_{mE}^v$	$10^3 \cdot \lambda_{sE}^v$	$10^3 \cdot \lambda_{Es}^v$	$10^3 \cdot V_\phi^0$	100.AARD (V_ϕ)	$10^6 \cdot \sigma(V_\phi)$ (m³/mol)	Source data
PPG + MgSO₄	404	25	22	0.010-0.850 0.000-0.250	1.0160± 0.0003	37.160±0.012	0.001069± 0.000001	-6.430± 0.001	4957± 23.598	-31.3600 ±0.098	-0.02311 ±0.00001	4.57 (0.40)	1.41 (9.24)	[7]
PPG + (NH₄)₂SO₄	404	25	8	0.605-0.772 0.100-0.500	41.2900±0.41 6	572.90±3.322	-0.09069± 0.0003	3.4750± 0.011	250000± 34.011	6.68100±0.79 5	-2.9290± 0.028	2.38 (0.04)	0.82 (0.57)	[34]
PPG + Na₂SO₄	404	25	8	0.550-0.780 0.100-0.500	-3.1910± 0.031	622.20±31.456	-0.02474± 0.0002	5.3160± 0.027	250000± 195.413	55780± 144.822	0.5540± 0.0066	8.45 (0.09)	1.74 (1.36)	[34]

a) 100.AARD values obtained from density data have been given in the parenthesis. *b* The standard deviations of density ($\sigma(d)/(kg/m^3)$) are reported in the parenthesis.

This table shows that the fitting quality of TNRF-mNRTL model is better than ternary-Wilson, ternary-mNRTL, and ternary-mWilson models. We also calculate the density values from apparent molar volumes estimated from these four models. The AARD and the standard deviation values obtained for density data have also been reported in Tables 3 and 4. As can be seen from these tables the reliability of density values predicted by TNRF-mNRTL model is better than the other three models. To see the performance of the studied models in a better manner, the difference between experimental and calculated apparent molar volume values for PEG4000 + NaClO₄ + H₂O system at 288.15K and the difference between experimental and calculated density values for PEG6000 + triammonium citrate + H₂O system at 308.15 K have been shown respectively in Figs. 3 and 4 as examples.

From Fig. 3 it is obvious that the fitting quality of ternary-Wilson, ternary-mWilson, and TNRF-mNRTL models is better than a ternary-mNRTL model for PEG4000 + NaClO₄ + H₂O system. However, for PEG6000 +triammonium citrate + H₂O system fitting quality of ternary-mNRTL and TNRF-mNRTL models is better than ternary-Wilson and ternary-mWilson models as shown in Fig. 4.

CONCLUSIONS

The new excess Gibbs energy equation was proposed for ternary polymer + electrolyte solutions (TNRF-mNRTL). This model along with Eyring absolute rate theory were applied to correlate the viscosity of ternary aqueous solutions of polymer + electrolyte considering temperature dependency. The local composition models which are available in the literature for correlating the thermodynamic properties of ternary polymer + electrolyte solutions (ternary-Wilson, ternary-modified NRTL, and ternary-modified Wilson) along with Eyring absolute rate theory were also used for fitting the viscosity values of ternary solutions. The fitting quality of Eyring-TNRF-mNRTL model was compared with these models. From the obtained results, we concluded that the reliability of Eyring-TNRF-mNRTL model in correlating the viscosity values of ternary polymer + electrolyte solutions is better than other local composition models investigated in this work. The necessary relations for excess molar volume of the TNRF-mNRTL, ternary-Wilson, ternary-mNRTL and ternary-mWilson models are not available in the literature. Therefore, these equations were derived for models investigated in this work and used in correlating the apparent molar volume and density values of ternary solutions of polymer +

Table 4: Comparison of the absolute average relative deviation (100.AARD) and standard deviation (σ) of the different local composition models in the correlation of the apparent molar volume values (V_ϕ) of the ternary aqueous solutions of polymer + electrolyte at different temperatures.

