ASEAN Journal of Chemical Engineering 2021, Vol. 21, No. 1, 38 – 51

Generalized Pitzer Correlation for Density Calculations of Ionic Liquids

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Submitted 22 October 2020 *Revised* 05 May 2021 *Accepted* 19 May 2021

Abstract. The density of ionic liquids is an important design parameter for its utilization as a chemical process solvent. In this study, a generalized Pitzer-type correlation for calculating the density of ionic liquids with the use of reduced temperature (T_R), reduced pressure (P_R), and acentric factor (ω) as parameters is proposed. Experimental density data were obtained from several references through the IUPAC Ionic Liquids Database. Expansion of the terms as well as integrating the ionic liquid molecular weight was attempted to determine the accuracy improvement of the model in predicting densities at 0.1 MPa. Then, the obtained model was modified by further truncation to include the pressure effects for densities at higher pressures. MATLAB software was used to determine the optimal virial coefficients for the proposed correlations. The percent average absolute deviation (%AAD) was applied to calculate the variation between the experimental and calculated density values. It was concluded that the eight (8) coefficient correlation equation with molecular weight for densities at 0.1 MPa had a %AAD of 4.7537%. Upon modifying the correlation to include pressure effects, the resulting modified equation had an overall %AAD of 4.7174%**.**

Keywords: Ionic liquids, Pitzer correlation, MATLAB, virial coefficients, percent average absolute deviation

INTRODUCTION

Ionic liquids (ILs) have gained interest in chemical engineering applications due to their favorable properties. ILs are feasible green solvents for process industries due to negligible vapor pressure, low flammability, and high thermal, chemical, and electrochemical stability. These are properties that make it possible to incur lesser emissions to the environment while utilizing a solvent that is reliable in performance. Combining different organic cations and organic or inorganic anions make up most of the ionic liquids (Shariati et al. 2013). In terms of its applications, the extraction or separation process of aromatics from aliphatics is of significant interest (Delgado-Mellado et al.

DOI: 10.22146/ajche.60787

2019) as it is observed to be superior to conventional solvents (Canales and Brennecke, 2016). Synthesis of ILs intended for a specified application will require information regarding their properties. Several challenges are encountered in attempts to experiment on ILs properties. ILs are expensive and tend to decompose upon approaching conditions of critical states (Valderrama et al. 2008). This has paved the way towards initiatives to utilize different methods in estimating the critical properties of ILs. One notable attempt was performed by Valderrama et al. (2008) in utilizing a group contribution method to estimate the critical properties, normal boiling point, and acentric factor of 200 ILs.

Density is a crucial design variable in chemical process industries. There are several means to predict ionic liquid densities, such as the use of the equation of states, correlations such as those based on the corresponding state principles, and group contribution methods based on molecular structure. Equation of state has its limitations when applied to the calculation of liquid densities. Meanwhile, the accuracy of correlation equations relies on the set experimental data used for its derivation (Roshan and Ghader 2012, Roshan and Ghader 2013). Zarei et al. (2019) modified a density correlation for liquid refrigerants called Nasrifar and Moshfeghian equation (Nasrifar and Moshfeghian, 1998) by removing the characteristic parameter that has a specified value for different ionic liquids and reducing the global constants. The resulted modified equation is generalized for many ionic liquids by requiring only critical parameters and the acentric factor. Zarei et al. (2019) further developed a correlation for calculations at higher pressures by again requiring only the critical temperature and pressure and the acentric factor. Keshavarz et al. (2016) developed a group contribution model in the form of multiple linear regression to calculate the density of ILs using its elemental compositions as variables and with correction factors to adjust the effects of ionic interactions. Valderrama et al. (2009) developed a method to predict ionic liquid densities using the classical group contribution method and artificial neural network (ANN) as the mathematical tool. Rostami et al. (2019) developed a method to estimate the densities of ILs by applying group contribution combined with the least square support vector machine trained by a genetic algorithm. In Roshan and Ghader's (2012) work, three equations for predicting the density of liquids were modified and integrated with adjustable parameters to fit their use for ionic liquid density calculations. Patel and Joshipura (2013) observed that less accurate predictions were obtained using the cubic equation of states. They improvised the Predictive-Soave-Redlich-Kwong (PSRK) approach by Khashayar et al. (1998) for predicting the liquid density of refrigerants by generating compound-specific adjustable parameters for 47 ILs. The optimized PSRK model is not a cubic equation of state, but it uses the cohesion factor expression of the Soave-Redlich-Kwong model. In all of the studies cited above, experimental data is essential to increase the model's accuracy and evaluate the suitability of the model for ILs densities.

Another version of an equation of state is expressed in virial form. Onnes (1902) formulated a virial equation of state written as a power series in reciprocal volume. The virial equation of states can be expanded to increase its accuracy in representing experimental data (Zohuri, 2018). A three-parameter corresponding state is suggested by Pitzer et al. (1955) for heavier fluids wherein a substance-specific parameter called an acentric factor, ω, is included. The general form of the correlation is expressed as $X = X^0 + \omega X^1$. Often, X represents a property of the fluid such as compressibility factor, enthalpy, entropy, and others. The use of the acentric factor is an extension of the two-parameter corresponding state principle to account for deviations that are typical of heavier fluids (Mesbah and Bahadori, 2016). The correction factors X^0 and X^1 expand in virial form and are often expressed as a function of pressure, temperature, and volume.

In this study, a Pitzer-type correlation, one that involves the use of the acentric factor, was derived to predict the density of ionic liquids across a wide range of temperatures at 0.1 MPa. The X variable in this correlation will be the density of ILs and the subsequent correction factors, X^0 and X^1, expands in virial form with the reduced temperature (T_R) and molecular weight (M) as parameters. Upon determining the coefficients in the generalized correlation equation for IL densities at 0.1 MPa, the model was further modified by truncation to account for pressure effects by integrating the reduced pressure (P_R) in the calculations. Finally, the model's accuracy was evaluated by calculating the percent average absolute deviation (% AAD) for each IL applied in the study. The purpose of selecting this method is to provide data regarding the accuracy and limitations of using the Pitzer model for ionic liquid densities.

