

# Molecular Interactions of Piperidinium Based Ionic Liquids with Water/Alcohol at Different Temperatures 

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Received: 2 September 2020;
Accepted: 28 October 2020;
Published online: 10 December 2020;
AJC-20198


#### Abstract

In this experimental investigation, the thermodynamic fundamental parameters of density $(\rho)$ and speed of sound(U) were calibrated for aqueous solution/alcoholic (1-propanol and 2-propanol) solutions of piperidinium based ionic liquids of 1-butyl-1-methylpiperidinium tetrafluoroborate $\left(\mathrm{BMPiBF}_{4}\right)$ in various concentrations within temperatures from 303.15 to 313.15 K . From these experimental determined values, various thermodynamic acoustic parameters of excess molar isentropic compressibility ( $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ ), excess molar volume ( $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ ) are expressed in specific and non-specific molecular interactions. Moreover, calibration of the partial molar volume's and partial isentropic compressibility's of both components shows strong interaction in $\mathrm{BMPiBF}_{4}+2$-proponol combination than any other executed binary composites. In addition to this, the FTIR characteristic spectrum of all combinations at different concentrations gives the more promising features such as interaction behaviour that helps our analysis to guide the interactions of individual bonds.


Keywords: Redlich-Kister equations, Ionic liquids, Piperidinium, Legendre polynomial, Partial isentropic compressibility.

## INTRODUCTION

The conceivable interactions in binary solutions of any one concentration has sharp applications rather than individual solution's applications [1,2]. In this context, the binary systems reinforce the molecular interactions at particular monumental point [3,4]. At this point, these molecular interactions are engineered into several applications alike rechargeable batteries, super capacitors, pharmaceutical, prevention of corrosions and peculiar solvent agent at room temperature range [5-10]. Noteworthy, these intramolecular interactions are explored with thermodynamic excess parameters alike excess molar volume ( $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ ) and excess molar isentropic compressibility $\left(\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}\right)$ [11,12]. Moreover, these excess features are accompanied with non-linear Redlich-Kister polynomial equations to divulge the information through entire concentrations of the binary solutions [13-16]. Since the highly reactiveness of the non-ideality of binary fluids could misprints the specific interactions. In order to show more specific interactions at low concentrations, the excess values are fitted into non-linear reduced Redlich-Kister polynomials equation with legendre co-efficients. In addition to that, to understand the intramolecular interactions
of binary fluids the partial molar volumes and partial isentropic compressibilities are computed [17]. Notwithstanding, the above parameters are experimentally computed with fundamental thermo physical features of density ( $\rho$ ) and speed of sound (U). In this present article, the binary alike water/1-propanol/ 2-propanol and piperidinium based ionic liquids of [BMPip]BF ${ }_{4}$ were prototyped within various concentrations at lukewarm temperature ranges [18]. Consequently, the above mixture suggests many applications from solvent agents to rechargeable battery as mentioned above [19-21]. Accordingly, these mixtures are replica to the major ionic liquids (solutions) that portrays the several applications at monumental point of concentration. Further, these isolated fluids and binary fluids are characterized with FTIR spectroscopy analysis to test the above template of molecular interactions [22,23].

## EXPERIMENTAL

At the outset, for evaluation of thermophysical features of ionic liquid binary systems, these were extracted with impurities by a Millipore instrument. Further, the chemical solvents of alike water, 1-propanol and 2-propanol are subjected to glass chromatography for removing additional impurities [24]. These

[^0]chemical data inventories of propanol isomers and [BMPip]$\mathrm{BF}_{4}$ have been shown in Table-1. Table-2 illustrated the density and speed of sound of pure fluids such as water, 1-propanol and 2-propanol with relevant citations. In addition to this, the unmapped density $(\rho)$ and speed of sound $(\mathrm{U})$ of $[B M P i p] \mathrm{BF}_{4}$. The specimens were correlated with standard literatures [25-29].

