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Research Article

Computational and Experimental investigations on binary green materials

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Abstract Computational and experimental FT-IR studies of two binary green systems ([Bmim][NTf2]/ [Bmim][Pf6] with aniline) are supported by the predictions related to the nature of molecular collaborations. Viscosity data has been evaluated for several mixture compositions of two binary systems in the temperatures range (298.15 to 323.15) K. The study categorically shows that the simultaneous analysis of deviations of viscosity is able to offer an extensive explanation for intermolecular interactions happening in the mixture systems, particularly if the part molecules have various sizes. The precise knowledge of the viscometric nature of the studied systems play essential part in many industrial applications.

Keywords: Computational FT-IR, [Bmim][NTf2], viscosity, [Bmim][Pf6].

1. Introduction

Due to the widespread and beneficial properties, ionic liquids (ILs) are used largely in various industrial and engineering purposes. The strange attributes of ILs namely – less vapour pressure, high solving ability and considerable thermal withstanding capacity be affected by created ILs as ecological helpful solvents as a good replacement to organic solvents. Additionally, the info concerning the thermodynamic nature of ILs + organic solvents is actually utmost important for many industrial uses [Rao et al., 2016, Mohan et al., 2010, Nadh ML et al., 2013].

The current study deals with two binary combination systems: [Bmim][NTf2] + aniline (system one) along with [Bmim][Pf_6] + aniline" (system two). The accurate information of computational, experimental and thermodynamic qualities of these investigated combinations can be of excellent value for the probable take advantage of theirs in the separation engineering, batteries, CO_2 absorption etc. [Rao et al., 2017].

2. Experimental Section

Vacuum treatment technique has been used to purify the ILs ([Bmim][NTf2]/[Bmim][Pf_6], Io-Li-Tec, Germany) for over twelve hours at a temperature of 343.15 K. Fractional distillation technique has been adopted to purify aniline (Sigma Aldrich, USA).

Infrared spectroscopy has been studied by utilizing "Agilent Cary 630 FT-IR spectrometer". The enhanced geometry and wave numbers of equimolar and pure compounds are estimated computationally from the DFT calculations using "6-311++G** and 6-311+G** sets". Gaussian computational package is utilized to perform these calculations [Becke AD, 1993, Frisch., et al., 2009 and Lee et al., 1988].

Viscosity (η) data is collected on Lovis 2000M micro viscometer from temperature (298.15 to 323.15) K at 0.1MPa.