METHODOLOGY

Collection of experimental data

The initial list of ionic liquids and corresponding critical properties such as critical temperature (T_c), critical pressure (P_c), acentric factor (ω), and molecular weight were obtained from Valderrama et al. (2008). Experimental density data at 0.1 MPa and high pressures were collected from the IUPAC Ionic Liquids Database. The data sets were plotted in a density vs. temperature graph for the trimming process. Data sets that exhibited deviation from the trend, with percent errors equal to or more than ± 10, and with less than three (3) available data points were excluded. Trimming of data points was one of the measures to improve the resulting correlation equation as it relies on the data set used. 78 ionic liquids from the study of Valderrama et al. (2008) were considered in this study due to sufficient available data in the IUPAC Ionic Liquids Database.

Proposed correlations as a function of reduced temperature for densities at 0.1 MPa

The virial equations were initiated starting with 6 coefficients and further expanded until the percent average absolute deviation (%AAD) can no longer be lowered. The objective function for the density correlation is expressed as:

$$\rho_{calc} = \rho^0 + \omega\rho^1 \qquad (1)$$

where ρ_{calc} is the calculated density in kg·m^{-3}, ω is the acentric factor of the IL, and ρ^0 and ρ^1 are the correction factors as a function of reduced temperature, T_R. For the six coefficients (α_1 - α_6) virial equation, ρ^0 and ρ^1 are defined as:

$$\rho^0 = \alpha_1 + \frac{\alpha_2}{T_R} + \frac{\alpha_3}{{T_R}^2} \qquad (2)$$

$$\rho^1 = \alpha_4 + \frac{\alpha_5}{T_R} + \frac{\alpha_6}{{T_R}^2} \qquad (3)$$

In the following discussions, Eq. (1) refers to the generalized Pitzer-type correlation for density, while the term virial equation refers to the different forms of the expansion of ρ^0 and ρ^1 used in this study.

Using MATLAB software, the values of α_1 - α_6 were maximized based on the experimental density data at 0.1 MPa. The calculated alpha, α, coefficients were plugged into Eqs. (2) and (3) to obtain ρ^0 and $\rho^{1,}$ which were plugged into Eq. (1) to determine the calculated density, ρ_{calc}. Similar procedures were performed for virial equations with 8, 10, and 12 coefficients. Eqs. (4) and (5) present the correction factors for the highest expansion of the model achieved in this study which contains 12 coefficients.

$$\rho^0 = \alpha_1 + \frac{\alpha_2}{T_R} + \frac{\alpha_3}{{T_R}^2} + \frac{\alpha_4}{{T_R}^3} + \frac{\alpha_5}{{T_R}^4} + \frac{\alpha_6}{{T_R}^5} \quad (4)$$

$$\rho^1 = \alpha_7 + \frac{\alpha_8}{T_R} + \frac{\alpha_9}{{T_R}^2} + \frac{\alpha_{10}}{{T_R}^3} + \frac{\alpha_{11}}{{T_R}^4} + \frac{\alpha_{12}}{{T_R}^5} \quad (5)$$

The accuracy for N number of data points for each ionic liquid was measured in terms of the %AAD:

$$\%AAD = \frac{1}{N}\sum_N \frac{|\rho_{calc} - \rho_{expt}|}{\rho_{expt}} * 100 \quad (6)$$

In this study, to determine the best expansion of the virial equation, each %AAD was obtained for comparison.

Proposed correlations as functions of molecular weight and reduced temperature for densities at 0.1 MPa

Assuming its direct relation to density, the effect of molecular weight, M, on the overall accuracy of the proposed correlations was also investigated. The equations for the correction factors, ρ^0 and ρ^1, were modified and then expressed as:

For 6 coefficients:

$$\rho^0 = \alpha_1 + \alpha_2\frac{M}{T_R} + \alpha_3\frac{M^2}{{T_R}^2} \quad (7)$$

$$\rho^1 = \alpha_4 + \alpha_5\frac{M}{T_R} + \alpha_6\frac{M^2}{{T_R}^2} \quad (8)$$

For 8 coefficients:

$$\rho^0 = \alpha_1 + \alpha_2\frac{M}{T_R} + \alpha_3\frac{M^2}{{T_R}^2} + \alpha_4\frac{M^3}{{T_R}^3} \quad (9)$$

$$\rho^1 = \alpha_5 + \alpha_6\frac{M}{T_R} + \alpha_7\frac{M^2}{{T_R}^2} + \alpha_8\frac{M^3}{{T_R}^3} \quad (10)$$

Eq. (1) was used to calculate ρ_{calc} after obtaining the correction factors ρ^0 and $\rho^{1,}$ while Eq. (6) was used to evaluate the %AAD for each model. The n coefficient virial equation with the lowest %AAD was used and modified to calculate the densities at higher pressures.

Proposed correlations as functions of molecular weight, reduced temperature, and reduced pressure for densities at high pressures

To incorporate the effects of pressure, additional terms were added to the most accurate n coefficient correlation for IL densities at 0.1 MPa. The additional terms in the expanded virial equation included the new coefficients for pressure effects, β, and added parameters of reduced pressure at high pressures, $P_{R,H}$, and reduced pressure at 0.1 MPa, $P_{R,1}$.

From the density calculations at 0.1 MPa, the correlation with eight (8) coefficients and molecular weight as an added parameter had the lowest overall %AAD. Further expansion was found to result in a divergence of the model. The obtained alpha coefficients from low-pressure calculations were retained for the modified equation to predict densities at higher pressures. Eqs. (11) and (12) show the correction factors, ρ^0 and ρ^1, for the correlation of ionic liquid densities at higher pressures.

$$\rho^0 = \alpha_1 + \alpha_2 \frac{M}{T_R} + \alpha_3 \frac{M^2}{{T_R}^2} + \alpha_4 \frac{M^3}{{T_R}^3} + \beta_1 \frac{M(P_{R,H} - P_{R,1})}{T_R} + \beta_2 \frac{M^2 {(P_{R,H} - P_{R,1})}^2}{{T_R}^2} + \beta_3 \frac{M^3 {(P_{R,H} - P_{R,1})}^3}{{T_R}^3} \quad (11)$$

$$\rho^1 = \alpha_5 + \alpha_6 \frac{M}{T_R} + \alpha_7 \frac{M^2}{{T_R}^2} + \alpha_8 \frac{M^3}{{T_R}^3} + \beta_4 \frac{M(P_{R,H} - P_{R,1})}{T_R} + \beta_5 \frac{M^2 {(P_{R,H} - P_{R,1})}^2}{{T_R}^2} + \beta_6 \frac{M^3 {(P_{R,H} - P_{R,1})}^3}{{T_R}^3} \quad (12)$$

The additional terms containing the β coefficients add the effects of increased pressure and mathematically give a value of zero at 0.1 MPa, since $P_{R,H}$ becomes equal to $P_{R,1}$. The modified correlation was simulated in MATLAB software using all data points to determine the β coefficients. After calculating ρ^0 and ρ^1, the ρ_{calc} and %AAD were determined using Eq. (1) and Eq. (6), respectively. The same procedure was repeated to obtain %AAD per ionic liquid as well as for each model.

