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DENSITY CALCULATION OF IONIC LIQUIDS

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Abstract. Recently, an interest from both academia and industry has been moved toward ionic liquids due to their environmentally friendly characteristics as green alternative for traditional volatile organic solvents (VOCs). In addition, because of their wide range of physicochemical properties they found unique applications in renewable energy sector. For using such substances, one needs reliable correlations for predicting their physical properties. In the present work, a new method for determining the density of ionic liquids has been proposed. It has been shown that density of ionic liquids appears to be correlated linearly with the refractive index parameter of these liquids. An average error of 12.27% for 45 ionic liquids was obtained. Several equations of state were compared with this method including, SRK, RK, Peng Robinson and Riazi and Roomi [1]. Using a sample of 29 ionic liquids, average errors of 88.72%, 65.79%, 39.10% and 66.07% were obtained for these equations of state, respectively. The estimated values from this method seems to be reasonable and can be applied to determine the density of ionic liquids at any temperature.

1. Introduction

Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of renewable energy. Although ionic liquids (ILs) have been known since the beginning of the last century (1814), [2] they are materials of recent advent in the field of green energy applications where their recognition as solvents or electrolytes has ever increased during the last decades.

The high thermal conductivity of ionic liquids introduces it as one of the most efficient media for thermal energy storage. As a result, it can be used in solar thermal power plant systems. An example of good thermal storage ionic liquid is $[C_8mim]$ $[PF_6]$ which has thermal energy storage (TES) density of 378 MJ/m^3 and liquid temperature range of -75 to 416℃. In comparison with other media such as Molten salts which has a melting temperature of about 142℃, which is considered low and it causes freezing of the pipeline and increase in the operating cost. Another media used in TES is thermal oil, which has the disadvantages of limited temperature range (below 300℃), low heat capacity and low density. Some ionic liquids overcome the disadvantages of other media due to their attractive properties and they can be one of the best thermal energy storage media [3].

Ionic liquids, also known as liquid electrolytes, is a term generally used to refer to salts that form stable liquids. They are currently defined as organic salts that melt at or below 100℃.

2. Ionic Liquids Properties

The knowledge and fundamental understanding of the physicochemical properties of ionic liquids (ILs) is important before its industrial applications. The most significant characteristic

properties of ionic liquids are melting point, density, diffusion, conductivity, viscosity, thermal stability, phase equilibrium study and the enthalpy of ionic liquids.

Ionic liquids are an environmentally friendly media and have been utilized in many research fields. Ionic liquids have many advantageous properties as follows: an extremely low vapor pressure for many ionic liquids, high-density values, very high Thermal and chemical stability, excellent solubility in both inorganic and organic chemicals, excellent electrochemical properties, low melting point. Many ionic liquids are liquid at temperatures as low as -60℃. This property is useful in the cold climates [4].

Refractive index (n) of a material is a measure of the change in speed of light as it passes from a vacuum or air as an approximation into the material. For ionic liquids, its value is above unity [1].

3. Ionic Liquids Applications

Considering the above properties, ILs have an incredible variety of application fields. They can be used as additives to paints to improve the finishing and the appearance of the color.

Ionic liquids are used in electrochemical conversion devices that depend on the transport of ionic species, since the ionic liquid has a good conductivity at room temperature in the range of (10^{-3} – 10^{-2}) it is used in electrochemical conversion devices like capacities, solar cells, li-ion batteries, fuel cells [5].

Biofuels like ethanol, butanol and biodiesel that are carbon natural resources produced from biomass store high energy in there lignocellulose. For the energy to be produced these lignocellulose should be broken down which requires a harsh chemical treatment, ionic liquids have inions with hydrogen bonds that can dissolve the lignocellulose by breaking the bonds in the biomass and hence producing energy [6].

The production of fossil fuels can be cleaner by the use of ionic liquids. For the production of the fossil fuels, a sulfur extraction from the petroleum feed stock is needed to protect the catalyst and the fuel cell, and to reduce the amount of SO_2 produced that is contaminating the air. Ionic liquids are very effective in sulfur extraction from fossil fuels [6].

The ability of the ionic liquid to dissolve the gasses and there low volatility at normal ambient temperatures allows them to be used in separation applications and gas capture [6].

ILs can also be used as catalyst in biodiesel production. Thus, ILs such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM]TfO) and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([BMIM]NTf_2) increases the biodiesel yield up to 96.3% which give the opportunity for future bio-refining processes.[7]

In the synthesis and applications of nanoparticles, it is always necessary to have solvents and stabilizing agents. Ionic liquids can be used as an alternative solvent and stabilizer that prevents the aggregation of nanoparticles. In addition, ionic liquids affect the nanoparticle size if they are used in there synthesis, the use of the ionic liquid in nanoparticles synthesis reduces the crystal growth resulting in a smaller particles produced [8].

Ionic liquid with its amazing properties and high chemical stability of some types of anion and cation lead it to be a part of the electrochemical devices application such as lithium batteries. They are used as electrolyte because of their non-flammability and low volatility properties which are useful in increasing the stability and safety .An example of the use of ionic liquids in lithium batteries is the stability that is offered by ILs to lithium electrochemistry in quaternary ammonium and phosphonium [NTf_2] [9].

