Applicability of different equations in modeling the thermodynamic and transport properties of aqueous and non-aqueous ionic liquid solutions

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A B S T R A C T

Applicability of different electrolyte based models has been tested in correlating the osmotic coefficient values of aqueous and nonaqueous binary ionic liquid solutions considering both the complete and partial dissociation of the ionic liquids. In local composition models the sum of a long-range and a short-range term is used. When the partial dissociation of ionic liquid is considered, the Pitzer–Debye–Hückel and Fowler–Guggenheim equations were used to calculate the long-range electrostatic interaction. In the Fowler–Guggenheim equation, for calculating Debye inverse length the necessary degree of association has been determined from osmotic coefficient data by Chemical Model (CM1). The correlation equations for excess molar volume of the NRTL–NRF, mNRTL, NRF–Wilson and NRF–mNRTL models for ionic liquid or electrolyte solutions were also derived. The performance of these equations was compared with the other available models for correlating the excess molar volume of ionic liquid solutions. Taking into account of complete or partial dissociation of ionic liquids, fitting quality of solution viscosities of various ionic liquids were examined using the Eyring's absolute rate theory and different electrolyte local composition models and Clegg–Pitzer equations.

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1. Introduction

A new class of compounds (room temperature ionic liquid (RTIL)) are considered as green solvents in reaction and separation processes [1,2]. Physicochemical properties including osmotic coefficient, viscosity and density are necessary to design any process involving ionic liquids (ILs). Also, knowledge of these physicochemical properties may be used for elucidating the structural interactions occurring in IL solutions. Therefore, knowing the dependence of osmotic coefficient, density and viscosity to the composition and temperature, i.e., modeling of IL solutions is an essential need. This aim can be reached by correlations of these properties using fully empirical, semi empirical and theoretical equations. Over the last years, Pitzer [3], extended Pitzer model of Archer [4] and reduced form of modified NRTL [5] models have been used for fitting of the osmotic coefficient values of IL mixtures. Excess molar volume and apparent molar volume are also important physical properties which can be calculated from density values of IL solutions. Excess molar volumes of these solutions have usually been fitted with Redlich–

kister equation [6–8]. The Redlich–Mayer and Pitzer models [9] have been used for fitting of apparent molar volumes. For correlating the viscosity of IL mixtures, however, only a few equations have been used. In most cases viscosity deviation or deviation in logarithm of viscosity has been correlated with the Redlich–Kister polynomial [6–8]. Seddon et al. [10] have used the exponential relation for fitting the viscosity of IL solutions. Recently, Wang et al. [11] have used liquid based Eyring–NRTL and Eyring–UNIQUAC equations for calculating the viscosity values of IL-cosolvent mixtures.

For IL solutions, the correlation equations used so far for representation of the thermodynamic and transport properties, ILs are considered to be either non-ionized or completely ionized systems. In this work, our interest in the study of thermodynamic properties of IL solutions is focused on testing the applicability of different electrolyte based models considering both the cases of the partial and complete dissociation of ILs. For this purpose, the reliability of well known electrolyte models (i.e., NRTL [12], Wilson [13], NRTL–NRF [14], NRF–Wilson [15], reduced form of mNRTL [5], mNRTL [16], NRF–mNRTL [17], TCPC [18], Pitzer [3], Clegg–Pitzer [19] and extended Pitzer model of Archer [4]) has been investigated for correlating the osmotic coefficient values of aqueous and nonaqueous binary IL solutions. In applying these models, both the complete and partial dissociation of IL are considered. In local composition models the sum of a long-range