RESULTS AND DISCUSSION

Effect of molecular weight parameter to the overall %AAD for models at 0.1 MPa

Table 1 presents the overall %AAD of the different models with n coefficients, with and without the effect of molecular weight. The 78 ILs with a combined 3982 data points were all used to derive those correlations. The overall %AAD was calculated using all density data at 0.1 MPa. It was concluded that the correlations incorporated the molecular weight had lower overall %AAD at even lesser truncated terms. Integrating the molecular weight in the equation has been proven to improve the model's accuracy, which indicates that this property should not be neglected in considering densities. In the virial equation for low pressure, raising the power of (M/T_R) above 3 resulted in the overall computation's divergence as the computed density started to increase dramatically. Therefore, only the eight (8) coefficient virial equation was achieved in the model, which integrates the molecular weight.

Table 1. The effect of truncating the terms in the virial equation model in terms of overall %AAD.

No. of coefficients	Overall %AAD	
	Without Molecular Weight	With Molecular Weight
6	5.4250	4.8528
8	5.3658	4.7537
10	5.1966	
12	5.1905	

In the modified equation for higher pressures, the same behavior of the divergence of the equations upon further truncation has occurred. Therefore, it was found that the expansion of the terms has a limit and the best model adopted is the one that has the lowest %AAD before approaching the limit.

The virial equation for ionic liquid density calculations at 0.1 MPa

The %AAD in calculating liquid density at low pressure (0.1 MPa) is presented in Table 2. The temperature range was based on the lower and upper limits of the 3982 data points obtained from IUPAC Ionic Liquids

Database. The model has exhibited reliable accuracy in predicting the densities of ionic liquids [emim][Ac] (0.40%), [pmpy][bti] (0.53%), [prmpyr][bti] (0.75%), [S221][bti] (0.92%), [py][EOESO$_4$] (0.70%), and [emim][ESO$_4$] (0.47%). [mim][HSO$_4$] has the largest average and maximum %AAD which are 21.40% and 21.78%, respectively. The range and average of experimental densities extracted from the database and the average calculated density for each ILs are also shown.

Table 2. %AAD in calculating the ionic liquid densities using the virial equation with eight (8) coefficients.

