Research Article

Measurement and Modeling of Solubility of Galactose in Aqueous Ionic Liquids, 1-Butyl-3-Methyl Imidazolium Bromide, 1-Hexyl-3-Methyl Imidazolium Bromide and 1-Butyl-3-Methylimidazolium Chloride at T = (298.15 And 308.15) K

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ABSTRACT

Background: Saccharides are considered as abundant, cheap and renewable starting materials for chemicals and fuels. Recently, ionic liquids have been used as green solvents for saccharides. The solubility values of galactose in aqueous ionic liquid solutions are not available. Thus, the main objective of this research was to determine the solubility of galactose in aqueous solutions containing ionic liquids, 1-butyl-3-methyl imidazolium bromide, [BMIm]Br, 1-butyl-3-methylimidazolium chloride [BMIm]Cl and 1-hexyl-3-methyl imidazolium bromide, [HMIm]Br at different mole fractions of ionic liquids at T = (298.15 and 308.15) K.
Methods: In this study, the gravimetric method was used to measure the solubility of galactose in aqueous ionic liquids solutions.
Results: The solubility values of galactose in water and aqueous ionic liquid solutions were correlated with the activity coefficient models of Wilson, NRTL, modified NRTL, NRF-NRTL, and UNIQUAC.
Conclusion: It was concluded that with increasing the mole fraction of ionic liquids, the solubility values of galactose decrease and in fact all of these ionic liquids show salting-out effect on aqueous galactose solutions and this behavior is stronger in ionic liquid 1-butyl-3-methylimidazolium chloride.

Introduction

One of the significant challenges in biorefinery is the use of alternative sources replaced to fossil fuel reserves.[1,2] Saccharides derived from lignocellulosic biomass are considered as abundant, cheap and renewable starting materials for chemicals and fuels.[3] However, there are some barriers such as their high complexity and low solubility in traditional solvents that impede the efficient conversion of these materials.[4] Recently, ionic liquids have been used as green solvents for pretreatment of lignocellulosic biomass.[5] The studies show that ionic liquids can dissolve the main components of biomass or total.[6,7] There are some advantages in pretreatment with ionic liquids compared to other methods.[8] In pretreatment with ionic liquids, significantly shorter time is required for conversion of biomass to fermentable sugars. Also, production of inhibitors and the degradation of saccharides is less. Furthermore, relatively mild conditions are required for dissolution and hydrolysis reactions.[8] Despite these numerous advantages, commercial utilization of ionic liquids is restricted due to problems such as the high price of ionic liquids, difficulty at recycling of pure ionic liquids and high viscosity of

solutions. To overcome these problems, researchers suggested that aqueous ionic liquid solutions instead of pure ionic liquid can be utilized for biomass pretreatment.[9-12] Fu *et al.*[9] achieved a higher amount of fermentable saccharides when 50% ionic liquid was used compared to using pure ionic liquid under the similar conditions. Zhang *et al.*[11] obtained 90% glucan digestibility using aqueous ionic liquid 1-butyl-3-methylimidazolium chloride solutions when 10–30% water was used.

Study of interactions between monomers of saccharides and ionic liquids in aqueous solution is essential to find the optimal conditions for converting saccharides. To achieve this goal, a systematic study of thermophysical properties is required. In this work, in continuation to our previous papers,[13-20] the solubility values of galactose in aqueous ionic liquids, 1-butyl-3-methyl imidazolium bromide, [BMIm]Br, 1-hexyl-3-methyl imidazolium bromide, [HMIm]Br and 1-butyl-3-methylimidazolium chloride [BMIm]Cl have been measured at different ionic liquid mole fractions at T = (298.15 and 308.15) K using the gravimetric method.

Table 1. Descriptions of the used Chemicals.

Material	Provenance	CAS number	Purity (mass fraction)	Purification method	Analysis method
N-Methylimidazole	Merck	616-47-7	>0.99	None	
1-Chlorobutane	Merck	109-65-3	>0.99	None	
1-Bromobutane	Merck	109-65-9	>0.99	None	
1-Bromohexane	Merck	111-25-1	>0.99	None	
Ethyl acetate	Merck	141-78-6	>0.99	None	
Galactose	Merck	59-23-4	0.98	Dried in vacuum over P_2O_5 at room temperature	
[BMIm]Cl	Synthesis		~0.98	Rotary evaporator and dried under vacuum	^{1}H NMR and FTIR
[BMIm]Br	Synthesis		~0.98	Rotary evaporator and dried under vacuum	^{1}H NMR and FTIR
[HMIm]Br	Synthesis		~0.98	Rotary evaporator and dried under vacuum	^{1}H NMR and FTIR

To model the experimental solubility data of galactose in water and aqueous ionic liquid solutions, models such as Wilson,[21] NRTL,[22] modified NRTL,[23] NRF-NRTL[24] and UNIQUAC[25] were used. In this study, the effects of anion type and chain length of ionic liquids on galactose - ionic liquid interactions have also been investigated.

Materials and Methods
Chemicals
The provenance, CAS number, purity, purification and analysis method of the utilized chemicals are represented in Table 1. Galactose was dried in vacuum over P_2O_5 at room temperature for at least 72 h. For the preparation of solutions, freshly doubly distilled water was used. Mass fractions of water in the synthesized ionic liquids 1-butyl-3-methyl imidazolium bromide, 1-hexyl-3-methyl imidazolium bromide, and 1-butyl-3-methylimidazolium chloride were 0.0034, 0.0050 and 0.0035, respectively. The water content was measured using a microprocessor based automatic Karl–Fischer Titrator and was considered in the preparation of the aqueous solutions.

Synthesis of ionic liquids
The ionic liquids, 1-butyl-3-methyl imidazolium bromide, [BMIm]Br , 1-hexyl-3-methyl imidazolium bromide, [HMIm]Br and 1-butyl-3-methylimidazolium chloride [BMIm]Clwere synthesized as described in the literature.[26–28] The purity of the prepared ionic liquids in mass fraction is about 0.98. ^{1}H NMR (Brucker Av-300, CDCl₃) and FTIR (Perkin Elmer, Spectrum RXI) spectra for the investigated ionic liquids are shown in Figure S1-S3 in the Supporting Information.