Nomenclature

Latin letters

A_0	Empirical adjustable parameters
A_1	Empirical adjustable parameters
A_ϕ	Debye–Hückel constant for osmotic coefficient
A_v	Limiting Debye–Hückel slope for apparent molar volume
a	Hard core collision diameter or distance of closest approach of ions in solution
a_+	Cationic radii
a_-	Anionic radii
C	Coordination number
c_i	Molar concentration of the solute species i
D	Dielectric constant of pure solvent
d	Density of solution
d_0	Density of the solvent
E_{me}	Parameters of NRF–Wilson model obtained from osmotic coefficient data
E_{me}^v	Parameters of NRF–Wilson model obtained from density data
E_{em}	Parameters of NRF–Wilson model obtained from osmotic coefficient data
E_{em}^v	Parameters of NRF–Wilson model obtained from density data
e	Electronic charge
g^{ex}	Excess Gibbs energy
g_{LR}^{ex}	Long-range electrostatic interaction term of excess Gibbs energy
g_{SR}^{ex}	Short-range interaction term of excess Gibbs energy
I_x	Ionic strength in mole fraction basis
K	Debye inverse length
k	Boltzmann constant
m	Molality
M	Molar mass
M_1	Molar mass of solvent
M_2	Molar mass of IL
N	Total number of data
N_A	Avogadro's number
N_i	Number of ionic species i in volume V_i
R	Universal constant of gases
S	Contribution of the shape and size of the solvent molecule
T	Absolute temperature
t	Temperature in the centigrade Celsius unit
V	Total volume of the solution
$\overline{V}$	Partial molar volume
V_i	Molar volume of component i
V_m^{ex}	Excess molar volume
x_1	Mole fraction of solvent
x_I	Mole fraction of component I
x_i	Mole fraction of component i
Z	Coordination number
z_c	Charge number of cation
z_a	Charge number of anion
z_i	Charge number of ion i

Greek letters

α	Degree of association
α_m	Nonrandomness factor in mNRTL model
β	Isothermal compressibility of the solvent
ε	Permittivity of vacuum
ϕ	Osmotic coefficient
ρ	Closest distance parameter
η	Solution viscosity
η_0	Solvent viscosity
η_i	Viscosity of component i
γ_1	Activity coefficient of solvent
γ_i	Activity coefficient of component i
λ_E	Parameters of NRF–mNRTL model obtained from osmotic coefficient data
λ_e	Parameters of NRTL–NRF model obtained from osmotic coefficient data
λ_E^v	Parameters of NRF–mNRTL model obtained from density data
λ_e^v	Parameters of NRTL–NRF model obtained from density data
λ_M	Parameters of NRTL–NRF model obtained from osmotic coefficient data
λ_m	Parameters of NRF–mNRTL model obtained from osmotic coefficient data
λ_M^v	Parameters of NRTL–NRF model obtained from density data
λ_m^v	Parameters of NRF–mNRTL model obtained from density data
$\tau_{ca,m}$	Parameters of mNRTL model obtained from osmotic coefficient data
$\tau_{ca,m}^v$	Parameters of mNRTL model obtained from density data
$\tau_{m,ca}$	Parameters of mNRTL model obtained from osmotic coefficient data
$\tau_{m,ca}^v$	Parameters of mNRTL model obtained from density data
$\omega_{ca,m}$	Parameters of mNRTL model obtained from osmotic coefficient data
$\omega_{ca,m}^v$	Parameters of mNRTL model obtained from density data
$\omega_{m,ca}$	Parameters of mNRTL model obtained from osmotic coefficient data
$\omega_{m,ca}^v$	Parameters of mNRTL model obtained from density data
ω_E	Parameters of NRF–mNRTL model obtained from osmotic coefficient data
ω_E^v	Parameters of NRF–mNRTL model obtained from density data
ω_m	Parameters of NRF–mNRTL model obtained from osmotic coefficient data
ω_m^v	Parameters of NRF–mNRTL model obtained from density data
ν_c	Stochiometric coefficients of cation
ν_a	Stochiometric coefficients of anion

Subscripts

0	Solvent
1	Solvent
2	IL
+	Cation
−	Anion
a	Anion
c	Cation
LR	Long-range
I	Component I
i	Component i
m	Solvent
SR	short-range
x	Mole fraction basis

Superscripts

ex	Excess