General procedure: The prepared binary fluids and pure fluids were cascaded into vials. These vials were covered with air tight lids to prevent evaporation and adsorption of atmospheric moisture. The fluids are weighed with the help of mass analytical balance (Mettler Toledo) which is having an accuracy 1011 kg . In this consequence, the uncertainty in measuring the final mole fraction for binary fluids should be less than 0.0001. The binary fluids of systems such as $[\mathrm{BMPip}] \mathrm{BF}_{4}+$ water (W), $[\mathrm{BMPip}] \mathrm{BF}_{4}+1$-propanol (1P) and [BMPip]BF $4+2$-propanol $(2 \mathrm{P})$ were prepared at specified concentrations, i.e. molefractions of these systems carried out 12 subsequent values in such way that the solvation concentration ranges from 0 to 1 .

Detection method: The temperature dependent thermophysical features of density ( $\rho$ ) was calibrated through an instrument vibrating-tube digital density meter. And the speed of sound (U) was extracted with sound analyzer with in temperature ranges from $303.15,308.15$ and 313.15 K over ambient atmospheric pressure. This temperature bath has been controlled through incorporated Peltier thermostat with an accuracy of $\pm 0.01 \mathrm{~K}$. In this consequence, the uncertainty in measuring the experimental density $(\rho)$ and speed of sound $(U)$ should be less than are equal to $0.01 \mathrm{~kg} \mathrm{~m}^{-3}$ and $0.5 \mathrm{~m} \mathrm{~s}^{-1}$, respectively.

## RESULTS AND DISCUSSION

The density $(\rho)$ and speed of sound $(\mathrm{U})$ were experimentally extracted for binary fluids of $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W}$, $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}$ +1 P and $[\mathrm{BMPip}] \mathrm{BF}_{4}+2 \mathrm{P}$ with temperature ranges 303.15,
308.15 and 313.15 K . The variations of these parameters are portrayed in Fig. 1a-b, which shows the non-linear trend. The observed features of non-linear increasing trend suggest that fluids have molecular interactions exists between them [30]. These non-linear trend decreases as the temperature increases. The excess thermodynamic acoustic parameters such as $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ and $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ for binary fluids have been esteemed with the literature [31-33]. The eventual expression as:

$$
\begin{equation*}
\mathrm{Y}^{\mathrm{E}}=\mathrm{Y}^{\mathrm{T}}-\mathrm{Y}^{\mathrm{id}} \tag{1}
\end{equation*}
$$

Here $\mathrm{Y}^{\mathrm{E}}=\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}, \mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ and $\mathrm{Y}^{\mathrm{r}}\left\{=\mathrm{V}_{\mathrm{m}}\right.$ (molar volume), $\mathrm{K}_{\mathrm{s}, \mathrm{m}}$ (molar isentropic compressibility) $\}$ are the real value of fluids. The ideal component of thermodynamic acoustic parameters for molar volume stands for

$$
\begin{equation*}
\mathrm{V}^{\mathrm{id}}=x_{1} \mathrm{~V}_{1}+\left(1-x_{1}\right) \mathrm{V}_{2} \tag{2}
\end{equation*}
$$

Here, $x_{1}$ is the mole fraction of component $\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}\right.$ (1) with respect to $\mathrm{W} / 1 \mathrm{P} / 2 \mathrm{P}(2) ; \mathrm{V}_{1}$ and $\mathrm{V}_{2}$ are the pure acoustic molar values of $[\mathrm{BMPip}] \mathrm{BF}_{4}(1)$ and $\mathrm{W} / 1 \mathrm{P} / 2 \mathrm{P}(2)$, respectively. The molar isentropic compressibility $\mathrm{K}_{\mathrm{s}, \mathrm{m}}$ was calculated from the equation

$$
\begin{equation*}
\mathrm{K}_{\mathrm{s}, \mathrm{~m}}=\mathrm{V}_{\mathrm{m}} \mathrm{~K}_{\mathrm{s}}=\frac{\mathrm{V}_{\mathrm{m}}}{\rho \mathrm{U}^{2}} \tag{3}
\end{equation*}
$$

