



Full Paper

Predicting Ionic Liquids' Second-Order Derivative Properties Based on a Combination of SAFT- γ EoS and a GC Technique

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ABSTRACT

Considering the high number of ionic liquids (ILs) and the impracticability of laboratory measurements for all properties of ILs, applying theoretical methods to predict the properties of this large family of ILs can be very helpful. In the present research, the thermophysical properties of ILs are predicted by a combination of statistical associating fluid theory and the group contribution concept (SAFT- γ GC EoS). The studied ionic liquids are 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][CF₃SO₃]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][CF₃SO₃]), 1,3-dimethylimidazolium methylsulfate ([mmim][MeSO₄]), 1-ethyl-3-methylimidazolium methylsulfate ([emim][MeSO₄]), 1-butyl-3-methylimidazolium methylsulfate ([bmim][MeSO₄]), 1-ethyl-3-methylimidazolium methanesulfonate ([emim][MeSO₃]) and 1-ethyl-3-methylimidazolium ethylsulfate ([emim][EtSO₄]). The thermophysical properties including the coefficient of thermal expansion, coefficient of thermal pressure, coefficient of isentropic compressibility, coefficient of isothermal compressibility, speed of sound, isochoric and isobaric heat capacities are estimated within broad ranges of pressure and temperature (0.1-60 MPa and 273-413 K). The comparison among the SAFT- γ predictions and some available experimental data shows good ability of SAFT- γ EoS to estimate the second-order derivative thermophysical properties of ILs.

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1. Introduction

Ionic Liquids can dissolve a large variety of substances. They have a wide range of liquidity, minor volatility and good chemical

and thermal stability [1-5]. Because of these desirable properties, the replacement of common organic solvents with ILs in various industrial processes is very demanded. The

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preparation of a medium for the absorption of CO₂, and the extraction of heavy metal ions from aqueous solutions, sulfur mixtures from gasolines and paraffins from aromatic compounds is among the industrial examples of ILs applications [1, 2, 6-10].

The accurate knowledge of the properties of the liquids is required to design many industrial processes involving ILs. However, considering the high number of ILs (approximately 10¹⁸) and the impracticability of experimental measurements for all these ILs, this knowledge is still inadequate for ILs [1, 2]. Therefore, predicting the thermodynamic properties of this large family of ILs using theoretical models can be a helpful method [11].

To investigate the phase behavior of complex fluids, SAFT-based equations of state (EoS) are very useful [11, 12]. Until now, several forms of SAFT EoS have been used to estimate the density and the gas solubility of ionic liquids [13-22], but a few researches have been focused on the second-order derivative properties of ILs (the coefficients of thermal expansion and thermal pressure, the coefficients of isothermal and isentropic compressibility, sound speeds, heat capacities and etc.) [11, 12].

Llovel et al. [17, 23] successfully predicted the density and coefficients of isothermal compressibility and thermal expansion of some ionic liquids by means of the soft-SAFT EoS [17, 23]. Maghari et al. [24] determined the density, sound speeds, thermal expansion and isothermal compressibility of some ILs by using the SAFT-Back EoS [24]. For some ILs with [PF₆], [Tf₂N] or [BF₄] anions, Bakhtazma and Alavi [25] obtained density and second-order thermodynamic derivatives including the density, sound velocity, heat capacities, the coefficients of isentropic and

isothermal compressibility and coefficients of thermal pressure and thermal expansion based on ePC-SAFT EoS [25]. Sun et al. [11] developed the ePC-SAFT equation to estimate the second-order derivatives and gas solubility of several ILs with various anions and cations [11].

In our previous works [21, 22], a combination of statistical associating fluid theory and the group contribution concept (SAFT- γ GC EoS) was applied to estimate density and CO₂ solubility of some imidazolium-derivative ILs with either [Tf₂N], [BF₄], [PF₆], [MeSO₄], [MeSO₃], [CF₃SO₃] or [EtSO₄] anions. In our recent work [26], this equation has also been used to estimate the density and thermophysical properties of some ionic liquids with imidazolium-based cations and [SCN], [DCA], [TCM] or [TCB] anions. The SAFT- γ GC EoS is able to consider various interactions including association interactions in IL systems. This GC EoS evaluates the anion and cation of IL separately and also considers the cation's alkyl chain as smaller groups of CH₃ and CH₂. These considerations make the model more comprehensive for a wider range of ILs [21, 22]. Furthermore, unlike the Ji and Adidharma's model [18], it is assumed in the SAFT- γ model that the heteronuclear segments connected together in a tangential direction as the consequence of thermodynamic perturbation theory of Wertheim [27-33]. The SAFT- γ GC technique is developed in the geometry of molecules by introducing the shape factor parameter. This factor indicates the share of a certain segment in the geometry of molecule [33].