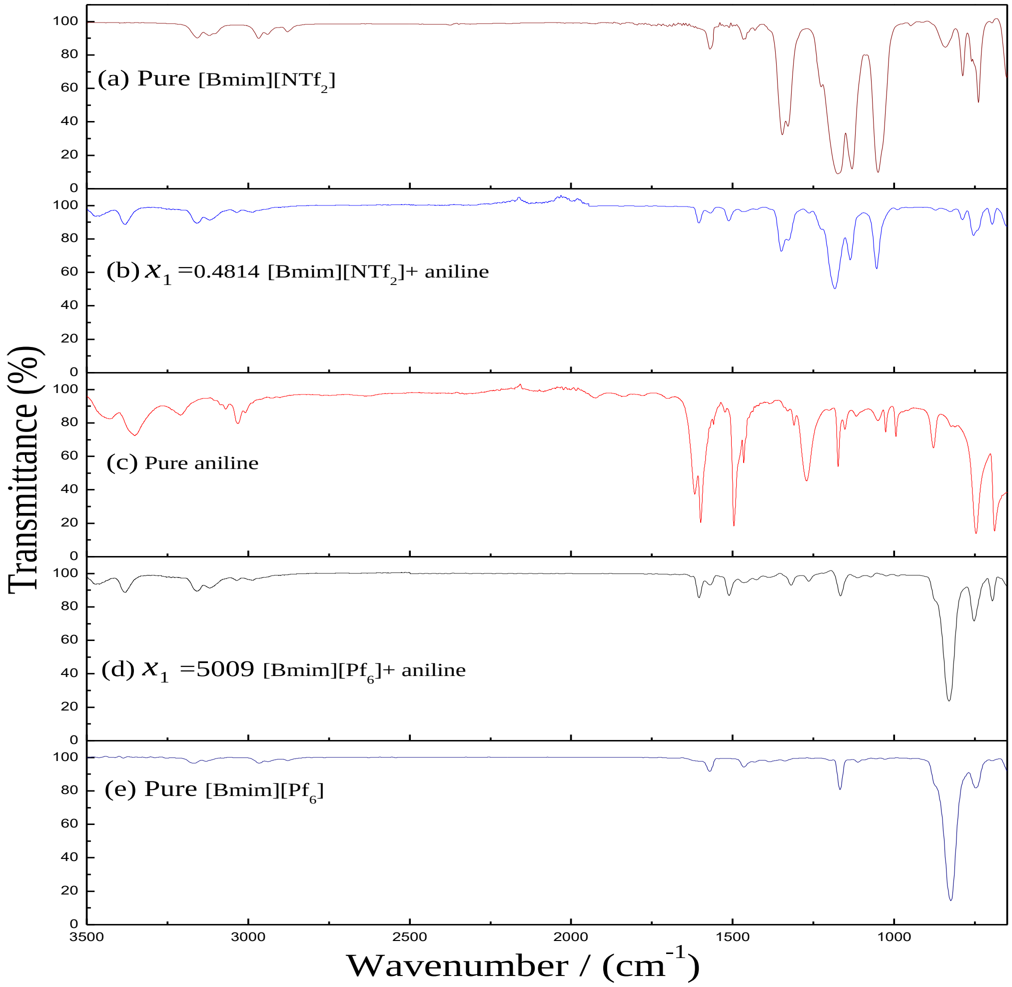
3. **Results and Discussion**

Computational and Experimental FT-IR Spectra

The FT-IR spectra of [Bmim][NTf2], [Bmim][Pf$_6$], aniline as well as for the molar mixture (0.4814) of system one and molar mixture (0.5009) of system two are captured within infrared zone of 500 to 3500 cm^{-1}. FT-IR of [Bmim][NTf2] (Figure 1 (a)) exhibits symmetric C–H stretching vibration at 3156 cm^{-1}. The crest at wave number 737 cm^{-1} resembles to S–N–S bending vibrations of [NTf$_2$] anion. Figure 1 (e) (FT-IR of [Bmim][Pf$_6$]) shows symmetric C–H stretching vibration at 3169 cm^{-1}. The crest at wave number 826 cm^{-1} is the F–P–F unevenness stretching vibrations of [Pf$_6$]$^-$ [Rao et al., 2017, Sharma D et al., 2012]. Figure 1 (c) (FT-IR of aniline) exhibits N–H extending vibrations at 3356 cm^{-1} [Silverstein et al., 1991].

Within system one (Figure 1 (b)), the increased wave numbers from 3356 cm^{-1} to 3381 cm^{-1} indicates the N–H extending vibration of aniline and it is because of the ion-dipole interface amid [Bmim][NTf2] and aniline. This interface will disperse the electron density left from the amine group. Figure 1 (d) (FT-IR of system two) represents symmetric C–H extending vibrations at 3159 cm^{-1}, F–P–F asymmetry extending vibrations of [Pf$_6$]$^-$ at 832 cm^{-1} and N–H extending at 3372 cm^{-1}[Silverstein et al., 1991].