Solubility measurement
In this study, the gravimetric method was used to measure the solubility of galactose in aqueous ionic liquids solutions. To prepare the aqueous ionic liquid solutions, an analytical balance with a precision of 1×10^{-7} kg (Shimadzu, 321-34553, Shimadzu Co., Japan) was used. The excess amount of galactose required for saturation was added. Then sealed vials containing galactose in the aqueous ionic liquid solutions were mixed using a magnetic stirrer (Behdad, Tehran, Iran) and placed in a bath with a constant temperature using a temperature controller (Julabo, MB, Germany) with a standard uncertainty of 0.01 K for three days to reach equilibrium. When a saturated solution was reached, the solid phase was removed by centrifugation (D-7200 Tuttlingen,

Hettich Co., America). The upper clear saturated solution was sampled using a syringe with a filter (Dura pore® membrane filters, type HV, 0.22 μm, Millipore, MA) and inserted into glass vessels, and immediately weighted. Then water of the solution was evaporated in a drying stove at 343.15 K for three days. To make sure that the weighed material did not contain water, a Karl Fisher titration on the solid residue was performed that show all of the water was completely removed in the drying oven. After the evaporation, the glass vessels with the samples were weighed. The solubility values of galactose in aqueous ionic liquid solutions were determined by the help of known initial ionic liquid concentration in the solution and the weight of the glass vessels in three conditions: (1) when they are empty, (2) with the saturated solution, and (3) with the dried sample. Each experimental data are represented as the average of three repetitive measurements.

Result and Discussion
Experimental result
The experimental solubility values of galactose in water and aqueous ionic liquids [BMIm]Br, [HMIm]Br, and [BMIm]Cl solutions at different mole fractions of ionic liquids are reported in Tables 2 and 3 at T = (298.15 and 308.15) K, respectively. The comparison of the obtained solubility values of galactose in pure water in this work with the literature[29,30] shows a good consistency between our data and literature at studied temperatures. Table 2 and 3 show that increase in the temperature from 298.15 K to 308.15 K enhances the solubility which means dissolution process of galactose in pure water and aqueous ionic liquid solution is endothermic. In Figure 1 and 2, the plot of solubility values of galactose in presence of studied ionic liquids at T = (298.15 and 308.15) K have been illustrated. According to these figures, in both temperatures, the solubility values decease by increasing the mole fraction of ionic liquids. This shows that interaction between galactose and investigated ionic liquids are unfavorable. In other words, these ionic liquids have a salting-out effect on aqueous galactose solutions. For three different ionic liquids considered in this study, our results show that the ionic liquid [BMIm]Cl has the strongest salting-out effect on aqueous galactose solutions.

In this study, we have studied the role of anion and cation of ionic liquids on solubility of galactose.

Table 2. Experimental solubility data for galactose in water and aqueous ionic liquid [BMIm]Br, [HMIm]Br and [BMIm]Cl solutions at T = 298.15 K and $P \approx$ 85 kPa.[a,b]

x_{IL}	x_{exp}
[BMIm]Cl	
0.0000	0.0462
0.0069	0.0438
0.0104	0.0424
0.0136	0.0414
0.0205	0.0389
[BMIm]Br	
0.0069	0.0440
0.0103	0.0430
0.0136	0.0418
0.0203	0.0399
[HMIm]Br	
0.0034	0.0455
0.0068	0.0450
0.0103	0.0444
0.0135	0.0440

[a] Standard uncertainties u for solubility, temperature and pressure are u (x) = 0.1, u (T) = 0.01 K, u (p) = 0.5 kPa, respectively.
[b] Relative standard uncertainty u_r for mole fraction of ionic liquids is u_r = 0.02.

Table 3. Experimental solubility data for Galactose in water and aqueous ionic liquid, [BMIm]Br, [HMIm]Br and [BMIm]Cl solutions at T = 308.15 K and $P \approx$ 85 kPa. [a,b]

x_{IL}	x_{exp}
[BMIm]Cl	
0.0000	0.0553
0.0036	0.0519
0.0066	0.0493
0.0105	0.0473
0.0170	0.0446
[BMIm]Br	
0.0032	0.0529
0.0068	0.0509
0.0101	0.0496
0.0135	0.0479
0.0170	0.0466
0.0201	0.0455
[HMIm]Br	
0.0067	0.0516
0.0102	0.0501
0.0135	0.0485
0.0168	0.0473
0.0202	0.0461

[a] Standard uncertainties u for solubility, temperature and pressure are u (x) = 0.1, u (T) = 0.01 K, u (p) = 0.5 kPa, respectively.
[b] Relative standard uncertainty u_r for mole fraction of ionic liquids is u_r = 0.02.

To see the effect of cation on solid - liquid equilibrium behavior of galactose, we compare the solubility values in aqueous ionic liquids [HMIm]Br and [BMIm]Br solutions. These ionic liquids have the same anion and different alkyl chain of cations. Our results show that the solubility values in the presence of ionic liquid [HMIm]Br are greater than the corresponding values in the presence of ionic liquid [BMIm]Br at both temperatures. This can be discussed based on different hydration behavior of ionic liquids. In our previous studies[15,16,19] we showed a higher affinity for water in ionic liquids having shorter alkyl chain. Our results showed that the activity coefficient values of ionic liquid [BMIm]Br in water are higher than the activity coefficient values of ionic liquid [HMIm]Br in water.[15,16,19]
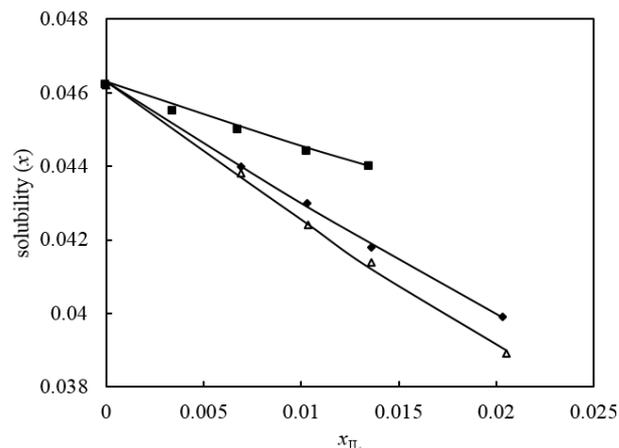
Figure 1. Solubility of galactose (x) in aqueous ionic liquid solutions at T = 298.15 K: ■, [HMIm]Br; ♦, [BMIm]Br; ∆, [BMIm]Cl; - NRTL mode.l.
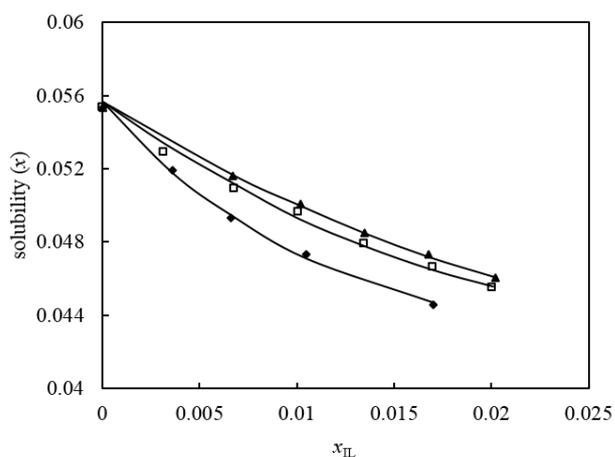
Figure 2. Solubility of galactose (x) in aqueous ionic liquid solutions at T = 308.15 K: ▲, [HMIm]Br; □, [BMIm]Br; ♦, [BMIm]Cl; - mNRTL model.