And the ideal component of molar isentropic compressibility can be calculated as follows:

$$
\begin{equation*}
\mathrm{K}_{\mathrm{s}, \mathrm{~m}}^{\mathrm{id}}=\sum_{\mathrm{i}=1}^{2} x_{\mathrm{i}}\left(\mathrm{~K}_{\mathrm{s}, \mathrm{~m}, \mathrm{i}}+\frac{\mathrm{TV}\left(\alpha_{\mathrm{i}}\right)^{2}}{\mathrm{C}_{\mathrm{p}, \mathrm{~m}, \mathrm{i}}}\right)-\left(\frac{\mathrm{T}\left(\sum_{\mathrm{i}=1}^{2} x_{\mathrm{i}} \mathrm{~V}_{\mathrm{i}}\right)\left(\sum_{\mathrm{i}=1}^{2} x_{\mathrm{i}} \alpha_{\mathrm{i}}\right)^{2}}{\sum_{\mathrm{i}=1}^{2} x_{\mathrm{i}} \mathrm{C}_{\mathrm{p}, \mathrm{~m}, \mathrm{i}}}\right) \tag{4}
\end{equation*}
$$

where $\mathrm{K}_{\mathrm{s}, \mathrm{m}, \mathrm{i}}, \mathrm{V}_{\mathrm{i}}, x_{\mathrm{i}}, \alpha_{\mathrm{i}}$ and $\mathrm{C}_{\mathrm{p}, \mathrm{m}, \mathrm{i}}$ are the molar heat capacity, molar volume, mole fraction, isobaric coefficient of thermal expansion and molar heat capacity of pure components in binary fluids, respectively. The isobaric thermal expansion coefficients of pure components were calculated as follows:

TABLE-1
SPECIFICATION OF SOURCE, CAS NUMBER, MASS FRACTION PURITY AND FURTHER PURIFICATION

| Name of the chemical | Source | CAS number | Mass fraction purity (\%) | Further purification methods |
| :---: | :---: | :---: | :---: | :---: |
| Water | Double Distillation Method | $7732-18-5$ | $>99.99$ | - |
| 1-Propanol | HiMedia Laboratories, India | $71-23-8$ | $>98.00$ | *GLPC |
| 2-Propanol | HiMedia Laboratories, India | $67-63-0$ | $>98.00$ | *GLPC |
| [BMPip]BF |  | HiMedia Laboratories, India | $886439-34-5$ | $>99.70$ |

*Gas-Liquid partition chromatography (GLPC) carried through inert gas Ar; **Impurities separation by filtration

TABLE-2
PHYSICAL PROPERTIES OF PURE COMPONENT WATER (W), 1-PROPANOL (1P), 2-PROPANOL (2P) AND [ $\mathrm{BMPip}^{2} \mathrm{BF}_{4}$ (IL) WITH LITERATURE AT SPECIFIC TEMPERATURES