Figure. 1 FT-IR spectra of (a) pure [Bmim][NTf$_2$] (b) x_1 = 0.4814 of [Bmim][NTf$_2$] + aniline (c) pure aniline (d) x_1 = 0.5009 of [Bmim][Pf$_6$] + aniline (e) pure [Bmim][Pf$_6$]



The comparability of experimental and computational spectroscopic data is shown in Table 1 [Pathak S et al., 2010]. The theoretical values are in fair correlation with regard to experimental data. The minimum energy molecular complexes attained using DFT study making use of Gaussian 09 for [Bmim][NTf2] (Figure.2**)**, [Bmim][Pf$_6$] (Figure.3**)**, aniline (Figure.4**)**, system one (Figure.5**)** and system two (Figure.6**)** are shown in figures.

The FT-IR study indicates that the mixing of [Bmim][NTf2]/[Bmim][Pf$_6$] with aniline effect (i) C–H tremors of [Bmim]$^+$; (ii) S–N–S bending vibrations of [NTf$_2$]$^-$ and F–P–F asymmetry extending of [Pf$_6$] anion as well as (iii) N–H extending of aniline. In this way, FT-IR investigation entitles the ion-dipole bondings concerning system one and system two.

Table.1. Investigational and Computational FT-IR analysis

Compound	**Band**	**Investigational**		**Computational**			
				Density Functional Theory(DFT - B3LYP)			
				6-311+G**		***6-311++G*****	
		υ (cm^{-1})	**$\Delta\upsilon$ (cm^{-1})**	**υ (cm^{-1})**	**$\Delta\upsilon$ (cm^{-1})**	**υ (cm^{-1})**	**$\Delta\upsilon$ (cm^{-1})**
[Bmim][NTf2]	CH S-N-S	3156 739	-	3152 736	-	3154 735	-
[Bmim][Pf$_6$]	CH F-P-F	3169 826	-	3173 829	-	3171 827	-
Aniline	NH	3356	-	3362	-	3359	-
System-1 ([Bmim][NTf2] +Aniline)	CH S-N-S NH	3165 755 3381	09 16 25	3162 750 3384	10 14 22	3165 752 3382	11 17 23
System-2 ([Bmim][Pf$_6$] + Aniline)	CH F-P-F NH	3159 832 3372	10 06 16	3166 837 3375	08 08 13	3160 834 3376	11 07 17