System	PEG+ NaClO$_4$	PEG+ NaClO$_4$	PEG+ NaClO$_4$	PEG +Triammonium Citrate	PEG +Triammonium Citrate	PEG +Triammonium Citrate	PEG +Triammonium Citrate
M_n (g.mol^{-1})	4000	4000	4000	6000	6000	6000	6000
Temperature range (°C)	15	25	35	25	30	35	40
N_P	12	12	12	29	29	29	29
Concentration range (w/w)	0.002-0.339 0.256-0.370	0.002-0.339 0.256-0.370	0.002-0.339 0.256-0.370	0.050-0.500 0.020-0.100	0.050-0.500 0.020-0.100	0.050-0.500 0.020-0.100	0.050-0.500 0.020-0.100
100.AARD ternary-Wilson	0.40 (0.06)[a]	0.37 (0.06)	11.2 (26.3)	9.81 (0.45)	29.19 (1.28)	24.30 (1.02)	20.62 (0.82)
$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) ternary-Wilson	0.15 (0.97)[b]	0.14 (0.88)	3.85 (26.3)	19.25 (5.63)	50.51 (13.83)	41.14 (11.04)	37.09 (8.99)
100.AARD ternary-mNRTL	12.43 (1.96)	6.35 (0.98)	6.81 (1.01)	2.45 (0.12)	3.40 (0.18)	4.75 (0.22)	5.53 (0.27)
$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) ternary-mNRTL	4.48 (26.83)	2.26 (13.08)	2.44 (14.22)	6.46 (1.76)	7.54 (2.72)	9.84 (2.75)	11.61 (3.26)
100.AARD ternary-mWilson	0.16 (0.02)	10.83 (1.66)	11.11 (1.62)	5.22 (0.25)	40.29 (1.79)	31.57 (1.31)	20.70 (0.91)
$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) ternary- mWilson	0.06 (0.40)	3.97 (27.31)	3.88 (26.36)	11.78 (3.45)	70.78 (24.96)	48.05 (15.41)	31.44 (11.06)
100.AARD TNRF_mNRTL	0.54 (0.09)	0.57 (0.09)	0.65 (0.10)	8.04 (0.39)	7.30 (0.38)	4.63 (0.23)	3.98 (0.17)
$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) TNRF_mNRTL	0.22 (1.38)	0.22 (1.37)	0.28 (1.76)	15.40 (5.4)	16.16 (5.17)	10.65 (3.02)	8.02 (2.15)
Source data	[5]	[5]	[5]	[32]	[32]	[32]	[32]

Table 4:

System	M_n (g.mol^{-1})	Temperature range (°C)	N_P	Concentration range (w/w)	100.AARD ternary-Wilson	$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) ternary-Wilson	100.AARD ternary-mNRTL	$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) ternary-mNRTL	100.AARD ternary-mWilson	$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) ternary- mWilson	100.AARD TNRF_mNRTL	$10^6 \cdot \sigma(V_\phi)$ (m^3 mol^{-1}) TNRF_mNRTL	Source data
PEG +Triammonium Citrate	6000	45	29	0.050-0.500 0.020-0.100	5.50 (0.21)	9.09 (2.84)	4.32 (0.18)	8.16 (2.47)	11.43 (0.33)	16.45 (4.68)	3.57 (0.15)	7.01 (1.99)	[32]
PEG + K$_3$PO$_4$	1000	20	7	0.130-0.220 0.105-0.122	2.37 (0.19)	2.12 (2.31)	3.35 (0.28)	2.66 (3.03)	5.00 (0.39)	3.92 (4.49)	1.73 (0.14)	1.54 (1.67)	[33]
PPG + MgSO$_4$	404	25	22	0.010-0.850 0.000-0.250	82.4 (2.31)	8.48 (42.99)	3.62 (0.18)	0.92 (2.74)	5.80 (0.35)	1.61 (6.76)	4.57 (0.40)	1.41 (9.24)	[7]
PPG + (NH$_4$)$_2$SO$_4$	404	25	8	0.605-0.772 0.100-0.500	3.93 (0.07)	1.23 (0.86)	3.92 (0.06)	1.16 (0.82)	3.14 (0.05)	1.02 (0.70)	2.38 (0.04)	0.82 (0.57)	[34]
PPG + Na$_2$SO$_4$	404	25	8	0.550-0.780 0.100-0.500	10.24 (0.11)	2.00 (1.55)	8.63 (0.10)	1.75 (1.35)	15.50 (0.21)	3.49 (2.37)	8.45 (0.09)	1.74 (1.36)	[34]
Overall					16.69 (2.72)	14.59 (9.38)	5.46 (0.46)	4.94 (6.25)	13.40 (0.74)	16.37 (10.66)	3.87 (0.19)	5.29 (2.92)	