In the present research, I estimate the second-order derivative properties of some ILs ([emim][CF₃SO₃], [bmim][CF₃SO₃], [mmim][MeSO₄], [emim][MeSO₄],

[bmim][MeSO₄], [emim][MeSO₃] and [emim][EtSO₄]) based upon the model of SAFT- γ GC EoS.

2. Model

In the present work, it is assumed that the IL system consists of the single-segment functional groups of CH₃, CH₂, cationic-head and anion [21, 22]. In the following, the symbols i (or j), k (or l) and a (or b) respectively express component i (or j), group k (or l) and the association site type a (or b). In the SAFT- γ model, each fused segment is defined by four parameters of diameter (σ_{kk}), shape factor (S_{kk}), dispersive energy (ϵ_{kk}) and its range (λ_{kk}). σ_{kl} , ϵ_{kl} , λ_{kl} are unlike potential parameters to characterize interactions between different groups. Also, ϵ_{klab}^{HB} and r_{klab}^c ($a = 1, \dots, NST_k$; $b = 1, \dots, NST_l$) are respectively the association energy parameter between association sites and the cut-off distance. In addition, NC , NG and NST_k are respectively the number of components, the number of functional groups and association site types' number of group k . Also, ρ , ρ_i , X_{ika} , n_{ka} , $v_{k,i}$ and x_i respectively indicate the number density of component i , the number density of mixture, the not-associated share of component i at the association sites type a on group k , the number of association site type a on group k , the number of group k in component i and the mole fraction of component i [21, 33].

The following equation shows the SAFT- γ model in the form of Helmholtz energy (A)

[33].

$$\frac{A}{Nk_B T} = \frac{A^{ideal}}{Nk_B T} + \frac{A^{mono}}{Nk_B T} + \frac{A^{chain}}{Nk_B T} + \frac{A^{assoc}}{Nk_B T} \quad (1)$$

where A^{ideal} and A^{mono} are the ideal Helmholtz energy and Helmholtz energy of hard-sphere dispersions and repulsions. Also, A^{chain} and A^{assoc} show the Helmholtz energy of the molecules' formation from hetero-nuclear segments and the Helmholtz energy of the associative bonding, and N , k_B and T respectively indicate the total number of molecules, Boltzman constant and temperature. The ideal Helmholtz energy is determined by Eq. (2) [21, 22, 33].

$$\frac{A^{ideal}}{Nk_B T} = \left(\sum_{i=1}^{NC} x_i \ln(\rho_i \Lambda_i^3) \right) - 1 \quad (2)$$

where Λ_i is the de Broglie wavelength of component i . It isn't required to precisely define Λ_i in the calculation of thermophysical properties [21, 33].

The Helmholtz energy of hard-sphere dispersions and repulsions is specified according to Eq. (3).

$$\frac{A^{mono}}{Nk_B T} = \frac{A^{HS}}{Nk_B T} + \frac{A_1}{Nk_B T} + \frac{A_2}{Nk_B T} \quad (3)$$

A^{HS} , A_1 and A_2 are respectively the hard-sphere free energy, the mean attractive energy and the second-order term of attractive energy that are determined by the following equations [21, 33].

$$\frac{A^{HS}}{Nk_B T} = \frac{6}{\pi \rho} \left[\left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1 - \zeta_3) + 3 \frac{\zeta_1 \zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3 (1 - \zeta_3)^2} \right] \quad (4)$$

$$\frac{A_1}{Nk_B T} = -\frac{\rho}{k_B T} \times \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j \sum_{k=1}^{NG} \sum_{l=1}^{NG} v_{k,i} v_{l,j} v_k^* v_l^* S_k S_l \alpha_{kl}^{vdw} g_{0,kl}^{HS} \quad (5)$$

$$\frac{A_2}{Nk_B T} = -\frac{K^{HS} \rho}{2} \left(\frac{1}{k_B T} \right)^2 \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j \sum_{k=1}^{NG} \sum_{l=1}^{NG} v_{k,i} v_{l,j} v_k^* v_l^* S_k S_l \epsilon_{kl} \alpha_{kl}^{vdw} \left(g_{0,kl}^{HS} + \zeta_3 \frac{\partial g_{0,kl}^{HS}}{\partial \zeta_{kl}^{eff}} \frac{\partial \zeta_{kl}^{eff}}{\partial \zeta_3} \right) \quad (6)$$

where ζ_0 , ζ_1 , ζ_2 and ζ_3 are the reduced densities and can be calculated by:

$$\zeta_m = \frac{\pi\rho}{6} \sum_{i=1}^{NC} x_i \sum_{k=1}^{NG} v_{k,i} v_k^* S_k \sigma_{kk}^m \quad m=0, 1, 2, 3 \quad (7)$$