The global warming caused by greenhouse gases has been increasing the amount of CO_2 in the atmosphere. As a result, the elimination of CO_2 by converting it to useful energy is highly recommended. Ionic liquids are used as a catalyst in a water gas shift reaction to convert CO_2 to fuel [10].

Selective ionic liquids can be used as an alternative to conventional solvents in catalytic reactions. They can change the reaction pathway and promote the selection and the yield of the product and the reaction proceeds more efficiently in comparison with the conventional solvents [8].

According to the wide applications of ionic liquids in process industry. The development of a reliable correlation for modeling the physical properties of ionic liquids would be useful from industrial point of view.

4. Results

Table 1 shows the calculated density values using the method proposed by this work compared to literature data and to the density values obtained from different equations of state for 45 ionic liquids.

Table 1. Literature data on density and refractive index, calculated refractive index parameter, I/d, and calculated density at 25℃ and the error percentage.

ILs Name	Literature ρ (kg/m^3)	n	I_{25}	I/d	Estimated ρ (kg/m^3)	Error %	Ref
[bmim][PF_6]	1365.7	1.4094	0.24743	0.00018117	1158.8	15.149	11
[emim][NTf_2]	1514.7	1.4225	0.25439	0.00016795	1191.4	21.343	11
[bmim][NTf_2]	1436.0	1.4265	0.25650	0.00017862	1201.3	16.342	11
[C_6mim][NTf_2]	1371.0	1.4295	0.25808	0.00018825	1208.7	11.836	11
[C_8mim][NTf_2]	1318.9	1.4326	0.25967	0.00019688	1216.1	7.791	11
[Bpyr][NTf_2]	1394.6	1.4230	0.25467	0.00018261	1192.7	14.475	16
[C_6mim][PF_6]	1292.4	1.4165	0.25120	0.00019437	1176.5	8.969	11
[C_8mim][PF_6]	1234.0	1.4235	0.25491	0.00020658	1193.9	3.251	11
[$P_{6\,6\,6\,14}$][NTf_2]	1065.4	1.4496	0.26855	0.00025206	1257.7	18.053	11
[emim] [BF_4]	1279.8	1.4121	0.24888	0.00019447	1165.6	8.922	13
[C_3mim] [BF_4]	1236.1	1.4211	0.25364	0.00020520	1187.9	3.897	13
[bmim][BF_4]	1199.4	1.4215	0.25385	0.00021165	1188.9	0.874	11
[C_5mim] [BF_4]	1171.9	1.4238	0.25507	0.00021765	1194.6	1.937	13
[C_6mim] [BF_4]	1146.3	1.4270	0.25675	0.00022398	1202.5	4.901	13
[C_{10}mim][NTf_2]	1278.3	1.4356	0.26124	0.00020437	1223.5	4.286	11
[C_{12}mim][N Tf_2]	1244.7	1.4376	0.26229	0.00021073	1228.4	1.308	11
[bmim][OTf]	1299.6	1.4366	0.26176	0.00020142	1226.0	5.665	11
[bmim][OAc]	1053.2	1.4938	0.29103	0.00027633	1363.0	29.416	11
[emim] [dca]	1101.0	1.5127	0.30042	0.00027286	1407.0	27.792	12
1-Et-3-Me-Im-FAP	1707.0	1.3691	0.22569	0.00013222	1057.0	38.077	12
1-Et-3-Me-Im-TCB	1028.0	1.4476	0.26750	0.00026021	1252.8	21.869	12
[emim] [SCN]	1115.0	1.5514	0.31924	0.00028631	1495.2	34.094	12
[emim] [HSO_4]	1367.0	1.4971	0.29267	0.00021410	1370.7	0.272	12
[emim] [mesy]	1241.0	1.4958	0.29202	0.00023531	1367.7	10.207	12
[emim] [ESO_4]	1237.0	1.4792	0.28367	0.00022932	1328.6	7.403	12
[prmpyr] [bti]	1427.0	1.4206	0.25338	0.00017756	1186.7	16.840	12
N-Me-Pr-PyrrN($SO_2F)_2$	1338.0	1.4425	0.26485	0.00019795	1240.4	7.293	12
Et-Py-N($SO_2F)_2$	1458.0	1.4703	0.27915	0.00019146	1307.4	10.328	12
Bu-Py-N($SO_2F)_2$	1369.0	1.4712	0.27961	0.00020425	1309.6	4.342	12