It means that [BMIm]Br-water interactions are stronger than [HMIm]Br-water interactions.[15,16,19] In ternary systems, it seems that ionic liquids with shorter alkyl chain have fewer tendencies to interact with galactose due to their higher tendency to interact with water. This behavior is consistent with the results obtained from vapor-liquid equilibrium behavior of {sucrose / fructose + [BMIm]Br / [HMIm]Br + water} systems in regard with sugar-ionic liquid interactions.[15,16] Our results are also consistent with the volumetric and viscometric results obtained by Shekaari and coworkers.[31] They studied density and viscosity of ternary {D-xylose + ionic liquids 1-hexyl-3-methyl imidazolium bromide or 1-octyl-3-methyl imidazolium bromide or 1-decyl-3-methylimidazoliume bromide + water} systems. Their results showed that the standard partial molar volumes (V_Φ^0) and the viscosity B-coefficient values increase as the alkyl chain length increases which indicate that when the chain length of ionic liquid increases, D-xylose-ionic liquid interactions become stronger.[31] In other study, they showed that the standard partial molar volumes of glucose in presence of ionic liquid 1-hexyl-3-methyl imidazolium

bromide have higher values in comparison to ionic liquid 1-pentyl-3-methyl imidazolium bromide.[32]

To see the effect of anion on solid - liquid equilibrium behavior of galactose, we compare the solubility values in the presence of ionic liquids [BMIm]Br and [BMIm]Cl. These ionic liquids have the same cation and different anions. Our results show that the solubility values in the presence of ionic liquid [BMIm]Br are greater than the corresponding values in presence of ionic liquid [BMIm]Cl. In our previous study,[19] we showed that an ionic liquid with smaller anion's size has stronger interaction with water than the ionic liquid with larger anion's size. Our results showed that the activity coefficient values of ionic liquid [BMIm]Cl in water are higher than the activity coefficient values of ionic liquid [BMIm]Br in water.[19] It means that [BMIm]Cl-water interactions are stronger than [BMIm]Br-water interactions.[19] The Gibbs energies of hydration for Cl⁻ and Br⁻ anions that are -340 kJ· mol⁻¹ and -315 kJ· mol ⁻¹, respectively[33] also fulfill this expectation. In ternary solution, Cl⁻ anion in comparison to Br⁻ anion due to higher hydration, shows less tendency to interact with galactose, therefore ionic liquid [BMIm]Cl has stronger salting-out effect on aqueous galactose solutions. The results obtained in this work are in agreement with those obtained by the Gibbs transfer energy values of fructose and sucrose in presence of ionic liquids 1-hexyl-3-methyl imidazolium bromide [HMIm]Br and 1-hexyl-3-methyl imidazolium chloride [HMIm]Cl reported in ref.[19]. Our results are also consistent with Kazempour[34] results in regard with the volumetric and viscometric properties of D-glucose in ternary aqueous solutions containing ionic liquids [HMIm]Br and [HMIm]Cl. They showed that standard partial molar volumes and viscosity *B*-coefficient values of D-glucose in presence of ionic liquid [HMIm]Br are higher compared with the corresponding values in presence of ionic liquid [HMIm]Cl which mean [HMIm]Br-glucose interactions are stronger than [HMIm]Cl-glucose interactions.[34]

Correlation of experimental solubility by activity coefficient models

For nonelectrolyte solutes, most thermodynamic models base the activity coefficient on the activity of hypothetical subcooled liquid solute, which is calculated using the enthalpy of fusion of the solute.[35] In this article, another procedure is used for correlating the solubility data of sugar in water and in presence of ionic liquids. This method has already been used for modeling of solubility of amino acid in water and aqueous ionic liquid solutions.[36,37] Here this is the first time that we evaluate the applicability of this procedure for modeling the solubility of a sugar in water and in presence of ionic liquids. The more details of this procedure can be found in detail in the literature.[37]

Thermodynamics of solubility of galactose in water

Solid -liquid equilibrium of galactose in water is expressed as the following equation:

$$K_s = x_A \gamma_A \qquad \text{Eq. (1)}$$

In the above equation, K_s is the solubility constant in mole fraction scale. x_A and γ_A are the mole fraction and activity coefficient of galactose in mole fraction scale, respectively. In this article, the following equation suggested by Chen[22] is used to express the relation of solubility constant to the temperature:

$$\ln K_s = a + \frac{b}{T} + c \ln T \qquad \text{Eq. (2)}$$

By equaling the equations 1 and 2, the following equation is obtained:

$$\ln x_A \gamma_A = a + \frac{b}{T} + c \ln T \qquad \text{Eq. (3)}$$

where *a*, *b* and *c* are adjustable parameters and can be estimated by minimizing the following objective function:

$$OF = \sum_j \left(x_j^{cal} - x_j^{exp} \right)^2 \qquad \text{Eq. (4)}$$

To determine the parameters *a*, *b* and *c*, the solubility data of galactose in water at different temperatures together with activity coefficient data are required. By inserting the binary energy parameters for galactose – water (obtained from correlating of water activity data reported in Ref. [38]) in the activity coefficient relation for each model, activity coefficient of galactose in any concentration is obtained. We used the solubility data for galactose in water within the temperature ranges from (298.15 to 348.15) K[29] and water activity data[38] to get parameters *a*, *b* and *c*. The obtained fitting parameters and the absolute relative percentage deviations (*Dev* %) are reported in Table 4. By *Dev%* values, we conclude that all the local composition models utilized in this study can be successfully used for the modeling the solubility of galactose in water.

Table 4. Solubility constants of galactose in water [a]

Models	*a*	*b*	*c*	*Dev%*
NRTL and mNRTL	-303.839	11959.571	45.772	0.656
NRF-NRTL	-328.094	13059.156	49.381	0.756
UNIQUAC	-224.973	8642.210	33.879	0.475
Wilson	-269.773	10440.495	40.687	0.525

[a] $Dev\% = \frac{1}{NP} \sum_{l=1}^{NP} \frac{\left| x_{w,l}^{exp} - x_{w,l}^{cal} \right|}{x_{w,l}^{exp}}$,NP is the number of experimental data points.