α_{kl}^{vdw} , $g_{0,kl}^{HS}$, K^{HS} and ζ_{kl}^{eff} are respectively van der Waals attractive parameter, the pair

$$\frac{A^{CHAIN}}{Nk_B T} = - \sum_{i=1}^{NC} x_i \left(\sum_{k=1}^{NG} v_{k,i} v_k^* S_k - 1 \right) \ln g_{ii}^{SW}(\bar{\sigma}_{ii}; \zeta_3) \quad (8)$$

$$\frac{A^{assoc}}{Nk_B T} = \sum_{i=1}^{NC} x_i \sum_{k=1}^{NG} v_{k,i} \sum_{a=1}^{NST_k} n_{ka} \left(\ln X_{ika} + \frac{1 - X_{ika}}{2} \right) \quad (9)$$

where $g_{ii}^{SW}(\bar{\sigma}_{ii}; \zeta_3)$ is the square-well radial distribution function at the effective contact distance ($\bar{\sigma}_{ii}$) and the actual packing fraction (ζ_3) of the mixture. $g_{ii}^{SW}(\bar{\sigma}_{ii}; \zeta_3)$, $\bar{\sigma}_{ii}$ and X_{ika} has been defined in Ref. [21, 33].

In the present work, one association site type b (electropositive site) on the cationic-head group and one association site type a (electronegative site) on the anionic group are taken into consideration for the associative bonding between the cationic-head and anionic group [21, 22]. In addition, the reported parameters by Lymperiadis et al. [34] are used for CH₃ and CH₂ groups. Also, our previously reported parameters are employed for the cationic-head and anion groups [21, 22] and σ_{kl} , ϵ_{kl} , λ_{kl} (unlike the potential parameters between different groups) are determined based on arithmetic relations [33].

The coefficients of the isothermal compressibility (κ_T) and thermal expansion (α) are obtained according to Eqs. (10) and (11) [25]:

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (10)$$

correlation function, the isothermal compressibility of the reference hard-sphere mixture and the effective packing fraction which are completely defined in Refs. [21, 33].

The contribution terms of A^{chain} and A^{assoc} are defined based on the following equations.

$$\alpha = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (11)$$

By dividing the coefficient of thermal expansion (α) by the coefficient of the isothermal compressibility (κ_T), the coefficient of thermal pressure (γ) is determined [25].

$$\gamma = \frac{\alpha}{\kappa_T} \quad (12)$$

The isobaric and isochoric heat capacities (C_P , C_V) are computed based upon Eqs. (13) and (14) [25].

$$C_P = C_V + \frac{T\alpha^2}{\rho\kappa_T} \quad (13)$$

$$C_V = C_P^{ig} - R - T \left(\frac{\partial^2 a^{res}}{\partial T^2} \right)_p \quad (14)$$

where C_P^{ig} , R and $\left(\frac{\partial^2 a^{res}}{\partial T^2} \right)_p$ are respectively

the isobaric heat capacity of the ideal gas, the universal gas constant and the second-order derivative of the residual molar Helmholtz free energy with respect to temperature. C_P^{ig} can be calculated employing Joback's group contribution model [35-37].

The sound speed (u) and the isentropic compressibility (κ_s) are also obtained by Eqs. (15) and (16) [25].

$$u = \sqrt{\frac{C_p}{C_v} \left(\frac{\partial \rho}{\partial P} \right)_T^{-1}} \quad (15)$$

$$\kappa_s = \kappa_T \frac{C_v}{C_p} \quad (16)$$

3. Results and discussion

The values of κ_T , α , γ , C_v , C_p , κ_s and u were estimated according to the SAFT- γ GC equation for [emim][CF₃SO₃], [bmim][CF₃SO₃], [mmim][MeSO₄], [emim][MeSO₄], [bmim][MeSO₄], [emim][MeSO₃] and [emim][EtSO₄]. The

SAFT- γ predictions of thermophysical properties were compared with the accessible experimental data. The AARD % (the average absolute relative deviation) among predicted and experimental properties is obtained by Eq. (17) [21]. The values of AARD % in the thermophysical properties of ILs are observed in Table 1.

$$\text{AARD \%} = \frac{1}{\text{ND}} \times \sum_{i=1}^{\text{ND}} \left| \frac{M_i^{\text{Exp.}} - M_i^{\text{Calc.}}}{M_i^{\text{Exp.}}} \right| \times 100 \quad (17)$$

where ND, $M_i^{\text{Calc.}}$ and $M_i^{\text{Exp.}}$ respectively define the number of the experimental data, and the values of calculated and experimental properties of ILs.

Table 1

The AARD % between the theoretical and experimental second-order thermodynamic derivative properties.