ILs Name	Literature ρ (kg/m^3)	n	I $_{25}$	I/d	Estimated ρ (kg/m^3)	Error %	Ref
He-Py-N(SO2F)2	1301.0	1.4709	0.27946	0.00021480	1308.8	0.603	12
1-Et-3-Me-Py-$N(SO_2F)_2$	1407.0	1.4719	0.27997	0.00019898	1311.2	6.807	12
1-Bu-3-Me-Im-$N(SO_2C_4F_9)_2$	1611.0	1.3880	0.23597	0.00014647	1105.2	31.400	12
[omim][BF_4]	1105.3	1.4342	0.26053	0.00023571	1220.2	10.396	14
[bmim][BF_4]	1201.3	1.4219	0.25407	0.00021148	1189.9	0.952	14
[emim] [AOC]	1099.3	1.5009	0.29457	0.00026796	1379.6	25.499	15
[C_2mim] [CH_3OHPO_2]	1208.3	1.4925	0.29037	0.00024031	1359.9	12.548	15
[emim] [TfO]	1385.9	1.4330	0.25988	0.00018751	1217.1	12.178	15
[bmim][PF_6]	1360.0	1.4100	0.24776	0.00018218	1160.4	14.678	17
2-hydroxy ethylammonium	1204.0	1.4772	0.28266	0.00023477	1323.8	9.953	18
[C_2CN Him]Br	1229.0	1.5287	0.30828	0.00025083	1443.8	17.477	19
[C_2CN Oim]Br	1176.6	1.5147	0.30142	0.00025618	1411.7	19.979	19
[C_2CN Bim]Br	1304.7	1.5454	0.31636	0.00024248	1481.7	13.563	19
[bdmim][BF_4]	1191.2	1.4330	0.25990	0.00021818	1217.2	2.184	20
[bmim][ClO_4]	1252.7	1.4725	0.28027	0.00022374	1312.7	4.786	21
[bmim][CF_3SO_3]	1303.8	1.4368	0.26188	0.00020086	1226.5	5.927	17
			Average I/d	0.00021352	AAD%	12.271	

Table 2. Comparison of the Density Values (Kg/m^3) Obtained with Equations of State at 25℃.

Method's Name	AAD%
SRK	88.72
REF[1]	66.07
Peng Robinson	39.10
RK	65.79
This Work	11.89

5. Discussion of Results

In this work, the density (ρ) and refractive index (n) at 25 ℃ for 45 ILs were collected [11,21]. Refractive index, which is an important property of any chemical material, was taken into consideration when developing the correlation, as it appears to be very efficient variable in increasing the accuracy of the results. This property was not considered in any equation of state model proposed before for ionic liquids.

By observation, a reliable correlation that describes the volumetric properties of ILs was found. This correlation was developed based on observing the density and the refractive index parameter (I) appears to be related linearly as shown in Fig. 1, and the equation takes the form of:

$$y = mx, \quad (1)$$

where x is the density while y is the refractive index parameter.

The value of refractive index parameter at 25℃ (I_{25}) was calculated based on the following equation:

$$I_{25} = \frac{n^2-1}{n^2+2}, \quad (2)$$

where n is the refractive index at 25℃.

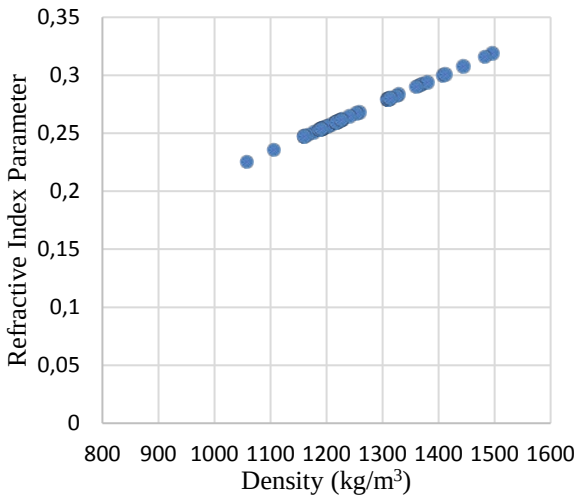

Fig. 1. Correlation of refractive index parameter and density for the 45 ILs.

The value of (m), or the slope, was found to be 0.00021352, which is the average value of dividing I_{25} by density at 25℃ for each component of the 45 ionic liquids as shown in Table 1.

Then, substituting the above parameters in equation 1. Hence, the proposed correlation takes the form of:

$$I_{25} = 0.00021352 * \rho_{25}. \quad (3)$$

An average error of 12.27% was the result when comparing the density values calculated by equation 3 with the literature values for the 45 ILs. This error is small compared to errors obtained using other EOS. Table 2 shows the comparison between the proposed correlation and other EOS.

For comparison, a sample of 29 ionic liquids was examined. Experimental data required for modelling and calculations were collected from the literature [22,23]. Will known equations of state such as SRK, PR, and RK were examined for density calculation of ionic liquids. The AARD % using SRK (Soave modification of Redlich-Kwong) was 88.72%, using Peng Robinson was 39.09%, using RK (Redlich-Kwong) was 38.08%, using Riazi-Roomi equation of state [1] was 66.07% and using the proposed correlation was 11.89%. It appears that the proposed correlation has much less average error when compared to other EOS. This proposed equation can be applied for ILs at any temperature.

6. Conclusion

ILs are materials with an incredible variety of application fields. In this work, a correlation for calculating the density of ionic liquids using refractive index was developed. In spite of the very simple form of the proposed correlation in this work, it showed very accurate results with small average error compared to other equations of state.

Variables Identification

ρ_{25}Density at 25℃
n Refractive Index
I_{25} Refractive Index Parameter

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