a) *100.AARD values obtained from density data have been given in parenthesis.* [b]*The standard deviations of density (σ(d)/(kg/m^3)) are reported in the parenthesis.*

electrolyte. Results obtained in this work showed that the performance of TNRF-mNRTL model in fitting the apparent molar volumes and densities of ternary solutions of electrolyte + polymer is better than ternary-Wilson, ternary-mNRTL, and ternary-mWilson models.

APPENDIX A

Ternary-Wilson equation for the excess molar volume

Using the excess Gibbs energy of ternary-Wilson model [14] the following equations are obtained for the excess molar volume of ternary polymer + electrolyte solutions
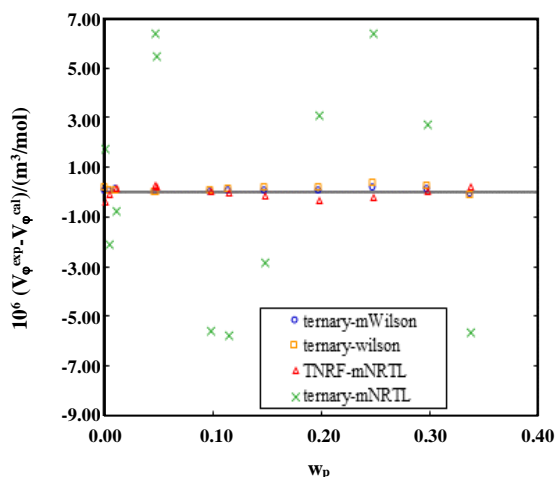
Fig. 3: Difference between experimental and calculated apparent molar volume values (V_ϕ) plotted against weight fraction of polymer (w_P) for PEG4000+ NaClO$_4$ +H$_2$O system at 288.15 K with different models.
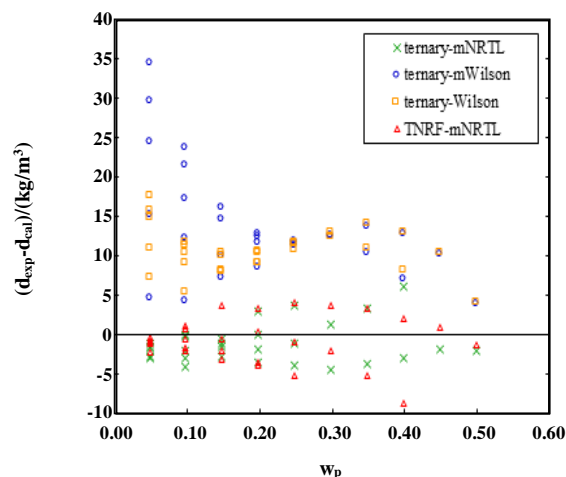

Fig. 4: Difference between experimental and calculated density values (d) plotted against weight fraction of polymer (w_P) for PEG6000 +triammonium citrate + H$_2$O system at 308.15K with different models.