Ionic Liquid	N	%AAD$_{ave}$	%AAD$_{min}$	%AAD$_{max}$	T(K) (range)	ρ_{expt} /kg · m^{-3} (range)	ρ_{expt} /kg · m^{-3} (average)	ρ_{calc}/kg·m^{-3}
[bmim][TFES]	10	5.3425	4.8670	5.8371	288.15 - 333.15	1318.8 - 1355.5	1337.09	1265.62
[emim][TFES]	7	10.6061	10.5650	10.6258	293.15 - 353.15	1385.8 - 1435.8	1410.71	1261.09
[bmim][HFPS]	4	9.1232	7.8685	10.2450	283.15 - 348.15	1364 - 1422	1395.00	1267.53
[bmim][TPES]	4	11.2069	9.2077	12.8952	283.15 - 348.15	1372 - 1439	1407.75	1249.63
[bmim][FS]	4	12.8820	11.0871	14.3826	283.15 - 348.15	1401 - 1462	1434.75	1249.63
[bmim][Ac]	119	8.2759	7.2052	10.3741	273.15 - 413.15	984.9 - 1112.5	1037.98	1123.79
[emim][Ac]	96	0.4045	0.0076	0.9026	273.15 - 363.15	1058.7 - 1115.3	1085.00	1089.35
[emim][BEI]	19	7.8765	6.4100	8.7124	273.15 - 363.15	1523.3 - 1621.6	1576.44	1452.08
[bmim][BEI]	23	7.1848	5.6271	7.6803	273.15 - 363.15	1446.1 - 1539.6	1500.27	1392.33
[dbim][bti]	36	2.0790	1.2617	3.6455	273.15 - 363.15	1282.5 - 1362.7	1322.70	1350.04
[dmim][bti]	32	3.7462	3.5021	3.9922	293.15 - 363.15	1503.2 - 1575	1543.76	1485.90
[bmpy][bti]	181	1.2741	0.0009	2.8350	278.15 - 373.15	1324.6 - 1498.1	1389.49	1407.00
[decmim][bti]	42	2.9662	1.3688	9.0373	293.15 - 473.15	1131.4 - 1308	1235.72	1271.76
[N-epy][bti]	40	2.6142	2.3796	2.8861	288.15 - 343.15	1491.87 - 1545.9	1519.35	1479.62
[hpmim][bti]	44	2.8894	1.0554	9.3686	278.15 - 473.15	1189.4 - 1373	1304.28	1340.91
[nmim][bti]	37	3.3023	1.5617	9.6707	278.15 - 473.15	1147.8 - 1316.4	1251.73	1292.18
[pmim][bti]	53	1.8152	0.0418	7.1665	278.15 - 473.15	1241.3 - 1443.6	1363.58	1387.17
[prmim][bti]	70	1.1637	0.0295	3.1079	278.15 - 473.15	1305.1 - 1515.1	1440.44	1430.30
[pmpy][bti]	79	0.5315	0.0107	1.3192	264.25 - 363.28	1386.7 - 1481.37	1430.89	1431.50
[N1123][bti]	23	2.1228	1.4084	2.9250	278.15 - 353.15	1352 - 1420.02	1384.25	1354.78
[N-bupy][bti]	97	1.0408	0.0647	2.0525	278.15 - 363.15	1389 - 1467.9	1429.84	1444.62
[prmpyr][bti]	67	0.7507	0.0092	1.6918	278.15 - 363.15	1370.5 - 1446.2	1410.51	1420.94
[N1444][bti]	19	2.2655	0.2289	3.4573	283.15 - 353.15	1217.5 - 1276	1248.89	1220.43
[N7222][bti]	8	2.1800	0.0657	3.9069	293.16 - 363.15	1213.8 - 1275.7	1245.13	1217.91
[N6222][bti]	41	1.6315	0.0005	3.4856	283.15 – 373.00	1231.1 - 1301.47	1264.44	1245.43
[N8222][bti]	25	2.9184	0.8104	4.1039	283.15 - 363.15	1195.8 - 1261.7	1227.86	1191.82
[S222][bti]	49	2.9009	2.4018	3.2923	278.15 - 353.15	1410.2 - 1479.7	1446.47	1488.38
[N1114][bti]	191	1.3946	0.0133	2.3355	278.15 - 414.93	1288.6 - 1480.6	1370.92	1351.77
[tmpa][bti]	10	3.3961	3.2790	3.4813	298.20 - 315.10	1414.2 - 1429.6	1422.63	1374.31
[Ph(CH2)mim][bti]	16	2.4483	1.7882	3.5122	278.15 - 323.15	1458 - 1512	1484.31	1520.58
[bdmim][bti]	80	1.3989	0.0307	2.4775	273.15 - 373.15	1328.4 - 1503.9	1402.35	1383.11
[mbpyr][bti]	25	1.2662	0.0149	2.6026	278.15 - 363.15	1352.7 - 1431	1390.80	1408.24
[bpyr][bti]	97	1.0521	0.0746	2.0660	278.15 - 363.15	1389 - 1467.9	1429.84	1444.78
[C12mim][bti]	34	3.1164	0.9004	8.3694	293.15 - 433.15	1133.7 - 1249.6	1206.32	1244.33
[mmim][bti]	32	4.9491	4.5609	5.2978	293.15 - 363.15	1503.2 - 1575	1543.76	1467.31
[S221][bti]	22	0.9166	0.7731	1.0302	278.15 - 353.15	1449.8 - 1520.5	1485.64	1499.25
[DEME][bti]	24	3.3162	1.7447	4.5905	283.15 - 368.15	1343.4 - 1420.6	1385.42	1339.30
[BMP][bti]	74	2.1505	0.8765	3.5788	283.15 - 373.15	1319 - 1395.6	1357.55	1386.61
[N222(12)][bti]	41	4.3950	0.4022	5.8851	283.15 - 373.00	1133.7 - 1199.67	1165.32	1115.63
[N2228][bti]	41	2.8133	0.4893	4.1635	283.15 - 373.00	1192.3 - 1261.7	1225.42	1190.73
[N2225][bti]	16	1.6183	0.0099	3.3357	298.00 – 373.00	1260.7 - 1321.5	1290.99	1270.34
[bmim][Br]	12	11.5943	11.5703	11.6388	308.39 - 362.86	1261.43 - 1299.64	1280.30	1131.86
[bmim][Cl]	40	1.2338	1.0807	1.5286	298.15 - 373.15	1000 - 1124	1057.60	1070.66
[hmim][Cl]	60	9.5430	9.0388	10.0411	288.15 - 373.15	997.1 - 1048	1022.30	1119.83
[omim][Cl]	50	15.2227	14.1502	16.3123	278.15 - 363.14	972.9 - 1021.2	997.52	1149.32
[emim][Cl]	18	9.0281	8.8026	9.1408	313.38 - 364.85	1106.3 - 1134.8	1118.78	1017.78
[bmim][dca]	223	8.6408	5.9498	11.1063	273.15 - 363.15	1001.1 - 1102.8	1046.77	1137.04

[emim][dca]	118	3.6111	1.5394	5.0920	273.15 - 363.15	1062.3 - 1145.4	1090.77	1130.03
[mbpyr][dca]	62	13.0643	11.0730	15.3106	273.15 - 358.15	980.7 - 1027.7	1006.67	1138.08
[mppyr][dca]	14	12.1739	10.9523	13.3405	298.15 - 363.15	990.8 - 1026.8	1008.59	1131.29
[dmim][DMPO4]	38	7.1392	6.7633	7.3924	293.15 - 363.20	1191.8 - 1315.1	1246.36	1157.37
[py][EOESO4]	12	0.6981	0.2452	1.0527	293.15 - 348.15	1244 - 1284	1264.17	1255.37
[emim][ESO4]	383	0.4668	0.0015	1.0291	253.15 - 391.27	1162.6 - 1295.1	1224.85	1230.50
[moim][PF6]	113	8.3810	4.3575	11.9316	273.10 - 373.15	1116 - 1312	1223.14	1120.32
[bdmim][PF6]	12	13.9573	12.7066	15.2266	308.17 - 364.63	1276.1 - 1344.6	1320.57	1136.14
[hpmim][PF6]	30	9.0602	6.7333	11.5345	292.97 - 364.45	1212.58 - 1266.7	1239.63	1127.08
[nmim][PF6]	30	7.5554	4.3114	10.9349	293.11 - 365.13	1163.68 - 1217	1190.62	1100.34
[pmim][PF6]	34	12.9466	11.1335	15.6068	267.86 - 363.15	1276.6 - 1351.9	1308.68	1139.00
[prmim][PF6]	22	18.1509	17.4172	19.1322	303.08 - 364.89	1359.36 - 1410.96	1381.33	1130.54
[emim][HSO4]	97	13.9509	13.5733	14.4759	283.15 - 363.15	1326.68 - 1376.7	1349.89	1161.54
[mim][HSO4]	9	21.4018	21.0566	21.7834	293.15 - 373.15	1412.9 - 1462.2	1437.02	1129.44
[bmim][I]	20	18.7420	18.5774	18.8389	282.94 - 364.72	1432.51 - 1496.03	1466.00	1191.24
[bmim][mesy]	9	4.9380	4.8675	5.0209	333.15 - 373.15	1125.8 - 1150.6	1138.09	1194.29
[emim][mesy]	89	3.1946	2.2298	3.9987	273.15 - 363.2	1198 - 1259.1	1228.45	1189.28
[dmim][MOESO4]	13	3.9382	3.7612	4.0635	293.15 - 353.15	1275 - 1317	1296.23	1245.19
[dmim][MSO4]	38	8.7416	7.9896	9.5176	283.15 - 353.15	1246.4 - 1338.2	1314.43	1199.57
[bmim][MSO4]	71	3.6684	3.4348	3.8580	278.15 - 358.14	1169.7 - 1231.26	1195.24	1239.09
[bmim][C8S]	83	10.6853	6.9662	12.9493	278.15 - 343.27	964 - 1126	1051.92	1164.17
[tibmp][pTSO3]	23	17.0572	14.9119	18.9605	283.15 - 353.15	1040.2 - 1082.4	1059.80	1240.44
[bdmim][BF4]	21	4.5747	2.4704	6.1296	288.15 - 373.15	1143.2 - 1199.9	1176.17	1122.20
[dmim][BF4]	17	4.2337	0.2757	8.2379	283.26 - 363.98	1028.48 - 1083.12	1055.25	1099.15
[prmim][BF4]	11	9.5716	8.8188	10.3074	293.15 - 343.15	1203 - 1239.3	1221.09	1104.16
[bpyr][BF4]	73	8.0857	6.9994	9.0456	278.15 - 353.15	1175.4 - 1250.4	1202.78	1105.46
[DEME][BF4]	15	5.1939	3.9946	6.4086	283.15 - 353.15	1141.8 - 1188.2	1164.65	1104.05
[bmim][tca]	86	10.4121	9.9101	10.6112	278.15 - 363.15	1031.73 - 1122.1	1057.66	1167.78
[emim][SCN]	73	2.3584	1.7905	3.0391	278.15 - 363.15	1078.7 - 1129.7	1104.88	1130.98
[omim][TfO]	27	4.3049	2.4630	5.9410	288.15 - 353.15	1152.68 - 1200.83	1175.76	1226.23
[dmpim][TMEM]	4	1.8397	1.1691	2.7788	283.15 - 348.15	1567 - 1612	1589.50	1618.85
	(Total) 3982	4.7537 (Mean)						