IL	κ_T	α	γ	C_v	C_p	κ_s	u	T (K)	P (MPa)	No.*	Ref.
[emim] [CF ₃ SO ₃]	18.16	14.73	22.24					293.15-393.15	0.1-35	65	Gardas et al. [39]
					14.81			313.15-353.15	0.1	3	Diedrichs and Gmehling [48]
					19.63			293.15, 313.15	0.1	2	Musial et al. [49]
							6.85	293.15-333.15	0.1	3	Musial et al. [49]
						11.99	12.48	293.15-333.15	0.1	3	Vercher et al. [42]
[bmim] [CF ₃ SO ₃]	15.03	5.36	0.63					293.15-393.15	0.1-10	42	Gardas et al. [50]
					10.84			293.15-353.15	0.1	4	Paulechka et al. [51]
					10.59			313.15-373.15	0.1	4	Diedrichs and Gmehling [48]
					9.52			293.15-373.15	0.1	5	Theoretical method of Ge et al. [37]
					2.86			293.15-353.15	0.1	4	Ge et al. [37]
					14.57			293.15, 313.15	0.1	2	Musial et al. [49]
							9.04	293.15-333.15	0.1	3	Musial et al. [49]
[mmim] [MeSO ₄]	7.23	5.72	14.09					313.15-333.15	0.1-25	34	Goldon et al. [52]
							1.49	318.15-333.15	0.1	4	Pereiro et al. [44]
[emim] [MeSO ₄]	7.58	9.23	15.57					293.15-393.15	0.1-35	60	Tome et al. [40]
							2.71	293.15-333.15	0.1	3	Requejo et al. [45]
[bmim] [MeSO ₄]	3.52	12.43	15.68					293.15-393.15	0.1-35	60	Matkowska and Hofmann [38]

				24.66				293.15-373.15	0.1	5	Theoretical method of Ge et al. [37]
							2.25	293.15-333.15	0.1	3	Pereiro et al. [46]
[emim] [MeSO ₃]	10.57	16.85	24.35					273.15-413.15	0.1-60	81	Safarov et al. [53]
				7.08	6.68	12.21	6.96	273.15-413.15	0.1-60	81	Musial et al. [41]
					10.433			283.15-333.15	0.1	4	Ficke et al. [43]
	35.94	10.28	26.64					293.15-393.15	0.1-35	60	Tome et al. [40]
[emim] [EtSO ₄]					19.62			313.15-353.15	0.1	3	Nieto de Castro et al.[54]
				23.07		20.54	293.15, 313.15	0.1	2		Garcia-Miaja et al. [55]
				12.28			293.15-373.15	0.1	5		Fernandez et al. [56]
				18.79			293.15-353.15	0.1	4		Ge et al. [37]
						19.09	293.15-333.15	0.1	3		Gomez et al. [57]
* Number of experimental data											

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Based on the data of Table 1, the average error in the values of the isothermal compressibility coefficient is 14.26 % for 402 data points. As an example, Figure 1 shows the κ_T values of [emim][CF₃SO₃] at different

temperatures and pressures. The κ_T values increase with the rise in temperature and decrease by increasing pressure. This behavior was also observed for other ILs investigated in the present research.

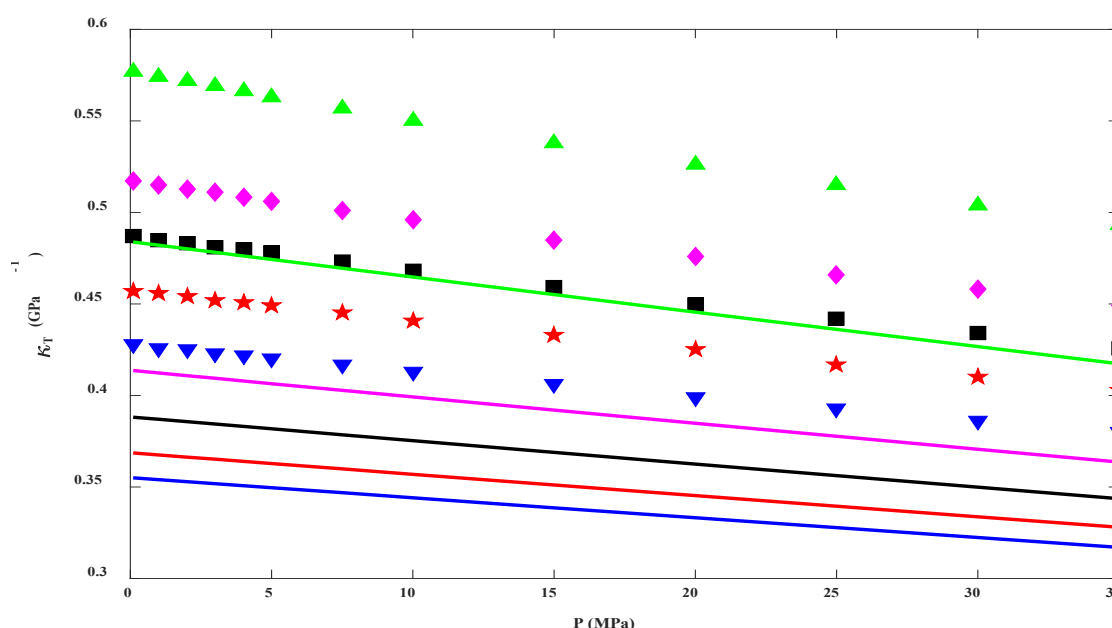


Figure 1. The isothermal compressibility coefficient (κ_T) versus pressure for [emim][CF₃SO₃] at different temperatures (393.15 (▲), 353.15 (◆), 333.15 (■), 313.15 (★) and 293.15 (▼) K). The experimental data of Gardas et al. [39] and the κ_T predictions of SAFT- γ EoS have been respectively shown by the symbols and the solid lines.