$$V^{ex, Wilson} = \quad (A.1a)$$

$$x_m \left(\frac{X_a E^v_{cam} H_{cam}}{CRT} + \frac{X_c E^v_{cam} H_{cam}}{CRT} + \frac{r_p X_s E^v_{sm} H_{sm}}{CRT} \right) \Big/ \left(r_p X_s H_{sm} + X_c H_{cam} + X_a H_{cam} + X_m \right) +$$

$$r_p x_p \left(\frac{X_a E^v_{cas} H_{cas}}{CRT} + \frac{X_c E^v_{cas} H_{cas}}{CRT} + \frac{X_m E^v_{ms} H_{ms}}{CRT} \right) \Big/ \left(r_p X_s + X_c H_{cas} + X_a H_{cas} + X_m H_{ms} \right) +$$

$$z_a x_a \left(\frac{r_p X_s E^v_{sca} H_{sca}}{CRT} + \frac{X_m E^v_{mca} H_{mca}}{CRT} \right) \Big/ \left(r_p X_s H_{sca} + X_c + X_m H_{mca} \right) +$$

$$z_c x_c \left(\frac{r_p X_s E^v_{sca} H_{sca}}{CRT} + \frac{X_m E^v_{mca} H_{mca}}{CRT} \right) \Big/ \left(r_p X_s H_{sca} + X_a + X_m H_{mca} \right)$$

$$H_{cam} = \exp\left(-\frac{E_{cam}}{CRT}\right) \quad , \quad H_{mca} = \exp\left(-\frac{E_{mca}}{CRT}\right) \quad (A.1b)$$

$$H_{cas} = \exp\left(-\frac{E_{cas}}{CRT}\right) \quad , \quad H_{sca} = \exp\left(-\frac{E_{sca}}{CRT}\right) \quad (A.1c)$$

$$H_{sm} = \exp\left(-\frac{E_{sm}}{CRT}\right) \quad , \quad H_{ms} = \exp\left(-\frac{E_{ms}}{CRT}\right) \quad (A.1d)$$

In these equations, *C* is the coordination number of the model which is set to 10. E_{cam}, E_{mca}, E_{cas}, E_{sca}, E_{sm}, and E_{ms}

are parameters for the excess Gibbs energy which are determined from fitting the viscosity data to the ternary-Wilson model in this work. E^v_{cam}, E^v_{mca}, E^v_{cas}, E^v_{sca}, E^v_{sm}, and E^v_{ms} are the adjustable parameters of the model which are obtained from pressure derivative of E_{cam}, E_{mca}, E_{cas}, E_{sca}, E_{sm} and E_{ms}, respectively.

Ternary-mNRTL model for the excess molar volume

The excess molar volume of the ternary-mNRTL model can be derived from the excess Gibbs energy of ternary-mNRTL model [15] as follow

$$V^{ex, mNRTL} = B_1 (\tau^v_{cam} G_{cam}(X_a + X_c) + r_p X_s \tau^v_{sm} G_{sm} - \quad (A.2a)$$

$$\alpha \tau_{cam} \tau^v_{cam} G_{cam}(X_a + X_c) - r_p \alpha X_s \tau_{sm} \tau^v_{sm} G_{sm}) +$$

$$B_1^2 [x_m (\alpha \tau^v_{cam} G_{cam}(X_a + X_c) + r_p \alpha X_s \tau^v_{sm} G_{sm}) \times$$

$$(\tau_{cam} G_{cam}(X_a + X_c) + r_p X_s \tau_{sm} G_{sm})] +$$

$$r_p x_p B_2 [\tau^v_{cas} G_{cas}(X_a + X_c) +$$

$$X_m \tau^v_{ms} G_{ms} - X_m \tau_{ms} \alpha \tau^v_{ms} G_{ms}] $$

$$+ r_p x_p B_2^2 [\tau_{cas} G_{cas}(X_a + X_c) + X_m \tau_{ms} G_{ms}) \times$$

$$(X_m \tau_{ms} \alpha G_{ms} + \alpha \tau^v_{cas} G_{cas}(X_a + X_c)] +$$

$$B_3 [\tau^v_{mca} (G_{mca} - 1) X_a X_m +$$

$$r_p(\tau_{sca}^v - \tau_{mca}^v)(G_{sca} - G_{mca})X_s X_m -$$

$$r_p(\tau_{sca} - \tau_{mca})(\tau_{sca}^v \alpha G_{sca} - \tau_{mca}^v G_{mca})X_s X_m +$$