Figure 1 shows the model's accuracy for predicting all density data and five (5) selected ionic liquids at 0.1 MPa (± 5%). The parity plot shows the range for both the experimental and calculated data values. The range of a strong agreement between the experimental and calculated values can be seen by how near the plots are at the diagonal line. For example, in [emim][Ac] (Figure 1b), a lot of predicted values agree with the experimental values, while for [pmpy][bti] (Figure 1c), the agreement occurs at a limited range. The values of the coefficients for the virial equation for IL density at 0.1 MPa (Eq. (9) and (10)) are $\alpha_1 = 635.4$, $\alpha_2 = 1.122$, $\alpha_3 = -3.884\times10^{-4}$, $\alpha_4 = 4.110\times10^{-8}$, $\alpha_5 = 343.6$, $\alpha_6 = -0.5424$, $\alpha_7 = -2.883\times10^{-4}$, and $\alpha_8 = 1.510\times10^{-7}$. The overall accuracy of the virial equation model is 4.75% for average %AAD for all the 78 ionic liquids considered in this study. Its application can be viable for the mentioned ionic liquids with an average %AAD of less than 1%.

The virial equation for ionic liquid density calculations at higher pressures

The virial equation initially derived for calculating density at 0.1 MPa has been modified by expanding the terms to account for the effects of increasing the pressure (see Eq. 11 and 12). The model provided accurate calculations for three ionic liquids [emim] [Ac], [pmim] [bti], and [emim] [ESO$_4$] with a %AAD of 0.38%, 0.41%, and 0.60%. Table 3 summarizes results for all ILs, and Figure 2 highlights the calculated values versus the experimental values in terms of a parity plot. Figure 2a displays the model's overall accuracy along with three ILs (Figures 2b, 2c, and 2d) with the lowest %AADs. The trend for [pmim][bti] and [emim][ESO4] (Figures 2c, 2d) means that the calculated values agree with the experimental values that at a fixed temperature, an increase in pressure increases density.

Meanwhile, the trend observed for [emim][Ac] shows how the calculated values do not agree with the experimental values as pressure increases at a fixed temperature. This varying trend has also been confirmed by analyzing the individual experimental values versus the calculated values for the other ionic liquids. This behavior is associated with the obtained optimized values of the coefficients than the actual IL. It is worth mentioning that for virial equation models, the values of the coefficients will change depending upon the training data sets adopted.