Thermodynamics of solubility of galactose in aqueous ionic liquid solution

In solid–liquid equilibrium, the solubility of sugar in an aqueous solution containing an electrolyte can be stated as:

$$x_A^{ter} \gamma_A^{ter} = x_A^{bin} \gamma_A^{bin} \qquad \text{Eq.(5)}$$

where "bin" and "ter" refer to binary and ternary systems, respectively. By equaling the equations 3 and 5, the following equation is obtained:

$$\ln x_A^{ter} \gamma_A^{ter} = a + \frac{b}{T} + c \ln T \qquad \text{Eq. (6)}$$

According to equation (6), the parameters *a*, *b* and *c* reported in Table 4 enable us to model solubility of galactose in aqueous ionic liquid solutions using an appropriate activity coefficient model for γ_A^{ter}. The required relation for activity coefficient of sugar in ternary solution is obtained by appropriate differentiation of the corresponding g^{ex} model. When the local composition models are used in the obtained activity coefficient relation, there are six parameters for each model. The binary sugar–water and ionic liquid –water interaction parameters are obtained by fitting the water activity data for these binary solutions to the corresponding relation for water activity. Galactose-ionic liquid parameters can be obtained from fitting of experimental solubility of galactose in ternary solutions.
In this work, we used the water activity data of (D-galactose + H₂O) system taken from Refs. [38, 39] to get the sugar-water energy parameters at *T* = (298.15 and 308.15) K. The water activity data for [HMIm]Br-H₂O, [BMIm]Br-H₂O and [BMIm]Cl-H₂O systems taken from Refs.[16,40-43] were used to get ionic liquid-water interaction parameters at *T* = (298.15 and 308.15) K. In this work, for modeling of solubility of galactose in aqueous ionic liquid solutions, for the first time, activity coefficient models such as Wilson,[21] NRTL,[22] modified NRTL,[23] NRF-NRTL[24] and UNIQUAC[25] have been utilized. In our previous studies[14-19], we found that the above models show good performance in modeling vapor-liquid equilibrium behavior for some (saccharide + ionic liquid + water) systems. In this work, the capability of these models has been examined for modeling the solubility of galactose in aqueous solutions containing ionic liquids 1-butyl-3-methyl imidazolium bromide, [BMIm]Br, 1-hexyl-3-methyl imidazolium bromide, [HMIm]Br and 1-butyl-3-methylimidazolium chloride [BMIm]Cl.

Activity coefficient models for (saccharide + ionic liquid + water)
For modeling the solubility of galactose in aqueous ionic liquid solutions, a suitable activity coefficient model is required. This relation is derived from the corresponding excess Gibbs energy relation. Excess Gibbs energies of (saccharide + ionic liquid + water) systems have two contributions (long range and short range):

$$\frac{g^{E}}{RT} = \frac{g^{E,LR}}{RT} + \frac{g^{E,SR}}{RT} \qquad \text{Eq.(7)}$$

In the above relation, the long-range (*LR*) and short-range (*SR*) interaction terms consider the electrostatic interactions between ions, and the non-electrostatic interactions between all species, respectively.
In this work, excess Gibbs energy of the Pitzer-Debye Hückel (PDH) equation is used for considering the long-range interaction term:[44, 45]

$$\frac{g^{ex.PDH}}{RT} = -\left(\sum_i x_i\right)\frac{4A_x I_x}{\rho}\ln\left(1+\rho I_x^{0.5}\right) \qquad \text{Eq. (8)}$$

where

$$A_x = \frac{1}{3}\left(\frac{2\pi N_A}{V_w}\right)^{\frac{1}{2}}\left(\frac{e^2}{4\pi\varepsilon D_w kT}\right)^{\frac{3}{2}} \qquad \text{Eq. (9)}$$

The parameters, ρ, N_A, k, ε and e represent the closest distance parameter, Avogadro's number, Boltzmann constant, permitivity of vacuum and electronic charge, respectively. x_i is the mole fraction of component i. I_x is the ionic strength in mole fraction basis. For aqueous solutions $\rho = 14.9$ was chosen. The V_w and D_w are the molar volume and dielectric constant of the solvent.
For short range contribution of $g^{E,SR}$, Wilson,[21] NRTL,[22] modified NRTL,[23] NRF-NRTL[24] and UNIQUAC[25] models have been considered.
The $g^{E,SR}$, in the Wilson model for (ionic liquid + sugar + water) system has the following form:[21]

$$\frac{g_{Wilson}^{E.SR}}{CRT} = -X_w \ln\left(\frac{X_m H_{mw} + (X_a + X_c)H_{ca,w} + X_w}{X_m + X_c + X_a + X_w}\right)$$
$$- X_m \ln\left(\frac{X_w H_{mw} + (X_a + X_c)H_{ca,m} + X_m}{X_m + X_c + X_a + X_w}\right)$$
$$- X_a \ln\left(\frac{X_m H_{m,ca} + X_c + X_w H_{w,ca}}{X_m + X_c + X_w}\right)$$
$$- X_c \ln\left(\frac{X_m H_{m,ca} + X_a + X_w H_{w,ca}}{X_m + X_a + X_w}\right)$$
Eq. (10a)

In the above equation, the subscripts *w*, *m*, *ca*, *c* and *a* denote water, sugar, electrolyte, cation and anion, respectively. X_i is the effective mole fraction:

$$X_i = x_i K_i$$

($K_i = Z_i$ For ions and $K_i = $ unity for molecules).
Eq.(10b)

In equation (10a), *C* is the effective coordination number in the system equal to 10 in this work, Z is the charge number; *H, h* and *E* are energy parameters.

$$H_{ij} = \exp\left(-\frac{(h_{ij} - h_{jj})}{CRT}\right) = \exp\left(-\frac{E_{ij}}{CRT}\right) \quad \text{Eq. (10c)}$$

$$H_{ij,kj} = \exp\left(-\frac{(h_{ij} - h_{kj})}{CRT}\right) = \exp\left(-\frac{E_{ij,kj}}{CRT}\right) \text{Eq. (10d)}$$

$$E_{cm} = E_{am} = E_{ca,m}, \qquad E_{cw} = E_{aw} = E_{caw} \quad \text{Eq. (10e)}$$

$$E_{m,ca} = E_{mc,ac} = E_{ma,ca}, \; E_{w,ca} = E_{wc,ac} = E_{wa,ca},$$
Eq. (10f)

$$E_{ac} = E_{ca} = E_{ca,ca} \qquad \text{Eq. (10g)}$$

In the above relations, species i, j and k are cation, anion, sugar or solvent molecule.