The average error of 11.58 % was observed between the experimental and SAFT- γ

predicted α values for 402 data points. Figure 2 indicates the α values of [bmim][MeSO₄]

versus pressure and temperature. The experimental α values of [bmim][MeSO₄] were determined based upon the density correlation of Matkowska and Hofmann [38].

Table 1 shows the average error of 18.40 % in the values of thermal pressure coefficient

for 402 data points. Figure 3 also displays the γ values for [emim][MeSO₄]. As seen in this figure, γ values decrease with the rise in temperature and pressure. This behavior was observed for other studied imidazolium, sulfate or sulfonate ILs.

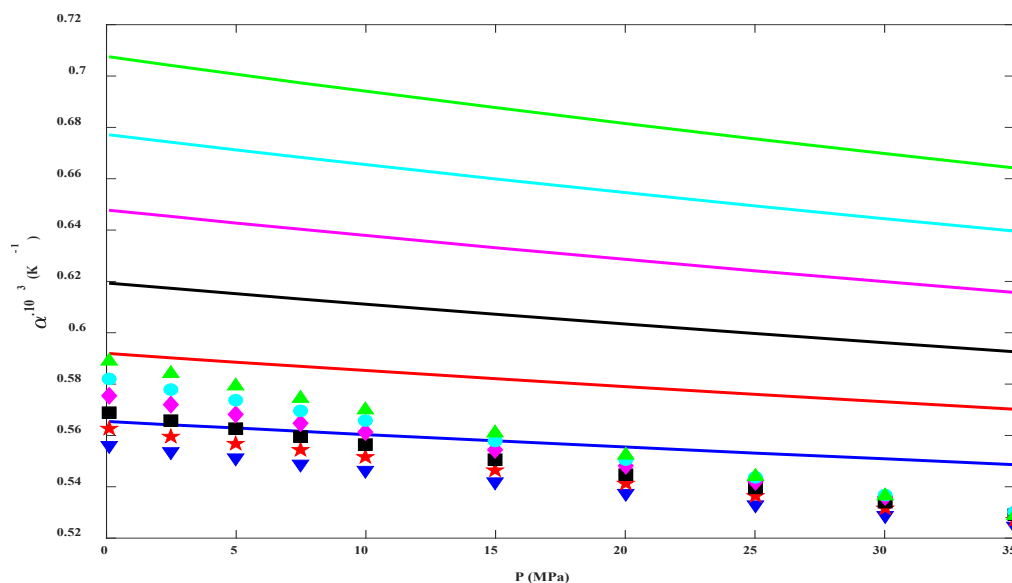


Figure 2. The thermal expansion coefficient (α) vs. pressure for [bmim][MeSO₄] at the temperatures of 393.15 (▲), 373.15 (●), 353.15 (◆), 333.15 (■), 313.15 (★) and 293.15 (▼) K. The experimental data have been indicated by the marks (these data have been obtained based upon the density correlation of Matkowska and Hofmann [38]) and the solid lines present the SAFT- γ GC estimations for α property.

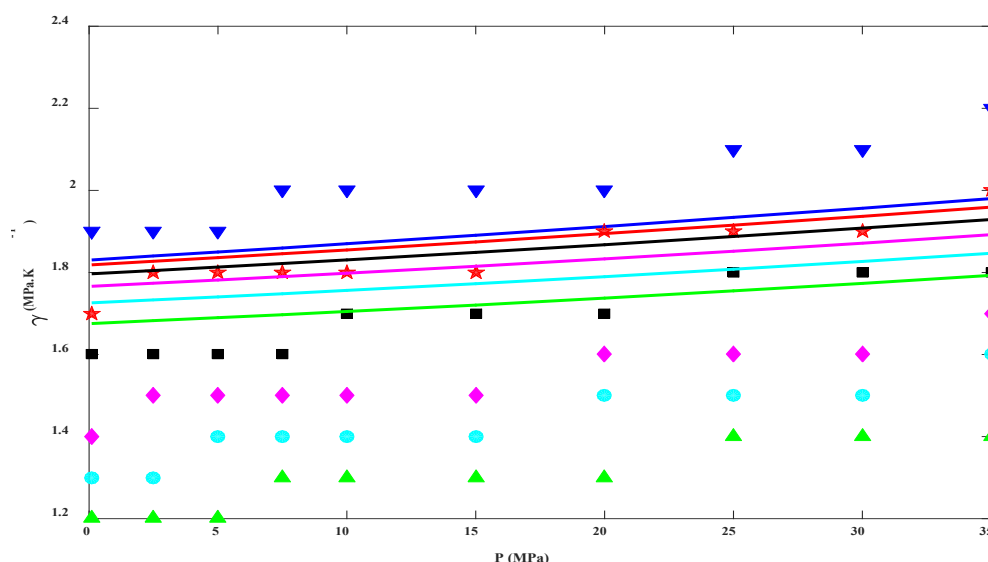


Figure 3. The thermal pressure coefficient (γ) of [emim][MeSO₄] vs. the pressure and at temperatures of 393.15 (▲), 373.15 (●), 353.15 (◆), 333.15 (■), 313.15 (★) and 293.15 (▼) K. The experimental data of Tome et al. [40] and the γ predictions of the SAFT- γ equation have been respectively shown by the symbols and the solid lines.