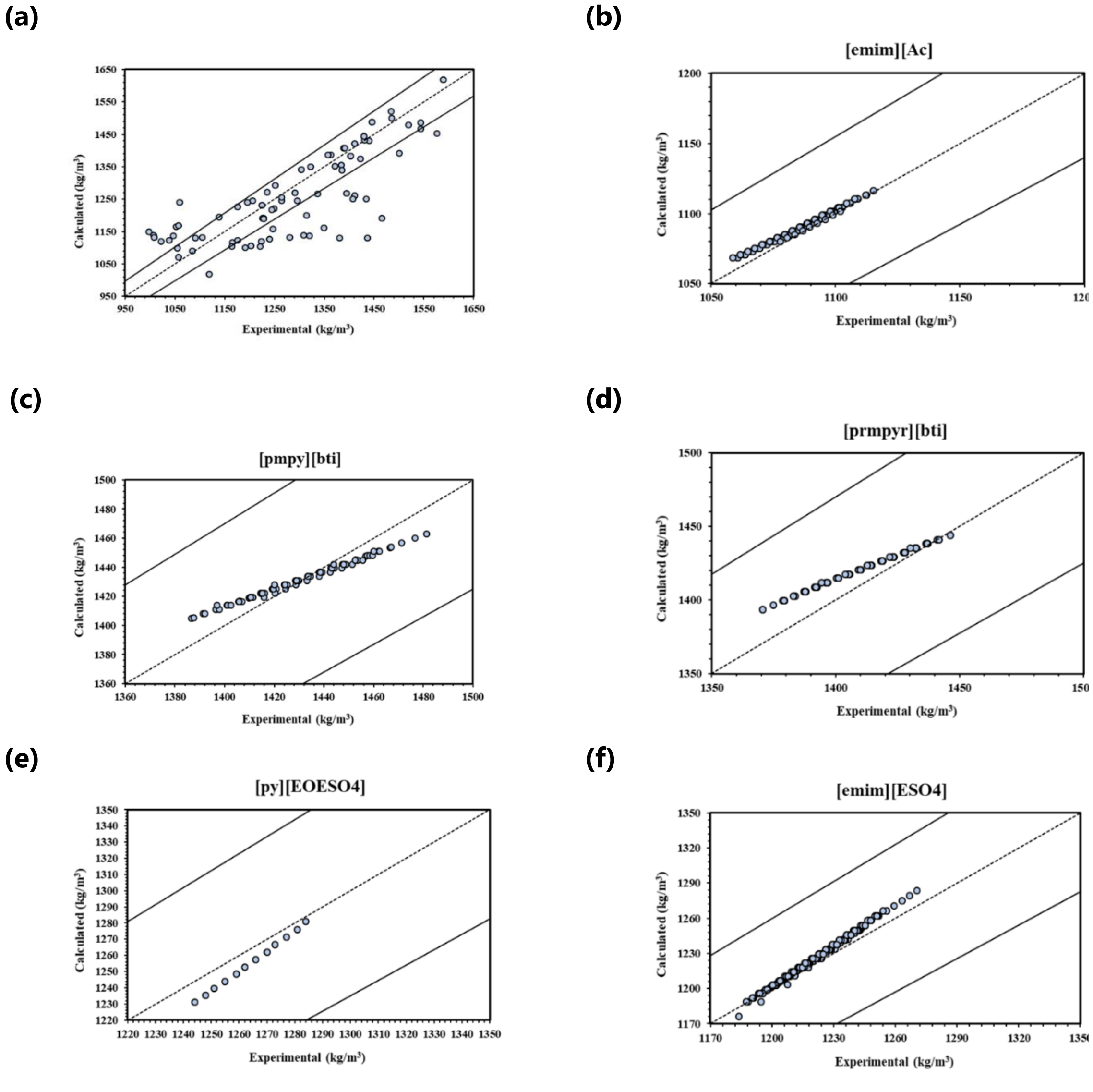

Fig. 1: Parity plot for (a) all density data, (b) [emim][Ac], (c) [pmpy][bti], (d) [prmpyr][bti], (e) [py][EOESO$_4$], and (f) [emim][ESO$_4$] at 0.1 MPa (±5% error).

Table 3. %AAD in calculating the ionic liquid densities at higher pressures.

Ionic Liquid	N	$\%AAD_{ave}$	$\%AAD_{min}$	$\%AAD_{max}$	T(K) (range)	P(kPa) (range)	$\rho_{expt}(kg/m^3)$	$\rho_{calc}(kg/m^3)$
[bmim][Ac]	313	4.8211	0.8748	10.3741	273.15 - 413.16	100 – 200000	1055.45	1105.81
[emim][Ac]	63	0.3828	0.0069	1.1219	293.14 - 353.2	100 – 25000	1087.64	1086.22
[bmpy][bti]	63	2.1321	0.0035	13.5863	278.15 - 398.15	100 – 120000	1413.50	1408.57
[decmim][bti]	80	1.3144	0.0001	4.0424	293.15 - 393.15	100 – 35000	1259.60	1274.93
[hpmim][bti]	96	1.6155	0.1819	4.7634	293.15 - 393.15	100 – 30000	1323.30	1344.37
[pmim][bti]	165	0.4163	0.0012	1.3541	298.15 - 333.15	100 – 59590	1408.64	1413.92
[prmim][bti]	165	1.1461	0.6248	1.6248	298.15 - 333.15	100 – 59590	1479.23	1462.25
[N1114][bti]	99	1.9711	0.0237	7.4623	278.15 - 414.95	100 – 120000	1379.22	1351.79
[bdmim][bti]	63	2.9964	0.1179	16.1996	278.15 - 398.15	100 – 120000	1419.12	1378.27
[bmim][Cl]	121	2.7306	0.0747	5.4157	352.1 – 452	100 – 200000	1066.69	1039.40
[bmim][dca]	324	5.7600	0.0034	12.3600	237.20 - 393.17	100 – 99920	1053.46	1113.40
[emim][dca]	85	1.2849	0.0025	3.7667	256.82 - 346.22	103.4 – 60101	1122.71	1122.51
[dmim][DMPO4]	63	8.7664	6.8116	10.8886	278.15 - 398.15	100 – 120000	1254.79	1144.61
[emim][ESO4]	646	0.6003	0.0030	3.6906	278.15 - 413.18	100 – 140209	1232.91	1230.24
[moim][PF6]	277	7.2913	0.4034	14.6642	293.15 - 472.3	100 - 200000	1219.49	1130.49
[bdmim][PF6]	63	13.7109	11.5049	16.5589	313.15 - 393.15	100 – 10000	1308.64	1128.97
[dmim][MSO4]	168	10.3053	8.8590	11.8324	318.15 - 428.15	100 – 60000	1288.61	1155.93
[bmim][MSO4]	360	3.1489	2.4054	3.7587	283.15 - 353.15	100 – 35000	1202.77	1240.63
[bmim][C8S]	338	10.8130	0.4487	20.4232	312.9 - 472.6	100 – 200000	1047.83	1159.81
[bpyr][BF4]	189	10.6150	6.9518	13.8688	283.15 - 353.15	100 – 65000	1217.60	1088.13
[bmim][tca]	134	9.8651	8.3735	10.6051	223.52 - 353.52	100 – 50956	1070.10	1175.62
[emim][SCN]	102	2.1040	0.7853	2.8973	285.69 - 348.16	100 – 50103	1108.09	1131.42
	3977	4.7174						