The NRTL model has also been used for modeling the solubility of galactose in presence of ionic liquids. In the NRTL model, $g^{E,SR}$, for (ionic liquid + sugar + water) system is expressed as:[22]

$$\frac{g_{NRTL}^{E,SR}}{RT} = X_w \left(\frac{X_m G_{mw} \tau_{mw} + (X_a + X_c) G_{ca,w} \tau_{ca,w}}{X_m G_{mw} + (X_a + X_c) G_{ca,w} + X_w} \right)$$

$$X_m \left(\frac{X_w G_{wm} \tau_{wm} + (X_a + X_c) G_{ca,m} \tau_{ca,m}}{X_w G_{wm} + (X_a + X_c) G_{ca,m} + X_m} \right)$$

$$+ X_a \left(\frac{X_w G_{w,ca} \tau_{w,ca} + X_m G_{m,ca} \tau_{m,ca}}{X_w G_{w,ca} + X_m G_{m,ca} + X_c} \right)$$

$$+ X_c \left(\frac{X_w G_{w,ca} \tau_{w,ca} + X_m G_{m,ca} \tau_{m,ca}}{X_w G_{w,ca} + X_m G_{m,ca} + X_a} \right),$$

$$\text{Eq. (11a)}$$

where G and τ are energy parameters:

$$G_{ij} = \exp\left(-\alpha_{ij} \frac{(g_{ij} - g_{jj})}{RT}\right) = \exp(-\alpha_{ij} \tau_{ij}) = \exp\left(-\alpha_{ij} \frac{a_{ij}}{RT}\right)$$

$$\text{Eq.(11b)}$$

$$G_{ij,kj} = \exp\left(-\alpha_{ij,kj} \frac{(g_{ij} - g_{kj})}{RT}\right) = \exp\left(-\alpha_{ij}, k_j \tau_{ij}, k_j\right)$$

$$= \exp\left(-\alpha_{ij}, k_j \frac{a_{ij,kj}}{RT}\right) \qquad \text{Eq. (11c)}$$

$$a_{cm} = a_{am} = a_{ca,m}, \qquad a_{cw} = a_{aw} = a_{ca,w} \quad \text{Eq. (11d)}$$

$$a_{m,ca} = a_{mc,ac} = a_{ma,ca} \qquad a_{w,ca} = a_{wc,ac} = a_{wa,ca}$$

$$\text{Eq. (11e)}$$

$$a_{ac} = a_{ca} = a_{ca,ca} \qquad \text{Eq. (11f)}$$

where α is the nonrandomness factor. The values of α utilized in this study have been explained in the next sections. The performance of modified NRTL (mNRTL) model[23] was also checked for modeling the solubility of galactose in (ionic liquid + water) systems. The modified NRTL model has been extended for the modeling of vapor–liquid equilibrium for (polymer + salt + water) systems.[23] In our previous studies,[14-17,19] we used this model for representing the vapor–liquid equilibrium of (ionic liquid + sugar + water) systems. $g^{E,SR}$, in the mNRTL model for (ionic liquid + sugar + water) system is expressed in Eq. 12.

In this work, for representing the solubility in these systems, we have also used NRF-NRTL model. This model has been presented for the correlation of vapor–liquid equilibrium of (polymer–salt-water) systems.[24] This model takes the following form (Eq. 13) for (ionic liquid + sugar + water) systems.

In this work, in order to obtain good performance of different version of NRTL models, the value of 0.4 was selected for the nonrandomness factor in galactose – water, [BMIm]Cl-water, [BMIm]Br-water and [HMIm]Br-water pairs at 298.15 K. For binary galactose -[BMIm]Br and galactose -[BMIm]Cl pairs at 298.15 K, the value of 0.1 was selected for α . However, the best quality of fitting in NRTL model was obtained when we choose nonrandomness factor for binary galactose - [BMIm]Cl pair as 0.4. The nonrandomness factor for galactose -[HMIm]Br pair was fixed at 0.4 at 298.15 K. At 308.15 K, the nonrandomness factor for galactose – water and [HMIm]Br -water, pairs was set at 0.4. At this temperature, the value of 0.1 was selected for [BMIm]Br –water and galactose -[BMIm]Cl.

$$\frac{g_{mNRTL}^{E,SR}}{RT} = X_w \left(\frac{X_m G_{mw} \tau_{mw} + (X_c + X_a) G_{ca,w} \tau_{ca,w}}{X_m G_{mw} + (X_a + X_c) G_{ca,w} + X_w} \right)$$

$$X_m \left(\frac{X_w G_{wm} \tau_{wm} + (X_{c_n} + X_{a_n}) G_{ca,m} \tau_{ca,m}}{X_w G_{wm} + (X_a + X_c) G_{ca,m} + X_m} \right)$$

$$+ X_a \left(\frac{X_w X_m (\tau_{m,ca} - \tau_{w,ca})(G_{m,ca} - G_{w,ca}) + X_w X_c \tau_{w,ca}(G_{w,ca} - 1) + X_m X_c \tau_{m,ca}(G_{m,ca} - 1)}{(X_w G_{w,ca} + X_m G_{m,ca} + X_c) B_c} \right)$$

$$+ X_c \left(\frac{X_w X_m (\tau_{m,ca} - \tau_{w,ca})(G_{m,ca} - G_{w,ca}) + X_w X_a \tau_{w,ca}(G_{w,ca} - 1) + X_m X_c \tau_{m,ca}(G_{m,ca} - 1)}{(X_w G_{w,ca} + X_m G_{m,ca} + X_a) A} \right)$$

$$\text{Eq. (12)}$$

$$A = X_s + X_a + X_w$$
$$B = X_s + X_c + X_w$$

$$\frac{g_{NRF}^{E,SR}}{RT} = X_w\left(\frac{X_m G_{mw}\tau_{mw} + (X_a + X_c)G_{ca,w}\tau_{ca,w}}{X_m G_{mw} + (X_a + X_c)G_{ca,w} + X_w} - \left(X_m\tau_{mw} + (X_a + X_c)\tau_{ca,w}\right)\right)$$

$$X_m\left(\frac{X_w G_{wm}\tau_{wm} + (X_a + X_c)G_{ca,m}\tau_{ca,m}}{X_w G_{wm} + (X_a + X_c)G_{ca,m} + X_m} - \left(X_w\tau_{wm} + (X_a + X_c)\tau_{ca,m}\right)\right)$$

$$+ X_a\left(\frac{X_w G_{w,ca}\tau_{w,ca} + X_m G_{m,ca}\tau_{m,ca}}{X_w G_{w,ca} + X_m G_{m,ca} + X_c} - \left(X_w\tau_{w,ca} + X_m\tau_{m,ca}\right)\right)$$

$$+ X_c\left(\frac{X_w G_{w,ca}\tau_{w,ca} + X_m G_{m,ca}\tau_{m,ca}}{X_w G_{w,ca} + X_m G_{m,ca} + X_a} - \left(X_w\tau_{w,ca} + X_m\tau_{m,ca}\right)\right)$$

Eq. (13)

In binary [BMIm]Cl-water pair, α was set at 0.01; however when we select it as 0.4 in NRF-NRTL model, we get the best quality of fitting. In galactose-[BMIm]Br pair, in mNRTL, NRF-NRTL and NRTL models, we set α at 0.1,0.1 and 0.4, respectively. In galactose-[HMIm]Br pair, in mNRTL, NRF-NRTL and NRTL models α was fixed at 0.1, 0.1, and 0.01, respectively.