$$r_p \tau_{sca}^v (G_{sca} - 1)X_a X_s - \alpha\tau_{mca}\tau_{mca}^v G_{mca}X_a X_w -$$

$$r_p \alpha\tau_{sca}\tau_{sca}^v G_{sca}X_a X_s \big] +$$

$$B_4 \big[(\tau_{mca}^v \alpha G_{mca}X_m + r_p X_s \alpha\tau_{sca}^v G_{sca})(\tau_{mca}(G_{mca} - 1) +$$

$$r_p \alpha\tau_{sca}\left(G_{sca}^{-1}\right)X_a X_s \big]$$

$$B_1 = \frac{1}{(X_a + X_c)G_{cam} + r_p X_s G_{sm} + X_m} \qquad (A.2b)$$

$$B_2 = \frac{1}{(X_a + X_c)G_{cas} + r_p X_s G_{sm} + X_m G_{ms}} \qquad (A.2c)$$

$$B_3 = \frac{z_a x_a + z_c x_c}{(r_p X_s + X_a + X_m)(X_m G_{mca} + r_p G_{sca} + X_a)} \qquad (A.2d)$$

$$B_4 = \frac{z_a x_a + z_c x_c}{(r_p X_s + X_a + X_m)(X_m G_{mca} + r_p G_{sca} + X_a)^2} \qquad (A.2e)$$

$$G_{cam} = \exp(-\alpha\tau_{cam}) \quad , \quad G_{mca} = \exp(-\alpha\tau_{mca}) \qquad (A.2f)$$

$$G_{cas} = \exp(-\alpha\tau_{cas}) \quad , \quad G_{sca} = \exp(-\alpha\tau_{sca}) \qquad (A.2g)$$

$$G_{sm} = \exp(-\alpha\tau_{sm}) \quad , \quad G_{ms} = \exp(-\alpha\tau_{ms}) \qquad (A.2h)$$

Where α is nonrandomness factor and in this work, its value is set to 0.2. τ_{cam}, τ_{mca}, τ_{cas}, τ_{sca}, τ_{sm} and τ_{ms} are parameters for the excess Gibbs energy which are determined from fitting the viscosity data to the ternary-mNRTL model in this work. τ_{cam}^v, τ_{mca}^v, τ_{cas}^v, τ_{sca}^v, τ_{sm}^v, and τ_{ms}^v are the adjustable parameters of the model which are obtained from derivative of pressure of τ_{cam}, τ_{mca}, τ_{cas}, τ_{sca}, τ_{sm} and τ_{ms}, respectively.

Ternary-mWilson equation for the excess molar volume

The differentiation of the excess molar Gibbs energy expression of the ternary-mWilson model [16] respect to pressure yields the following equations for the excess molar volume of a ternary polymer + electrolyte solution

$$V^{ex,mWilson} = \qquad (A.3a)$$

$$-\frac{r_p x_p \left(\dfrac{-X_c E_{cas}^v H_{cas}}{CRT} - \dfrac{X_a E_{cas}^v H_{cas}}{CRT} - \dfrac{X_m E_{ms}^v H_{ms}}{CRT} \right)}{r_p X_s + X_c E_{cas} + X_a E_{cas} + X_w} -$$

$$\frac{Z_c x_c \left(\dfrac{-r_p X_s E_{sca}^v H_{sca}}{CRT} - \dfrac{X_m E_{mca}^v H_{mca}}{CRT} \right)}{r_p X_s H_{sca} + X_a + X_m H_{mca}} -$$

$$\frac{Z_a x_a \left(\dfrac{-r_p X_s E_{sca}^v H_{sca}}{CRT} - \dfrac{X_m E_{mca}^v H_{mca}}{CRT} \right)}{r_p X_s H_{sca} + X_a + X_m H_{mca}} -$$

$$\frac{x_m \left(\dfrac{-r_p X_s E_{sm}^v H_{sm}}{CRT} - \dfrac{X_c E_{cam}^v H_{cam}}{CRT} \right)}{r_p X_s H_{sm} + X_a H_{cam} + X_c H_{cam} + X_m} -$$