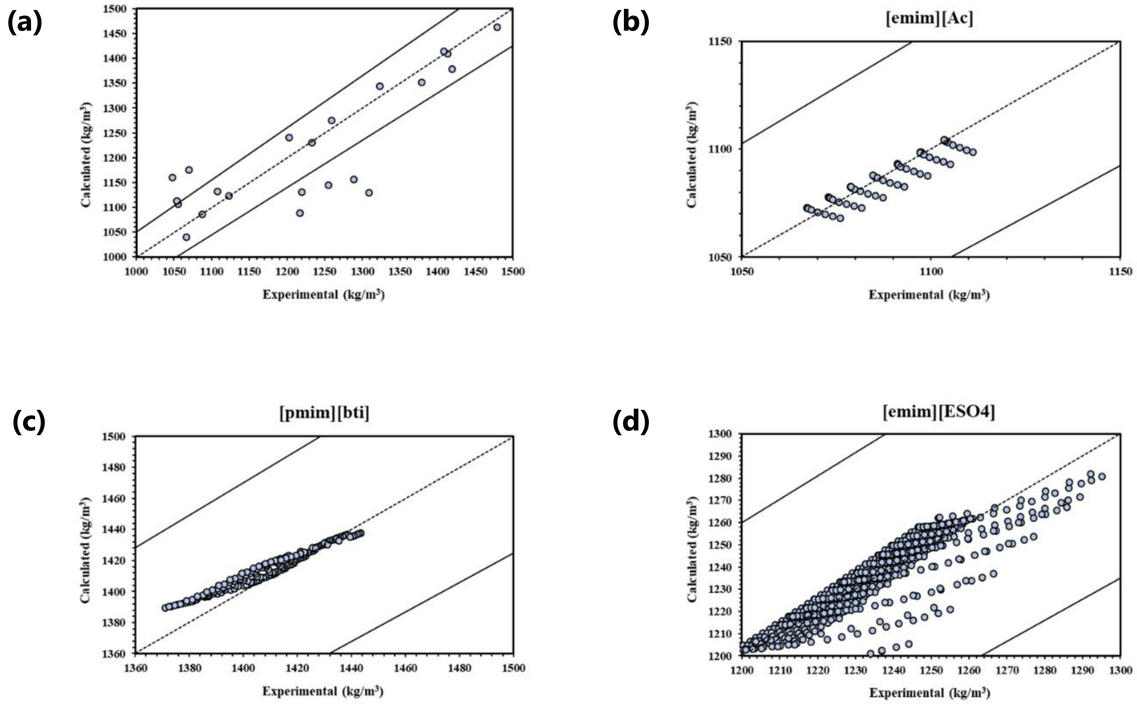

Fig. 2: Parity plot for (a) all density data, (b) [emim][Ac], (c) [pmim][bti], (d) [emim][ESO_4] at high pressures (±5% error).

The modified equation has an overall %AAD of 4.72%. It was initially attempted to recreate a new model, which is also based on virial equations for calculating densities at higher pressures with new coefficients; however, it provided less accurate results than extending the virial equation for lower pressures. Modifying the equation is convenient in a way that it expounds on the effects of pressure, and adding it to the previous equation emphasizes the basic concept that an increase in pressure corresponds to an increase in density. 3977 data points were extracted from IUPAC Ionic Liquids Database. Application of the equation must consider the minimum and maximum temperature and pressure for its range of validity. Thus, Table 3 provides the range of temperature and pressure for reference.

The beta coefficients for the modified model are $\beta_1 = 3.678\times10^{-3}$, $\beta_2 = -2.196\times10^{-8}$, $\beta_3 = -5.682\times10^{-13}$, $\beta_4 = -9.115\times10^{-3}$, $\beta_5 = 1.445\times10^{-7}$, and $\beta_6 = 6.853\times10^{-14}$. The values are relatively small compared to the alpha coefficients since these are intended to serve as pressure effect correction factors. It is pointed out once again that further expansion resulted in a divergence of the model. Privat et al. (2009) provided insights regarding the divergence of the virial equation for high densities into which ionic liquids fall. The reason why divergence has occurred and the coefficients are known to have significance in terms of molecular interaction is not the scope of this study. However, it is worth noticing that for some ionic liquids, the equation derived can be usable in the prediction of their respective densities. Additionally, the methods used in this study can be adopted, and new coefficients can be derived for ionic liquids, which the model has the accurate predicting capability.

Comparison with other models

Table 4 is data adopted from Zarei et al. (2019), which compares the %AAD obtained from different models used to calculate ionic liquid densities. ZN, the Zarei et al. (2019) model, was a modification of the model by Nasrifar and Moshfeghian (1998), which is also included in the table as NM. GC is the group contribution method combined with the artificial neural network by Valderrama et al. (2009). Meanwhile, YW is the model by Yen and Wood (1966), which is one of the early attempts to apply computer calculations on creating a generalized equation for IL densities. Rackett (1970) proposed an equation of state model for saturated liquids, which is indicated as RA. A modification of the Rackett equation was developed by Yamada and Gun (1973), indicated as YG. HT is a correlation by Hankinson and Thomson (1979) for saturated densities of liquids. In the present study using Pitzer correlation, prediction of densities for five (5) ionic liquids: [bmpy][bti], [N7222][bti], [N1444][bti], [N6222][bti], and [N2225][bti] provided excellent results compared to recently developed models such as ZN, NM, and GC. It can also be seen that several calculations in the current model provided %AAD values with high deviations similar to earlier developed models such as YW, RA, YG, and HT. In Table 2, ionic liquids [emim][Ac],

[pmpy][bti], [prmpyr][bti], [S221][bti], [py][EOESO$_4$], and [emim][ESO$_4$] have a %AAD of 0.40%, 0.53%, 0.75%, 0.92%, 0.70%, and 0.47% respectively. All of which were not compared as in Table 4 due to limited data.

Data for comparing the Pitzer correlation for higher IL densities to other models is still adopted from the work of Zarei et al. (2019) as shown in Table 5. NAM is the model by Zarei et al. (2019) for higher pressures. The extended Tait equation by Thomson et al. (1982) is a method to calculate densities of nonpolar and slightly polar liquids and mixtures at higher pressures. Chang and Zhao (1990) is an equation for calculating the volumes and densities of compressed liquids. Both Taylor's series expansion and Padé's approximation are developed by Roshan and Ghader (2013).

Table 4. Comparison of %AAD with different models of IL densities at 0.1 MPa.