|  | Parameter | 303.15 K |  |  | 308.15 K |  |  | 313.15 K |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Exp. | Lit. | Lit. | Exp. | Lit. | Lit. | Exp. | Lit. | Lit. |
| 2P | $\rho\left(\mathrm{kg} \mathrm{m}^{-3}\right)$ | 782.00 | $781.50^{\text {a }}$ | $776.85{ }^{\text {e }}$ | 772.50 | $772.00^{\text {a }}$ | $772.49^{\text {c }}$ | 760.20 | $760.10^{\text {a }}$ | $768.05^{\text {e }}$ |
|  | $\mathrm{U}\left(\mathrm{m} \mathrm{s}^{-1}\right)$ | 1122.40 | $1122.20^{\text {a }}$ | $1121.43^{\text {e }}$ | 1106.00 | $1106.20^{\text {a }}$ | $1103.94^{\text {e }}$ | 1088.64 | $1088.80^{\text {a }}$ | $1086.62^{\text {e }}$ |
| 1P | $\rho\left(\mathrm{kg} \mathrm{m}^{-3}\right)$ | 798.52 | $798.50{ }^{\text {d }}$ | $775.97^{\text {e }}$ | 793.30 | $793.30^{\text {d }}$ | $791.89^{\text {e }}$ | 787.02 | $786.90^{\text {d }}$ | $787.77^{\text {e }}$ |
|  | $\mathrm{U}\left(\mathrm{m} \mathrm{s}^{-1}\right)$ | 1189.24 | $1189.20^{\text {d }}$ | $1189.26^{\text {e }}$ | 1171.74 | $1171.80^{\text {d }}$ | $1172.37^{\text {e }}$ | 1150.10 | $1150.00^{\text {d }}$ | $1155.53^{\text {e }}$ |
| W | $\rho\left(\mathrm{kg} \mathrm{m}^{-3}\right)$ | 995.64 | $995.67^{\text {b }}$ | $995.70^{\text {c }}$ | 994.04 | $994.04^{\text {b }}$ | $994.03^{\text {c }}$ | 992.21 | $992.23^{\text {b }}$ | $992.16^{\text {c }}$ |
|  | $\mathrm{U}\left(\mathrm{m} \mathrm{s}^{-1}\right)$ | 1509.12 | $1509.25^{\text {b }}$ | $1509.25^{\text {c }}$ | 1519.82 | $1519.82^{\text {b }}$ | $1519.82^{\text {c }}$ | 1528.90 | $1528.89^{\text {b }}$ | $1528.89^{\text {c }}$ |
| IL | $\rho\left(\mathrm{kg} \mathrm{m}^{-3}\right)$ | 1410.54 | - | - | 1392.24 | - | - | 1374.56 | - | - |
|  | $\mathrm{U}\left(\mathrm{m} \mathrm{s}^{-1}\right)$ | 1484.22 | - | - | 1462.12 | - | - | 1443.22 | - | - |

*The calibrated uncertainties are $\operatorname{Uc}(\rho)=0.038 \mathrm{~kg} \mathrm{~m}^{-3}, \mathrm{U}_{\mathrm{c}}(\mathrm{U})=0.416 \mathrm{~m} \mathrm{~s}^{-1}, \mathrm{U}_{\mathrm{c}}\left(\mathrm{x}_{1}\right)=0.000027, \mathrm{U}_{\mathrm{c}}(\mathrm{T})=0.01 \mathrm{~K}$ are carried at ambient atmospheric pressure references ${ }^{\text {a }}$ [Ref. 25], ${ }^{\mathrm{b}}$ [Ref. 26], ${ }^{\mathrm{c}}\left[\right.$ Ref. 27], ${ }^{\mathrm{d}}\left[\right.$ Ref. 28], ${ }^{\mathrm{C}}$ [Ref. 29]


Fig. 1. Plot of thermo physical features versus mole fraction (a) density and (b) speed of sound

$$
\begin{equation*}
\alpha=-\frac{1}{\rho}\left(\frac{\partial \rho}{\partial \mathrm{~T}}\right) \tag{5}
\end{equation*}
$$

The molar heat capacity $\mathrm{C}_{\mathrm{p}, \mathrm{m}, \mathrm{i}}$ and isobaric thermal coefficient for pure samples ionic liquid calculated from group contribution method of estimation of heat capacity $[34,35]$. The formula for group contribution method are

$$
\begin{equation*}
C_{p, m}=R\left[A+B\left(\frac{T}{100}\right)+D\left(\frac{T}{100}\right)^{2}\right] \tag{6}
\end{equation*}
$$

where R is a universal gas constant. T is the temperature measured in Kelvins. A, B and D are group contribution parameters can be calculated [36] from as follows:

$$
\begin{equation*}
\mathrm{A}=\Sigma_{\mathrm{i}}^{\mathrm{k}} \mathrm{n}_{\mathrm{i}} \mathrm{a}_{\mathrm{i}}, \mathrm{~B}=\Sigma_{\mathrm{i}}^{\mathrm{k}} \mathrm{n}_{\mathrm{i}} \mathrm{~b}_{\mathrm{i}}, \mathrm{D}=\Sigma_{\mathrm{i}}^{\mathrm{k}} \mathrm{n}_{\mathrm{i}} \mathrm{~d}_{\mathrm{i}} \tag{7}
\end{equation*}
$$

whereas the heat capacity of structural isomers of propanol, water was collected from the standard article. These are catalogued as illustrated in Fig. 3.