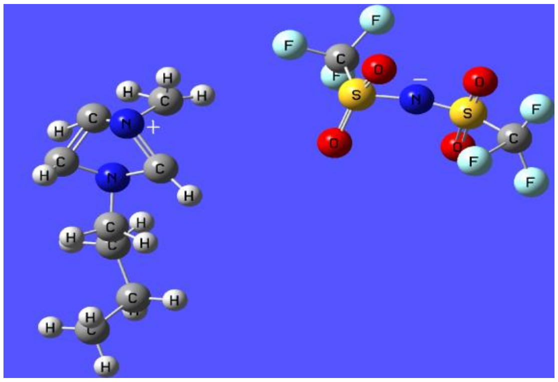


Figure.2 ([Bmim][NTf2]) by DFT - B3LYP *6-311+G***

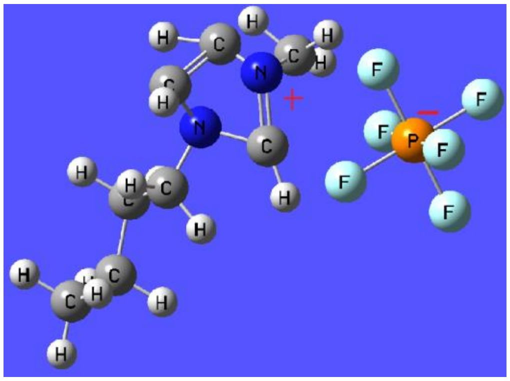


Figure.3 ([Bmim][Pf$_6$]) by DFT - B3LYP *6-311+G***

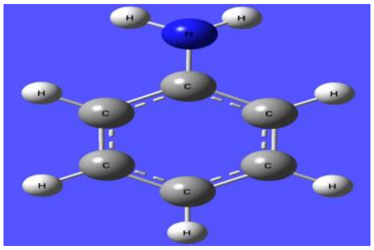


Figure.4 Aniline by DFT - B3LYP *6-311+G***

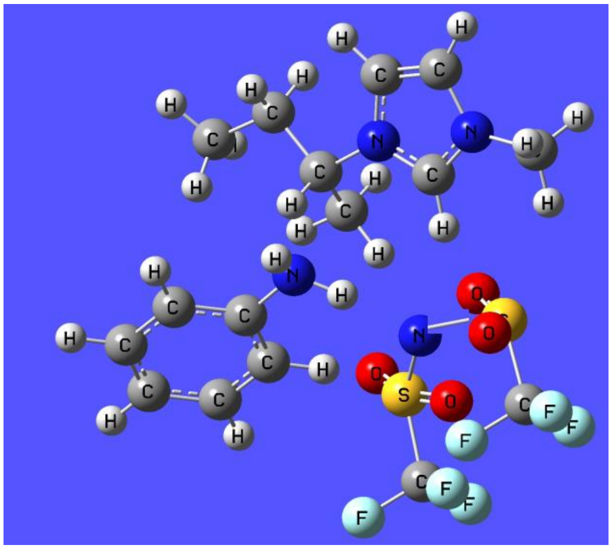


Figure.5 [Bmim][NTf2] + Aniline by DFT - B3LYP *6-311+G***

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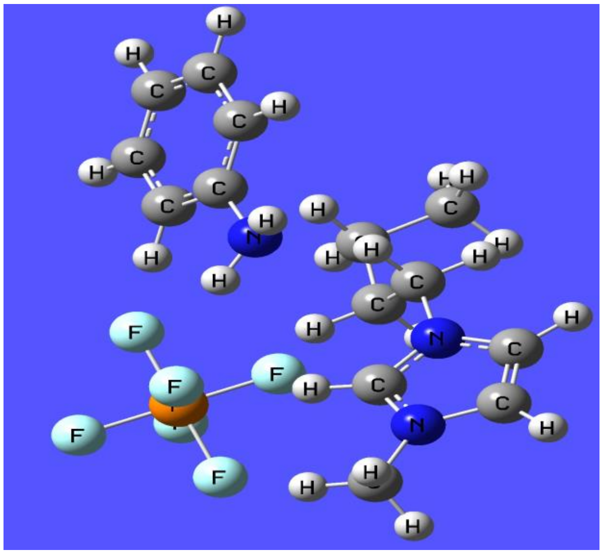


Figure.6 [Bmim][Pf_6] + Aniline by DFT - B3LYP *6-311++G***

$$\eta = \eta_0 \exp\left[\frac{B}{T-T_0}\right] \qquad (1)$$

where η_0, B and T_0 represent fitting coefficients. The values of fitting coefficients and Average absolute Relative Deviation (ARD) are shown in Tables 2 and 3.

Table.2. η_0 , B , T_0 and ARD for viscosity at various values of x_1 in [Bmim][NTf_2] + aniline