$$\frac{Z_c x_c (r_p X_s E_{sca}^v + X_m E_{mca}^v)}{(r_p X_s + X_a + X_c)RT} -$$

$$\frac{Z_a x_a (r_p X_s E_{sca}^v + X_m E_{mca}^v)}{(r_p X_s + X_a + X_c)RT}$$

$$H_{cam} = \exp\left(-\frac{E_{cam}}{CRT}\right) \quad , \quad H_{mca} = \exp\left(-\frac{E_{mca}}{CRT}\right) \qquad (A.3b)$$

$$H_{cas} = \exp\left(-\frac{E_{cas}}{CRT}\right) \quad , \quad H_{sca} = \exp\left(-\frac{E_{sca}}{CRT}\right) \qquad (A.3c)$$

$$H_{sm} = \exp\left(-\frac{E_{sm}}{CRT}\right) \quad , \quad H_{ms} = \exp\left(-\frac{E_{ms}}{CRT}\right) \qquad (A.3d)$$

In these equations, *C* is the coordination number of the model which is set to 10. E_{cam}, E_{mca}, E_{cas}, E_{sca}, E_{sm} and E_{ms} are the excess Gibbs energy parameters which are determined from fitting the viscosity data to the ternary-mWilson model in this work. E_{cam}^v, E_{mca}^v, E_{cas}^v, E_{sca}^v, E_{sm}^v and E_{ms}^v are the adjustable parameters of the model which are obtained from pressure derivative of E_{cam}, E_{mca}, E_{cas}, E_{sca}, E_{sm} and E_{ms}, respectively.

Nomenclature
Latin letter

A	Empirical adjustable parameter
A_0	Temperature-dependence parameter
A_1	Temperature-dependence parameter
A_v	Limiting Debye-Hückel slope for apparent molar volume
A_ϕ	Debye-Hückel constant for osmotic coefficient
C	Coordination number
c_i	Molar concentration of the solute species i, mol/L
d	Density of solution

D_m	Dielectric constant of pure solvent
d_m	Density of water, kg/m^3
E_{cam}	Adjustable parameter of Wilson and mWilson models
E_{cam}^v	Adjustable parameter of Wilson and mWilson models for apparent molar volume
E_{cas}	Adjustable parameter of Wilson and mWilson models
E_{cas}^v	Adjustable parameter of Wilson and mWilson models for apparent molar volume
E_{mca}	Adjustable parameter of Wilson and mWilson models
E_{mca}^v	Adjustable parameter of Wilson and mWilson models for apparent molar volume
E_{ms}	Adjustable parameter of Wilson and mWilson models
E_{ms}^v	Adjustable parameter of Wilson and mWilson models for apparent molar volume
E_{sca}	Adjustable parameter of Wilson and mWilson models
E_{sca}^v	Adjustable parameter of Wilson and mWilson models for apparent molar volume
E_{sm}	Adjustable parameter of Wilson and mWilson models
E_{sm}^v	Adjustable parameter of Wilson and mWilson models for apparent molar volume
e	Electronic charge, C
g_a^0	Reference states Gibbs energy for cells with central anion
g_c^0	Reference states Gibbs energy for cells with central cation
g_m^0	Reference states Gibbs energy for cells with central solvent
g_s^0	Reference states Gibbs energy for cells with central segment
g_{ii}	Eergies of interaction between i-i pairs of species
g_{ji}	Energies of interaction between j-i pairs of species
g^{ex}	Excess molar Gibbs energy, J/mol
$g^{ex,F\text{-}H}$	Excess molar Gibbs energy of Flory-Huggins relation, J/mol
$g^{ex,PDH}$	Excess molar Gibbs energy of Pitzer-Debye-Hückel theory, J/mol
$g^{ex,TNRF\text{-}mNRTL}$	Excess molar Gibbs energy of TNRF-mNRTL model, J/mol
I_x	Ionic strength in mole fraction basis
k	Boltzmann constant, J/K
M_m	Molar mass of solvent, kg/mol
m	Molality of the solution, mol/kg
N_A	Avogadro's number, mol^{-1}
p	Pressure
R	Gas universal constant, J/mol.K
r_i	Number of the segment of component i
T	Absolute temperature, K
t	Temperature, °C
X_{ii}	The effective local mole fractions of species i and i
X_{ji}	The effective local mole fractions of species j and i
x_i	Mole fraction of species
x_p	Mole fraction of polymer molecule
x_m	Mole fraction of solvent
V^{ex}	Molar excess volume of the solution
$V^{ex,F\text{-}H}$	Molar excess volume of Flory-Huggins relation
$V^{ex,LC}$	Molar excess volume of local composition model
$V^{ex,PDH}$	Molar excess volume of Pitzer-Debye-Hückel theory
$V^{ex,mWilson}$	Molar excess volume of mWilson model
$V^{ex,mNRTL}$	Molar excess volume of mNRTL model
$V^{ex,TNRF\text{-}mNRTL}$	Molar excess volume of TNRF-mNRTL model
$V^{ex,Wilson}$	Molar excess volume of Wilson model
V_ϕ	Apparent molar volume of the solution
V_ϕ^0	Limiting apparent molar volume of the solution
Z	Nonrandom factor
z_a	Charge number of anion
z_c	Charge number of cation
z_i	Charge number of ion i