Redlich-Kister polynomial analysis: The conventional non-linear curve fitting strategy for attributes of binary fluids pertains Redlich-Kister polynomial regression, which contains Legendre coefficients.

$$
\begin{equation*}
\mathrm{Y}_{\mathrm{RK}}^{\mathrm{E}}=x_{\mathrm{i}}\left(1-x_{1}\right) \sum_{\mathrm{p}=0}^{\mathrm{p}=\mathrm{n}} \mathrm{~A}_{\mathrm{p}, \mathrm{~T}} \mathrm{~L}_{\mathrm{p}}\left(2 x_{\mathrm{i}}-1\right) \tag{8}
\end{equation*}
$$

Here, ( $\mathrm{Y}_{\mathrm{RK}}^{\mathrm{E}}$ ) means excess thermodynamic feature which contain any value (i.e. $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}, \mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ ) has been taken. The standard deviation was also calibrated for the consequence.

$$
\begin{equation*}
\sigma\left(\mathrm{Y}_{\mathrm{RK}}^{\mathrm{E}}\right)=\sqrt{\sum_{\mathrm{i}=1}^{\mathrm{i}=\mathrm{n}} \frac{\left(\mathrm{Y}_{\mathrm{i}, \text { exp }}-\mathrm{Y}_{\mathrm{i}, \mathrm{cal}}\right)^{2}}{(\mathrm{~m}-\mathrm{n})}} \tag{9}
\end{equation*}
$$

where $m$ is the number of experimental values and $n$ is the adjustable parameter. These excess values are examined with Redlich-Kister polynomial non-linear regression with legendre coefficients. And these values of $\mathrm{A}_{\mathrm{i}, \mathrm{T}}(\mathrm{i}=0,1,2,3)$ are determined along with standard deviation for the experimental values. Table-3 summarized the whole values of all the composites. The abnormality of thermodynamic acoustic axcess parameters of $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ and $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ are shown in Fig. 2a \& 2b, respectively. Due to thermal agitations of all fluids, temperature rise ushers to descend the excess parameters. The abnormality of excess molar volume at all temperatures has been shown in Fig. 2a
over an entire concentration for all composites [37,38]. The values of $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ are attributes positive or small negative for high concentrations of water (W), 1-propanol (1P) and 2-propanol $(2 \mathrm{P})$ and the trend turns to negative during the increasing concentration of [BMPip] $\mathrm{BF}_{4}$ in the respective composites. The negative value of excess molar volume $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ are greater in [BMPip] $\mathrm{BF}_{4}+2 \mathrm{P}$ than compared to the other fluids such [BMPip]BF4 + 1P and [BMPip]BF4 + W (Fig. 2a). Here the negative sign of $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ clearly distinguishes the formation of H bond, which is stronger at higher concentration and weaker in lower concentrations of composites. In addition to that, formation of H -bond is very weak at high concentrations of water, 1-propanol and 2-propanol. The negative value of excess molar volume $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ are greater in $[\mathrm{BMPip}] \mathrm{BF}_{4}+2 \mathrm{P}$ than compared to the other fluids such $[\mathrm{BMPip}] \mathrm{BF}_{4}+1 \mathrm{P}$ and $[\mathrm{BMPip}] \mathrm{BF}_{4}+$ W (Fig. 2b). The abnormality sign of $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ plays a vital role in assessing the compactness due to molecular interactions in multi-component mixtures through electric charge transfer, dipole-dipole interactions and dipole-induced dipole interactions in between bonds of successive constituent elements. It also suggests interstitial accommodation and oriental ordering leading to more compact structure making, which enhances to negative values. Fort and Moore [39] indicated that the binary fluids having distinct molecular sizes and shapes mix well there by reducing the volume, which causes values of $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ to be negative. The $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ value of negative was greater in $\left[\mathrm{BMPip}^{\mathrm{K}}\right] \mathrm{BF}_{4}$ +2 P than compared to the other composites of $[\mathrm{BMPip}] \mathrm{BF}_{4}+$ 1 P and $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W}$, respectively. This also clearly distinguishes a greater steric hindrance to the formation of hydrogen bonds in the respective composites. The sign of $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ and $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$ values, leads the strength of the intermolecular interactions are $[$ BMPip $] \mathrm{BF}_{4}(1)+2 \mathrm{P}(2)>\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}(1)+1 \mathrm{P}(2)>[$ BMPip $]-$ $\mathrm{BF}_{4}(1)+\mathrm{W}(2)$.