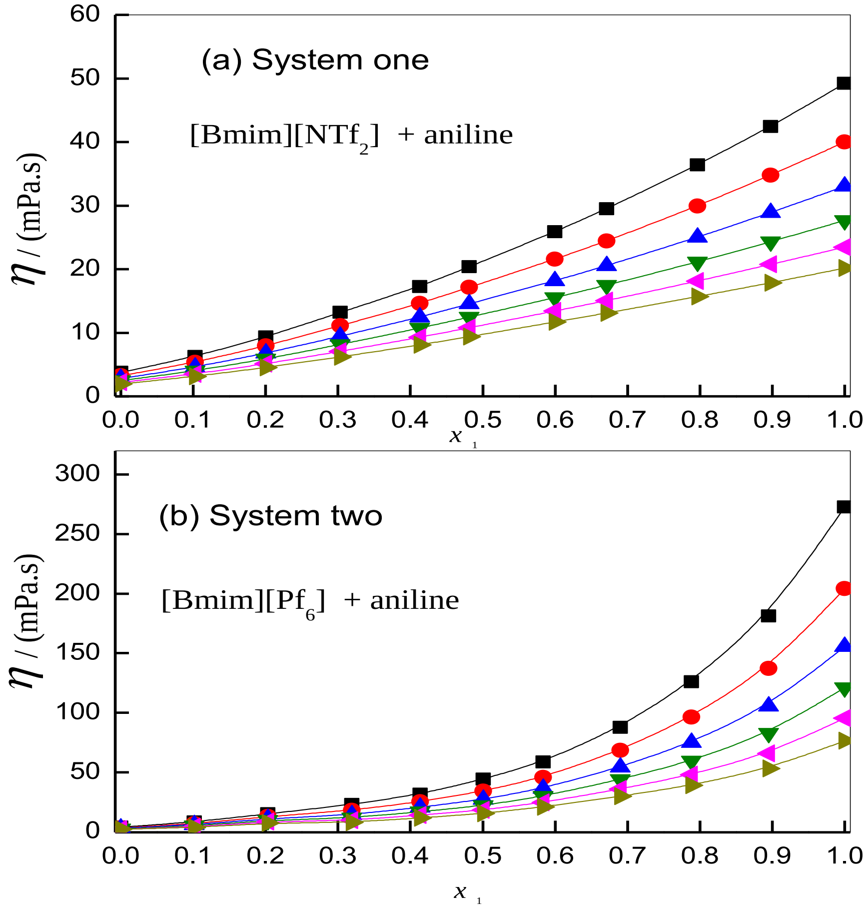
x_1	η_0	B	T_0	ARD
0	0.0601	545.650	166.301	0.0631
0.1028	0.0715	597.275	164.552	0.2784
0.2004	0.1101	568.315	170.156	0.0796
0.3031	0.1075	639.680	165.233	0.0461
0.4128	0.0322	1145.174	115.898	0.1812
0.4814	0.0806	849.812	144.534	0.0840
0.5995	0.2046	615.700	170.927	0.1058
0.6714	0.2435	588.077	175.543	0.0428
0.7968	0.3019	563.409	180.575	0.0220
0.8981	0.2248	661.644	171.897	0.0880
1	0.3009	599.592	180.531	0.1645

The behaviour of η, with regard to mole fraction (x_1) and temperature (*T*) in system one as well as system two, is revealed in Figure 7. For examined temps, η values have been rising as well as rising IL concentration in the two systems. Additionally, in the studied combinations, η values are observed to be dwindling with rising *T*. The nature of η with concentration and temp, represents that the thermo physical qualities of ionic liquids might be customized for a desired purpose with the addition of aniline or by altering temperature.

Table.3. η_0 , B , T_0 and ARD for viscosity at various values of x_1 in [Bmim][Pf$_6$] + aniline

x_1	η_0	B	T_0	ARD
0	0.0601	545.650	166.301	0.0631
0.1017	0.0826	538.176	181.065	0.2724
0.2032	0.0514	837.168	149.496	0.3186
0.3192	0.0135	1356.623	115.531	0.3386
0.4135	0.0205	1327.958	117.503	0.2858
0.5009	0.1557	725.884	169.570	0.3554
0.5836	0.0376	1208.751	133.819	0.4081
0.6901	0.0463	1179.190	141.561	0.3479
0.7886	0.0324	1283.904	142.293	0.3644
0.8955	0.0663	1078.906	161.793	0.0854
1	0.0685	1142.183	160.379	0.2391

Figure.7. η vs x_1 in the systems (a) system one and (b) system two.