The applicability of UNIQUAC activity coefficient model has also been examined in description of solubility of galactose in (ionic liquid + water) solutions. There are two terms for representation of the UNIQUAC group contribution model: a combinatorial (enthalpic) and a residual (entropic) term. In this work, the extended UNIQUAC model[25] was used for phase equilibrium behavior of (galactose + ionic liquid + water) system. For any component i, the $g^{ex, SR}$ in UNIQUAC model equation has the following form:

$$\frac{g_{UNIQUAC}^{E,SR}}{RT} = \frac{g_{(combinatorial)}^{E,SR}}{RT} + \frac{g_{(residual)}^{E,SR}}{RT}$$

$$\frac{g_{(combinatorial)}^{E,SR}}{RT} = \sum_{i=1}^{m} x_i \ln\frac{\psi_i^*}{x_i} + \frac{z}{2}\sum_{i=1}^{m} q_i x_i \ln\frac{\theta_i}{\psi_i^*}$$

$$\frac{g_{(residual)}^{E,SR}}{RT} = -\sum_{i=1}^{m} q_i' x_i \ln\left(\sum_{i=1}^{m}\theta_i'\tau_{ji}\right)$$

Eq. (14a)

Segment fraction ψ_i^* and area fractions θ_i, θ_i', and τ_{ji} (energy parameters) are given by:

$$\psi_i^* = \frac{r_i x_i}{\sum_i r_i x_i}$$

Eq. (14b)

$$\theta_i = \frac{q_i x_i}{\sum_i q_i x_i}$$

Eq. (14c)

$$\theta_i' = \frac{q' x_i}{\sum_i q' x_i}$$

Eq. (14d)

$$\tau_{ji} = \exp\left(-\frac{\Delta u_{ji}}{RT}\right)\exp\left(-\frac{a_{ji}}{T}\right)$$

Eq. (14e)

In the above equations, q_i and q_{0i} are relative molecular surface area. r_i is relative molecular volume. z is the coordination number in the system equal to 10. Basically, q_0 is equal to q except for water and alcohols.[25] These values obtained from the literature.[46-48] For galactose, [BMIm]Br, [HMIm]Br and [BMIm]Cl, the values 5.8028, 7.081, 8.897 and 5.467, respectively have been used for r. For galactose, [BMIm]Br, [HMIm]Br and [BMIm]Cl, the values 4.84, 5.69, 7.613 and 4.574, respectively have been used for q.

Table 5-10 enlist the parameters of the used activity coefficient models. The *Dev %* values of Wilson, NRTL, mNRTL, NRF-NRTL and UNIQUAC models obtained from fitting the solubility values of galactose in aqueous ionic liquid solutions show that all of these models can satisfactorily correlate the experimental solid-liquid equilibrium data for the studied systems at T = (298.15 and 308.15) K. In (galactose + [BMIm]Cl + water) system, however, higher *Dev %* values obtained with the Wilson , NRTL and UNIQUAC models at T = 308.15 K, show the lower capability of these models in fitting solubility data at this temperature.

Table 5. Values of parameters of Wilson, NRTL, mNRTL, NRF- NRTL and UNIQUAC models (J·mol^{-1}) for {galactose + [BMIm]Cl + H$_2$O} system at T = 298.15 K.

Wilson model

E_{mw}	E_{wm}	$E_{ca,w}$	$E_{w,ca}$	$E_{ca,m}$	$E_{m,ca}$	*Dev%*
7830.512	-11976.733	-29246.3846	59440.7568	1354.8166	42791.2902	0.130

NRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
-0.4280	-3.4170	-2.4926	5.1090	-0.7964	4.9469	0.202

mNRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
-0.4280	-3.4170	-2.0690	4.5422	-24.2182	-68.2670	0.154

Table 5 Continued.

NRF model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
2.9687	1.5783	-2.1144	4.6592	17.4370	4.3930	0.242

UNIQUAC model

Δu_{mw}	Δu_{wm}	$\Delta u_{ca,w}$	$\Delta u_{w,ca}$	$\Delta u_{ca,m}$	$\Delta u_{m,ca}$	Dev%
-589.504	-976.099	-58.910	-1719.797	203.161	2579.294	0.158

Table 6. Values of parameters of Wilson, NRTL, mNRTL, NRF- NRTL and UNIQUAC models (J·mol^{-1}) for {galactose + [BMIm]Br + H$_2$O} system at T = 298.15 K.

Wilson model

E_{mw}	E_{wm}	$E_{ca,w}$	$E_{w,ca}$	$E_{ca,m}$	$E_{m,ca}$	Dev%
7830.512	-11976.733	-26894.939	56486.876	-22120.336	61442.588	0.094

NRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
-0.4280	-3.4170	-1.9665	4.4867	-13.6427	14.9620	0.107

mNRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
-0.4280	-3.4170	-1.2578	3.8446	6.6466	9.2711	0.141

NRF model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
2.9687	1.5783	-1.1920	3.9386	90.0353	-92.4746	0.140

UNIQUAC model

Δu_{mw}	Δu_{wm}	$\Delta u_{ca,w}$	$\Delta u_{w,ca}$	$\Delta u_{ca,m}$	$\Delta u_{m,ca}$	Dev%
-589.504	-976.099	-1386.553	839.290	-913.128	2275.506	0.125

Table 7. Values of parameters of Wilson, NRTL, mNRTL, NRF- NRTL and UNIQUAC models (J·mol^{-1}) for {galactose + [HMIm]Br + H$_2$O} system at T = 298.15 K.

Wilson model

E_{mw}	E_{wm}	$E_{ca,w}$	$E_{w,ca}$	$E_{ca,m}$	$E_{m,ca}$	Dev%
7830.512	-11976.733	-28446.636	62546.044	-37886.179	174388.281	0.105

NRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
-0.4280	-3.4170	-2.0103	5.1629	-14.4910	27.9530	0.150

mNRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
-0.4280	-3.4170	-1.3039	4.6594	12117.9910	17.5540	0.171

NRF model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
2.9687	1.5783	-1.1180	4.7132	2.8699	17.0324	0.210

UNIQUAC model

Δu_{mw}	Δu_{wm}	$\Delta u_{ca,w}$	$\Delta u_{w,ca}$	$\Delta u_{ca,m}$	$\Delta u_{m,ca}$	Dev%
-589.504	-976.099	-1481.013	1481.013	-2898.024	42972.558	0.135

Table 8. Values of parameters of Wilson, NRTL, mNRTL, NRF- NRTL and UNIQUAC models (J·mol^{-1}) for { galactose + [BMIm]Cl + H$_2$O} system at T = 308.15 K.