No.	**Ionic Liquid**	**%AAD**							
		This work	ZN[a]	NM[b]	GC[c]	YW[d]	RA[e]	YG[f]	HT[g]
1	[emim][BEI]	7.88	1.75	0.97	1.57	4.36	18.13	1.15	1.39
2	[bmim][BEI]	7.18	1.95	1.68	1.76	5.31	23.74	5.20	5.45
3	[dmim][bti]	3.75	1.29	0.63	1.66	7.33	5.28	2.38	1.96
4	[bmpy][bti]	1.27	1.57	0.82	1.76	1.01	3.56	1.49	1.74
5	[N-epy][bti]	2.61	1.37	0.39	0.76	8.50	6.55	4.22	3.82
6	[N7222][bti]	2.18	2.42	0.75	2.25	2.08	7.69	10.03	9.77
7	[emim][mesy]	3.19	3.02	0.27	1.51	38.45	22.7	4.49	4.39
8	[N1444][bti]	2.27	2.42	0.75	2.25	2.08	7.69	10.03	9.77
9	[N6222][bti]	1.63	2.03	0.76	1.96	0.79	4.57	7.66	7.46
10	[N8222][bti]	2.92	2.66	0.84	2.25	2.47	10.10	11.69	11.30
11	[bmim][Br]	11.59	0.43	0.01	3.63	4.42	1.51	0.48	0.75
12	[tmpa][bti]	3.40	1.14	0.13	2.09	13.04	9.94	0.73	0.54
13	[hmim][Cl]	9.54	1.04	0.03	2.24	5.10	2.39	0.42	0.88
14	[emim][Cl]	9.03	2.19	0.27	3.97	10.04	7.68	9.05	9.33
15	[DEME][bti]	3.32	1.72	0.58	2.04	3.47	1.92	2.44	2.50
16	[BMP][bti]	2.15	1.26	1.26	2.29	1.93	3.93	10.24	10.10
17	[N2225][bti]	1.62	1.65	0.60	1.62	1.32	1.20	5.05	4.90
18	[omim][Cl]	15.22	1.08	0.17	4.65	3.58	7.73	4.11	3.46
19	[hpmim][PF6]	9.06	1.59	0.08	0.92	9.11	7.36	6.92	5.41
20	[mim][HSO4]	21.40	1.18	0.17	3.80	37.60	42.52	7.70	7.15
21	[nmim][PF6]	7.56	1.09	0.25	0.90	7.59	13.19	11.85	10.12
22	[DEME][BF4]	5.19	0.70	2.17	0.91	26.00	25.79	6.18	7.89
23	[bmim][I]	18.74	2.13	0.09	4.20	1.19	4.35	1.42	1.16
24	[bmim][mesy]	4.94	0.59	0.16	3.69	17.20	14.10	1.13	1.17
25	[dmim][MOESO4]	3.94	2.00	0.28	1.24	13.50	11.31	1.37	1.30
26	[tibmp][pTSO3]	17.06	1.05	0.59	1.01	0.53	12.50	11.80	11.26
27	[bdmim][BF4]	4.57	1.89	0.34	3.73	8.72	8.72	8.21	6.38
28	[prmim][BF4]	9.57	1.28	0.88	2.58	12.90	12.90	1.76	1.58
29	[omim][TfO]	4.30	2.85	0.59	4.67	2.67	2.67	8.80	8.55

[a]*Zarei et al. (2019);* [b]*Nasrifar and Moshfeghian (1998);* [c]*Valderrama et al. (2009);* [d]*Yen and Wood (1966);* [e]*Rackett (1970);* [f]*Yamada and Gun (1973);* [g]*Hankinson and Thomson (1979).*

Table 5. Comparison of %AAD with different models of IL densities at higher pressures (adopted from Zarei et al. (2019).

No.	**Ionic Liquid**	**%AAD**					
		This work	NAM[a]	Tait[b]	CZ[c]	Taylor[d]	Padé[d]
1	[emim][Ac]	4.82	1.11	1.13	1.10	1.04	1.18
2	[pmim][bti]	0.42	0.86	1.35	0.93	1.03	0.98
3	[prmim][bti]	1.15	0.77	0.87	0.82	0.73	1.14
4	[bdmim][bti]	3.00	1.01	1.58	1.08	1.35	1.05
5	[bmim][Cl]	2.73	1.52	2.54	3.40	3.96	4.02
6	[bmim][dca]	5.76	3.25	3.13	3.30	2.41	2.93
7	[dmim][DMPO4]	8.77	1.82	1.96	2.14	1.63	3.02
8	[emim][ESO4]	0.60	0.99	0.98	1.04	0.95	1.03
9	[bdmim][PF6]	13.71	2.96	3.11	3.05	3.02	3.16
10	[dmim][MSO4]	10.31	2.28	1.53	1.67	1.40	1.37
11	[bmim][MSO4]	3.15	1.00	0.99	1.04	0.95	1.03
12	[hpmim][bti]	1.62	2.85	3.16	2.99	3.04	2.98

[a]Zarei et al. (2019); [b]Thomson et al. (1982); [c]Chang and Zhao (1990); [d]Roshan and Ghader (2013)

The accuracy of the equation for predicting the densities of [pmim][bti], [emim][ESO4], and [hpmim][bti] were excellent compared to other models. The ILs [emim][Ac] and [pmim][bti] with %AADs of 0.38% and 0.41% (Table 3) were not compared with other models due to limited data. In Table 5, significant deviations from the present model are observed compared to other models. The comparison of the models is given to show the limitation of the Pitzer correlation for IL densities. Similar to the observed improvement in the overall %AAD obtained by the addition of molecular weight, it should be considered that other parameters which are characteristic of each ILs may improve the accuracy of the model.

CONCLUSIONS

Application of the Pitzer correlation for ionic liquid density calculations has been attempted in this study. Improvement of the model's accuracy by truncating the terms in the virial equation and including reduced temperature, reduced pressure, acentric factor, and molecular weight as variables has been shown. The results show that 6 of the 78 ionic liquids considered in this study fits well into the model for density calculations at 0.1 MPa; while 3 of the 22 ionic liquids used in the higher-pressure density calculations fits well into the extended virial equation.

There are several generalized correlation equations available for ionic liquid densities. The Pitzer correlation, which yields accurate results when applied for gases at low to moderate densities, has its limitations when applied for the density calculations of ionic liquids. It should be considered that the coefficients obtained for the model depend on the adopted data set, therefore indicating that this approach in calculation can further be improved and modified. Further expansion of the terms in the virial equations has resulted in a divergence in terms of a dramatic increase in calculated %AAD. The divergence of the calculated values upon further expansion also reveals the optimum accuracy of the form of equation used. However, it should not be overlooked how accurate predictions were obtained for some ionic liquids where the use of the model derived may be feasible.

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