Greek letter

α	Nonrandomness factor
ε	Permittivity of vacuum, C^2/N.m^2
η	Viscosity of solution, Pa.s
η_m	Viscosity of solvent, Pa.s
ρ	Closest distance parameter
λ_{Em}	Adjustable parameter of TNRF-mNRTL model
λ_{Em}^v	Adjustable parameter of TNRF-mNRTL model for apparent molar volume

λ_{Es}	Adjustable parameter of TNRF-mNRTL model
λ_{Es}^{v}	Adjustable parameter of TNRF-mNRTL model for apparent molar volume
λ_{mE}	Adjustable parameter of TNRF-mNRTL model
λ_{mE}^{v}	Adjustable parameter of TNRF-mNRTL model for apparent molar volume
λ_{ms}	Adjustable parameter of TNRF-mNRTL model
λ_{ms}^{v}	Adjustable parameter of TNRF-mNRTL model for apparent molar volume
λ_{sE}	Adjustable parameter of TNRF-mNRTL model
λ_{sE}^{v}	Adjustable parameter of TNRF-mNRTL model for apparent molar volume
λ_{sm}	Adjustable parameter of TNRF-mNRTL model
λ_{sm}^{v}	Adjustable parameter of TNRF-mNRTL model for apparent molar volume
τ_{cam}	Adjustable parameter of mNRTL model
τ_{cam}^{v}	Adjustable parameter of mNRTL model for apparent molar volume
τ_{cas}	Adjustable parameter of mNRTL model
τ_{cas}^{v}	Adjustable parameter of mNRTL model for apparent molar volume
τ_{mca}	Adjustable parameter of mNRTL model
τ_{cam}^{v}	Adjustable parameter of mNRTL model for apparent molar volume
τ_{ms}	Adjustable parameter of mNRTL model
τ_{ms}^{v}	Adjustable parameter of mNRTL model for apparent molar volume
τ_{sca}	Adjustable parameter of mNRTL model
τ_{sca}^{v}	Adjustable parameter of mNRTL model for apparent molar volume
τ_{sm}	Adjustable parameter of mNRTL model
τ_{sm}^{v}	Adjustable parameter of mNRTL model for apparent molar volume
ν_a	Stochiometric coefficients of anion
ν_c	Stochiometric coefficients of cation

Subscript

a	Anion
c	Cation
ca	Electrolyte
E	Electrolyte

i	Species i
m	Solvent
p	Polymer
s	Segment of polymer
x	Mole fraction basis

Superscript

ex	Excess
mNRTL	Modified non-random two-liquid model
mWilson	Modified Wilson model
PDH	Pitzer-Debye-Hückel model
TNRF-mNRTL	Ternary nonrandom factor-modified non-random two-liquid model
Wilson	Wilson model

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