Wilson model

E_{mw}	E_{wm}	$E_{ca,w}$	$E_{w,ca}$	$E_{ca,m}$	$E_{m,ca}$	Dev%
3875.762	-8292.044	5359.556	-38540.023	49783.136	375340.002	1.960

NRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
-0.4019	-3.2930	3.3867	-11.9226	-24.2844	198.3691	2.133

mNRTL model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
-0.4019	-3.2930	-12.2252	45.9306	-24.2581	-65.7513	0.358

NRF model

τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	Dev%
1.961	0.386	4.568	3.165	17.479	-55.475	0.275

UNIQUAC model

Δu_{mw}	Δu_{wm}	$\Delta u_{ca,w}$	$\Delta u_{w,ca}$	$\Delta u_{ca,m}$	$\Delta u_{m,ca}$	Dev%
-726.348	-797.139	-339.295	-1786.27	-364.782	33045.433	1.584

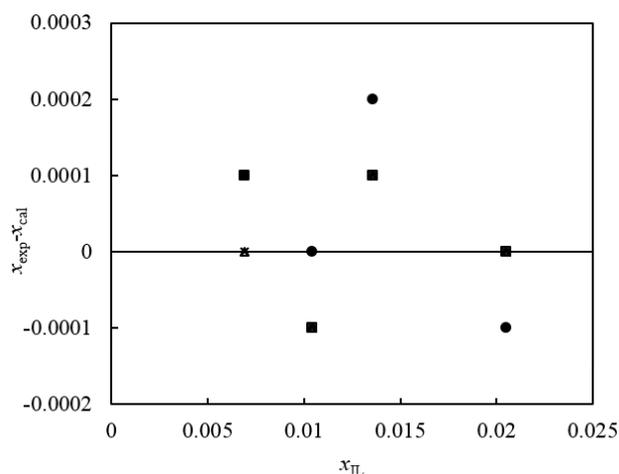**Table 9.** Values of parameters of Wilson, NRTL, mNRTL, NRF- NRTL and UNIQUAC models (J·mol^{-1}) for { galactose + [BMIm]Br + H$_2$O} system at T = 308.15 K.
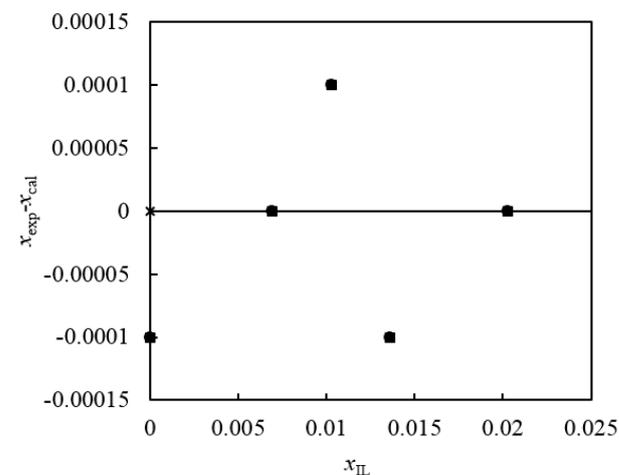
Wilson model						
E_{mw}	E_{wm}	$E_{ca,w}$	$E_{w,ca}$	$E_{ca,m}$	$E_{m,ca}$	*Dev%*
3875.762	-8292.044	-28485.383	60632.884	-30067.281	490936.580	0.847
NRTL model						
τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
-0.4019	-3.2930	-2.1700	5.0587	-94.8137	362.6702	0.484
mNRTL model						
τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
-0.4019	-3.2930	1.9404	16.4121	-22.2702	-71.8715	0.513
NRF model						
τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
1.96120	0.38563	-31.1782	98.4555	0.0846	104.9152	0.425
UNIQUAC model						
Δu_{mw}	Δu_{wm}	$\Delta u_{ca,w}$	$\Delta u_{w,ca}$	$\Delta u_{ca,m}$	$\Delta u_{m,ca}$	*Dev%*
-726.348	-797.139	-1105.204	398.097	37988.914	-647.043	1.285

Table 10. Values of parameters of Wilson, NRTL, mNRTL, NRF- NRTL and UNIQUAC models (J·mol^{-1}) for {galactose + [HMIm]Br + H$_2$O} system at T = 308.15 K.

Wilson model						
E_{mw}	E_{wm}	$E_{ca,w}$	$E_{w,ca}$	$E_{ca,m}$	$E_{m,ca}$	*Dev%*
3875.762	-8292.044	-31060.259	70290.832	-33726.431	504238.979	0.458
NRTL model						
τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
-0.4019	-3.2930	-2.2682	6.0798	-48.4281	549.7495	0.256
mNRTL model						
τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
-0.4019	-3.2930	-1.8609	5.9007	-20.9121	-53.1965	0.289
NRF model						
τ_{mw}	τ_{wm}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\tau_{ca,m}$	$\tau_{m,ca}$	*Dev%*
1.9612	0.3856	-1.7407	5.9007	51.6855	-61.3089	0.180
UNIQUAC model						
Δu_{mw}	Δu_{wm}	$\Delta u_{ca,w}$	$\Delta u_{w,ca}$	$\Delta u_{ca,m}$	$\Delta u_{m,ca}$	*Dev%*
-726.348	-797.139	7845.7564	-1958.1397	125663.263	3414.046	1.055

In Figure 3-8, we have depicted the difference between experimental and calculated solubility data obtained from different models for these systems to see the performances of all the models used in this work.