Figures 4 and 5 respectively present the values of C_V and κ_S for [emim][MeSO₃] at different temperatures and pressures. Both C_V and κ_S values increase with the rise in

temperature. The κ_S values decrease by increasing the pressure. The C_V values do not change considerably by increasing pressure.

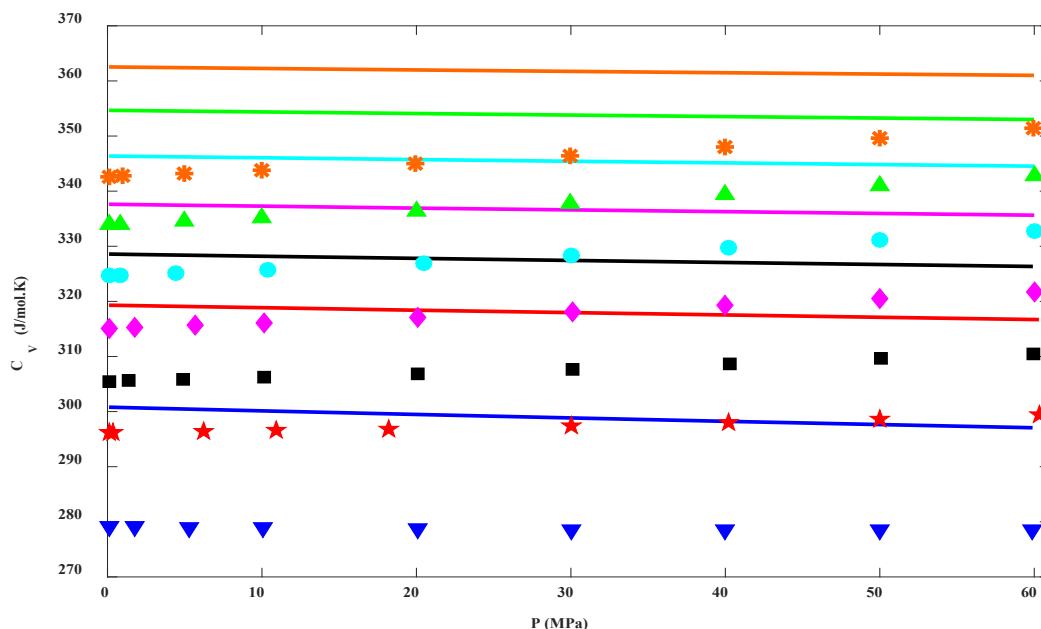


Figure 4. The isochoric heat capacity (C_V) vs. pressure for [emim][MeSO₃] at the temperatures of 413.15 (*), 393.15 (\blacktriangle), 373.15 (\bullet), 353.15 (\blacklozenge), 333.15 (\blacksquare), 313.15 (\star) and 273.15 (\blacktriangledown) K. The experimental data of Musial et al. [41] and the C_V predictions of SAFT- γ EoS have been respectively indicated by the marks and the solid lines.