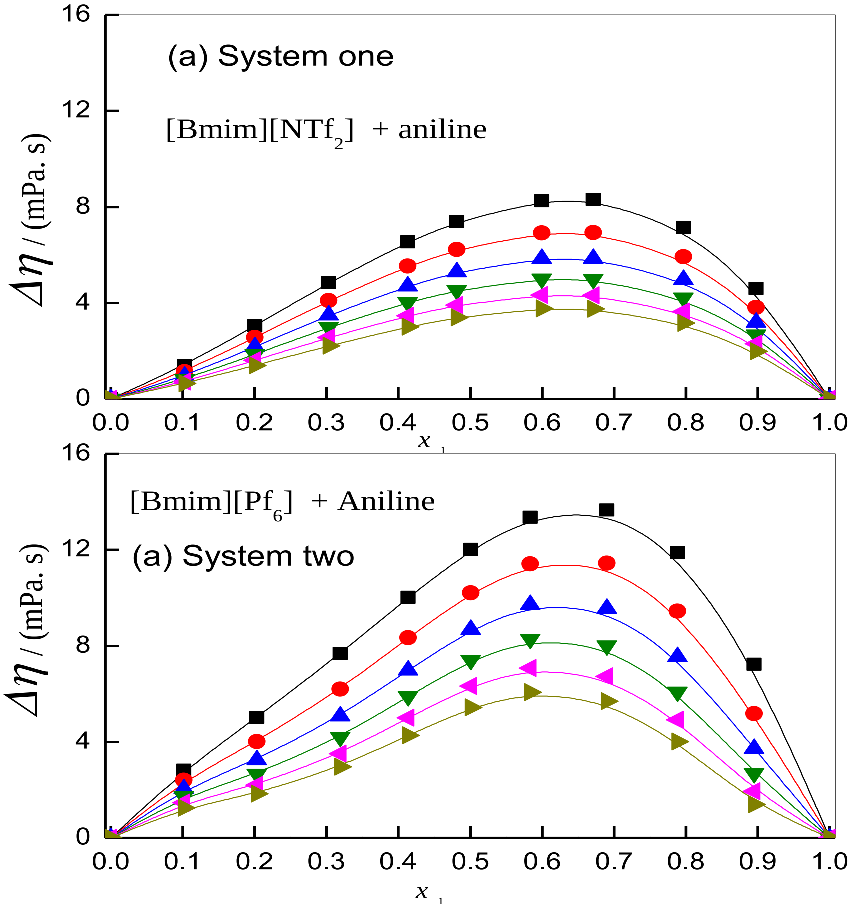


The formula for calculating deviation in viscosity ($\Delta\eta$) is given by,

$$\Delta\eta = \eta - exp\left[x_1 \ln\eta_1 - x_2 \ln\eta_2\right] \tag{2}$$

where η_1 , η_2 and η denote respectively viscosities of pure ionic liquid, aniline and mixture.

Figure.8. $\Delta\eta$ vs x_1 in (a) system one and (b) system two.



Usually, the distribution as well as chemical bond shattering interactions give negative $\Delta\eta$ data whereas, bond developing interactions cause positive $\Delta\eta$ data. In present study, positive $\Delta\eta$ data (Figure 8) has been found for both the studied systems with complete x_1 range of IL at each studied temperature. These tendencies label that, structural rearrangements are occurring in the combinations by ion-dipole mechanism. Additionally, the high positive data of $\Delta\eta$ in system two, specify the intensity of chemical associations as ([Bmim][Pf$_6$] + aniline) > ([Bmim][NTf$_2$] + aniline).

4. Conclusions

In this study, the occurrence of ion-dipole bondings between ionic liquids ([Bmim][NTf2], [Bmim][Pf$_6$]) and aniline has been confirmed through the computational and experimental spectroscopic investigations. Viscosity data has been evaluated for several mixture compositions of two binary systems (system one ([Bmim][NTf2] + aniline) as well as system two ([Bmim][Pf$_6$] + aniline) for studied temperatures. The nature of viscosity entitles that the physico-chemical behaviour of ionic liquids can be altered in a desired way by combining aniline. Quantitative examination of positive deviation of viscosity indicates the stronger interactions in system two compared to system one.

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