good performances of the above local composition models considered in this work in representing solubility of galactose in (ionic liquid + water) solutions. Reported parameters in Table 5-10, enable us to calculate the solubility of galactose in aqueous ionic liquid solutions at T = (298.15 and 308.15) K with different models. These values are presented in Table S1-S6.
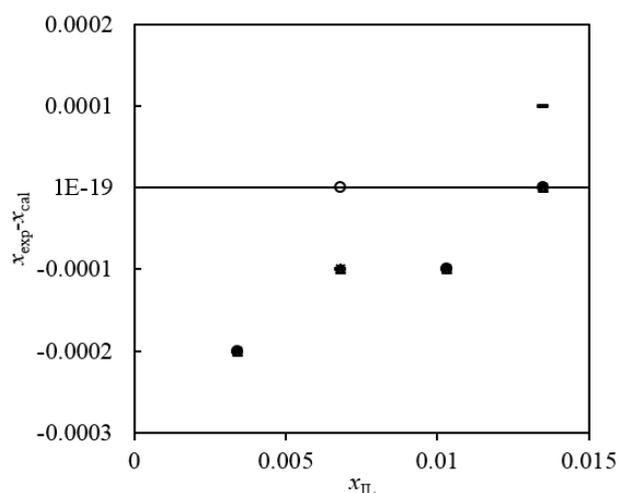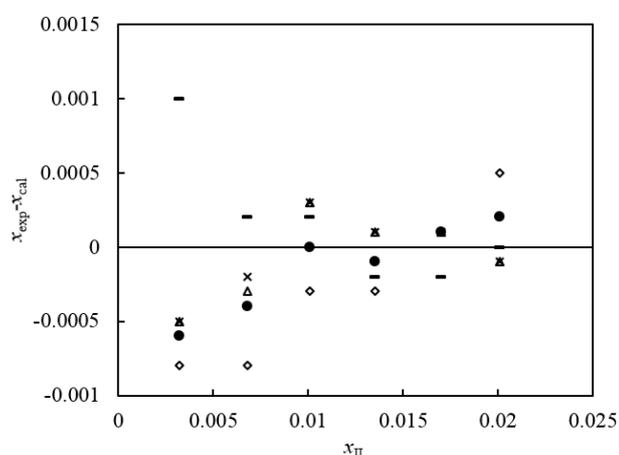

Figure 3. Plot of the difference between the experimental and calculated solubility values, against mole fraction of ionic liquid [BMIm]Cl; •, NRTL model; ◊ , Wilson model; ×, mNRTL model; △, NRF- NRTL model; □, UNIQUAC model at T = 298.15 K.

According to these figures, small differences between experimental and calculated solubility data indicate the

Figure 4. Plot of the difference between the experimental and calculated solubility values, against mole fraction of ionic liquid [BMIm]Br; ○, NRTL model; ◊ , Wilson model; △, mNRTL model; △ ,NRF- NRTL model; ■, UNIQUAC model at T = 298.15 K.
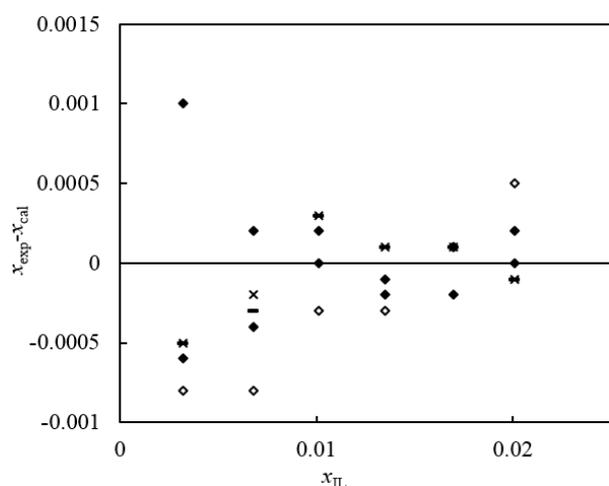
Figure 5. Plot of the difference between the experimental and calculated solubility values, against mole fraction of ionic liquid [HMIm]Br; ×, NRTL model; ◊ , Wilson model; △, mNRTL model; - ,NRF- NRTL model; ○, UNIQUAC model at *T* = 298.15 K.
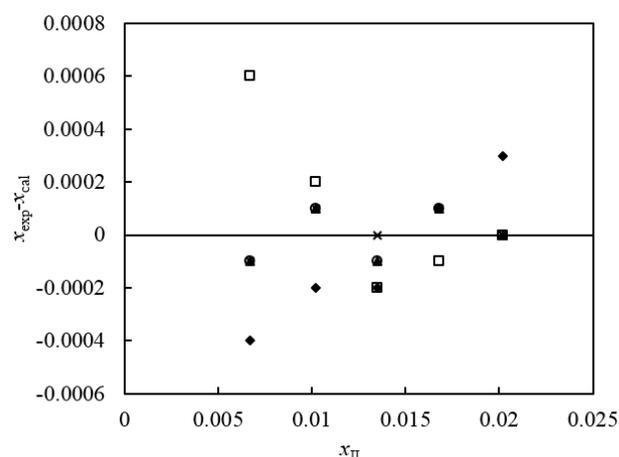

Figure 6. Plot of the difference between the experimental and calculated solubility values, against mole fraction of ionic liquid [BMIm]Cl; ×, NRTL model; ◊ , Wilson model; △, mNRTL model; •, NRF- NRTL model; -,UNIQUAC model at *T* = 308.15 K.

Figure 7. Plot of the difference between the experimental and calculated solubility values, against mole fraction of ionic liquid [BMIm]Br; ×, NRTL model; ◊ , Wilson model; -; mNRTL model; △,NRF- NRTL model ; ♦,UNIQUAC model at *T* = 308.15 K.

Figure 8. Plot of the difference between the experimental and calculated solubility values, against mole fraction of ionic liquid [HMIm]Br; ×, NRTL model; ♦ , Wilson model; ○, mNRTL model; ▲, NRF- NRTL model; □,UNIQUAC model at *T* = 308.15 K.

Conclusion

The solubility of galactose in aqueous solutions containing ionic liquids, 1-butyl-3-methyl imidazolium bromide, [BMIm]Br, 1-hexyl-3-methyl imidazolium bromide, [HMIm]Br and 1-butyl-3-methylimidazolium chloride [BMIm]Cl has been measured at different ionic liquids mole fractions at $T = (298.15$ and $308.15)$ K using the gravimetric method. To model the experimental solubility data, the activity coefficient models of Wilson, NRTL, modified NRTL, NRF-NRTL and UNIQUAC were utilized. The results show that all of these models can be successfully used to model the solubility of galactose in aqueous ionic liquids solutions. However, in (galactose + [BMIm]Cl + water) system, higher *Dev %* values obtained with the Wilson , NRTL and UNIQUAC models at $T=308.15$ K, show the lower capability of these models in fitting solubility data at this temperature. The experimental solubility data obtained in this work show that with increasing the mole fraction of ionic liquids, the solubility values of galactose decrease and in fact the studied ionic liquids have a salting-out effect on aqueous galactose solutions at $T = (298.15$ and $308.15)$ K. Our results for three different ionic liquids considered in this study show that ionic liquid [BMIm]Cl has the strongest salting-out effect in comparison to other studied ionic liquids which is due to its high tendency to interact with water.

Acknowledgements

Conflict of interests
The authors claim that there is no conflict of interest.

Supplementary Materials
Supplementary file contains Figure S1-S3 and Table S1-S6 is available on the journal's web site along with the published article

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