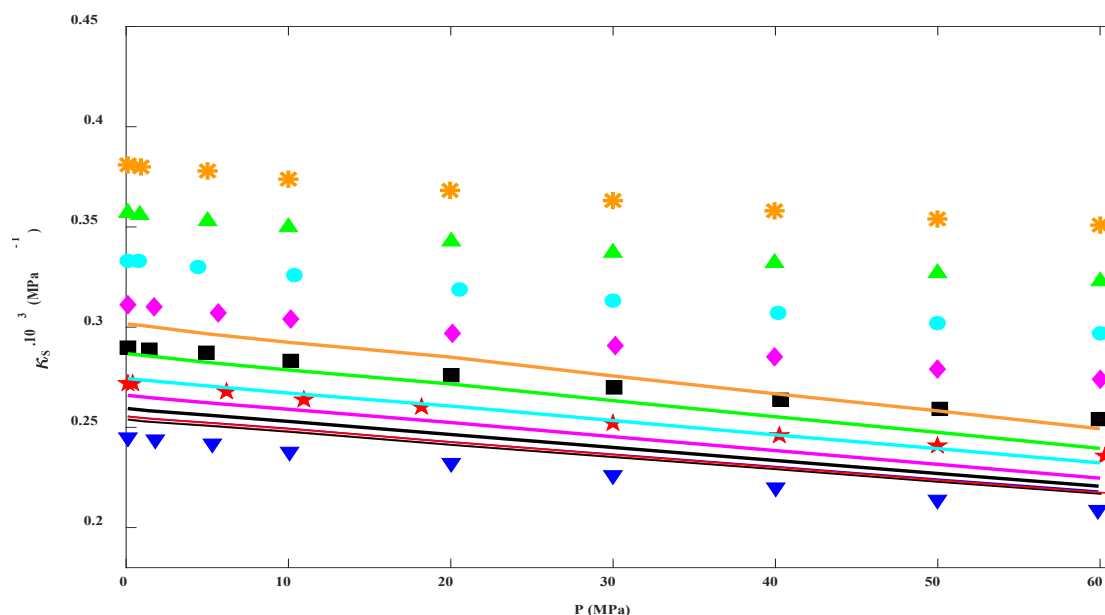


Figure 5. The isentropic compressibility coefficient (κ_S) vs. pressure for [emim][MeSO₃] at the temperatures of 413.15 (*), 393.15 (\blacktriangle), 373.15 (\bullet), 353.15 (\blacklozenge), 333.15 (\blacksquare), 313.15 (\star) and 273.15 (\blacktriangledown) K. The experimental data of Musial et al. [41] and the κ_S predictions of the SAFT- γ model have been respectively displayed by the signs and the solid lines.

The C_p values of [emim][CF₃SO₃], [bmim][CF₃SO₃] and [emim][MeSO₃] versus temperature have been shown in Figure 6 at a pressure of 0.1 MPa. As it is seen in this figure, the C_p values increase with the rise in temperature. In addition, our results did not show a significant change in the isobaric heat capacity of the studied ILs by increasing pressure.

Figure 7 presents the sound speeds versus temperature for [mmim][MeSO₄], [emim][MeSO₄], [bmim][MeSO₄],

[emim][CF₃SO₃] and [bmim][CF₃SO₃] at 0.1 MPa of pressure. According to this figure, the u values decrease by increasing temperature. This decreasing trend is more noticeable for the experimental data. The results also show a decrease in the speed values by increasing the length of the alkyl chain. Moreover, our results showed a slight increase in the u values by increasing pressure. This increasing trend is also in agreement with the experimental observations.

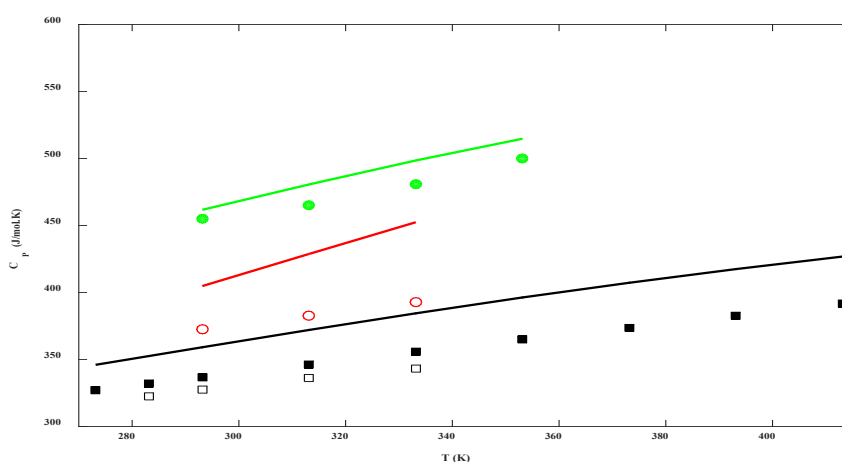


Figure 6. The diagram of the isobaric heat capacity (C_p) vs. temperature for [bmim][CF₃SO₃] (●, Ge et al. [37]), [emim][CF₃SO₃] (○, Vercher et al. [42]), [emim][MeSO₃] (■, Musial et al. [41]) and [emim][MeSO₃] (□, Ficke et al. [43]) at a pressure of 0.1 MPa. The solid lines illustrate the C_p predictions by SAFT- γ EoS.

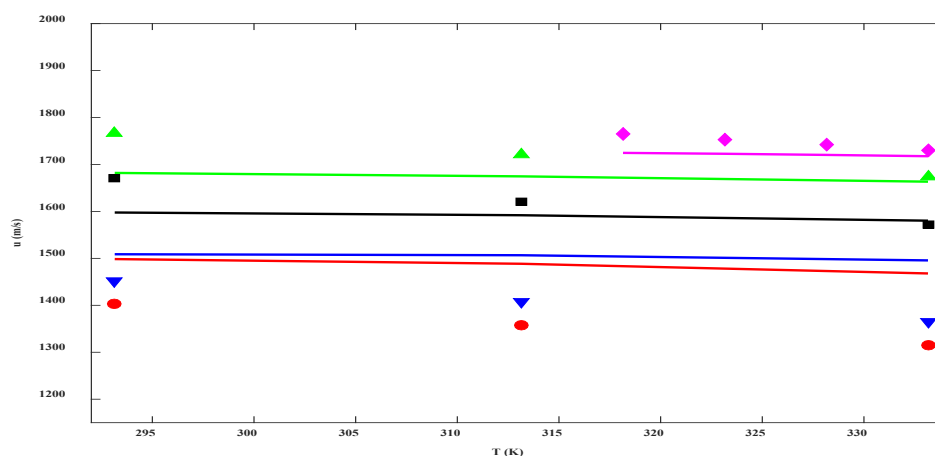


Figure 7. The speed of sound (u) versus temperature for [mmim][MeSO₄] (◆, Pereire et al. [44]), [emim][MeSO₄] (▲, Requejo et al. [45]), [bmim][MeSO₄] (■, Pereire et al. [46]), [emim][CF₃SO₃] (▼, Vercher et al. [42]) and [bmim][CF₃SO₃] (●, Seoane et al. [47]) at the pressure of 0.1 MPa. The lines illustrate the u predictions by the SAFT- γ model.

The results demonstrate a good capability of the SAFT- γ GC technique to estimate the second-order derivative thermophysical properties of ILs with imidazolium-based cations and sulfate or sulfonate anions.

4. Conclusions

The second-order derivative thermophysical properties of some ILs including [emim][MeSO₃], [mmim][MeSO₄], [emim][MeSO₄], [bmim][MeSO₄], [emim][EtSO₄], [emim][CF₃SO₃] and [bmim][CF₃SO₃] were predicted by means of SAFT- γ GC EoS within vast ranges of pressure and temperature (0.1-60 MPa and 273-413 K). The comparison of the predicted second-order derivative properties including the coefficients of thermal expansion and thermal pressure, sound speeds, isobaric and isochoric heat capacities, the coefficients of isentropic and isothermal compressibility with some accessible experimental data showed the good performance of the SAFT- γ model to estimate the properties of ILs. The average error in the values of κ_T , α and γ was respectively 14.26 %, 11.58 % and 18.40 % for 402 data points. Although not much experimental data of heat capacities (C_P , C_V), sound speeds (u) and the coefficient of isentropic compressibility (κ_S) were available, acceptable errors were observed among the SAFT- γ predictions and the limited experimental data.

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Nomenclature

Roman symbols

α	thermal expansion coefficient [K ⁻¹].
α^{vdw}	van der Waals attractive parameter.
γ	thermal pressure coefficient [MPa.K ⁻¹].

ε	energy of dispersion [J].
ε^{HB}	energy of association [J].
κ_T	isothermal compressibility coefficient [GPa ⁻¹].
κ_S	isentropic compressibility coefficient [MPa ⁻¹].
Λ_i	de Broglie wavelength of component i [m].
λ	range of dispersion.
ρ	mass density [kg.m ⁻³], number density [m ⁻³].
σ	segment diameter [m].
$\overline{\sigma_{ii}}$	effective contact distance [m].
ζ_m	reduced density.
ζ^{eff}	effective packing fraction.

Letters

A	energy of Helmholtz [J].
A ₁	mean attractive energy [J].
A ₂	second-order term of attractive energy [J].
A ^{HS}	hard-sphere free energy [J].
a	molar Helmholtz energy [J.mol ⁻¹].
AARD	average absolute relative deviation (in percentage).
%	
C _P	isobaric heat capacity [J.mol ⁻¹ .K ⁻¹].
C _V	isochoric heat capacity [J.mol ⁻¹ .K ⁻¹].
g ₀ ^{HS}	pair correlation function.
g ^{SW}	square-well radial distribution function.
k _B	Boltzmann constant [m ² .kg.s ⁻² .K ⁻¹].
K ^{HS}	isothermal compressibility of reference hard-sphere mixture [Pa ⁻¹].
M	thermodynamic property.
n	number of electronegative or electropositive association sites.
N	molecules' number.
NC	components' number.
ND	number of experimental data.
NG	group types' number.
NST	number of association site types.
P	Pressure [Pa].
r _{klab} ^c	cut-off distance [m].
R	universal gas constant [J.mol ⁻¹ .K ⁻¹].
S	shape factor.
T	Temperature [K].
u	speed of sound [m/s].
v _{k,i}	number of group k in constituent k.
v _k [*]	fused segments' number of group k.
x	mole fraction of a component.
X	non-associated portion of a constituent.

Superscripts

assoc	contribution of association energy.
chain	contribution of molecules' formation from hetero-nuclear segments.
Calc.	calculated (predicted) property.
Exp.	experimental property.
ideal	contribution of ideal Helmholtz energy.
ig	ideal gas.
mono	contribution of hard-sphere dispersions and repulsions.
res	residual.

Subscripts

a	type of association site.
b	type of association site.
i	data, component.
j	component.
k	type of group.
l	type of group.

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