Reduced Redlich-Kister polynomial analysis: The Redlich-Kister approach sporadically misguides the dissimilar composites. In conjunction to that it deceives interactions of molecules at low concentration regions in composites. Consequently, Desnoyers and Perron [40] suggested a contemporary befitted Reduced Redlich-Kister (RRK) polynomial analysis to address more specific features in composites [41,42]


Fig. 2. Plot of excess thermo physical features versus mole fraction (a) excess molar volume and (b) excess molar isentropic compressibility


Fig. 3. Plot of alpha and heat capacity of samples are illustrated in (a) and (b)
TABLE-3
COEFFICIENTS OF REDLICH-KISTER EQUATION PARAMETERS AND STANDARD DEVIATION FOR EXCESS MOLAR QUANTITIES AT DIFFERENT TEMPERATURES

| Combination | T (K) | Redlich-kister equation coefficients |  |  |  | $\begin{gathered} \text { Error } \\ \sigma\left(\mathrm{Y}_{\mathrm{RK}}^{\mathrm{E}}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{A}_{0 . \mathrm{T}}$ | $\mathrm{A}_{1 . \mathrm{T}}$ | $\mathrm{A}_{2 . \mathrm{T}}$ | $\mathrm{A}_{3 . \mathrm{T}}$ |  |
| $\mathrm{V}_{\mathrm{m}}{ }^{\mathrm{E}}\left(10^{-6} \mathrm{~m}^{3} \mathrm{~mol}^{-1}\right)$ |  |  |  |  |  |  |
|  | 303.15 | -12.0126 | -21.9486 | -9.3576 | -15.2959 | 0.2749 |
| $\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}(1)+\mathrm{W}(2)\right.$ | 308.15 | -10.3155 | -19.8914 | -8.6691 | -13.7641 | 0.2625 |
|  | 313.15 | -8.6372 | -17.8426 | -7.9794 | -12.2404 | 0.2501 |
| $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}\left(10^{-15} \mathrm{~m}^{2} \mathrm{~N}^{-1}\right)$ |  |  |  |  |  |  |
|  | 303.15 | -1.0751 | -0.0245 | 0.0077 | -0.0074 | $1.64 \times 10^{-7}$ |
| $\left[\mathrm{BMPip}^{\text {] }} \mathrm{BF}_{4}(1)+\mathrm{W}(2)\right.$ | 308.15 | -1.0153 | -0.0172 | 0.0054 | -0.0052 | $9.6 \times 10^{-8}$ |
|  | 313.15 | -0.9519 | -0.0109 | 0.0034 | -0.0033 | $4.8 \times 10^{-8}$ |
| $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}\left(10^{-6} \mathrm{~m}^{3} \mathrm{~mol}^{-1}\right)$ |  |  |  |  |  |  |
|  | 303.15 | 6.0972 | -15.3599 | -5.9189 | 0.053 | 0.0288 |
| $\left[\mathrm{BMPip}^{\text {a }} \mathrm{BF}_{4}(1)+1 \mathrm{P}(2)\right.$ | 308.15 | 7.468 | -13.2754 | -5.4188 | 0.8831 | 0.0084 |
|  | 313.15 | 6.7375 | -12.1472 | -4.9142 | 0.7789 | 0.0120 |
| $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}\left(10^{-15} \mathrm{~m}^{2} \mathrm{~N}^{-1}\right)$ |  |  |  |  |  |  |
| $[\mathrm{BMPip}] \mathrm{BF}_{4}(1)+1 \mathrm{P}(2)$ | 303.15 | -0.3815 | -0.0001 | 0 | 0 | $1.0 \times 10^{-9}$ |
|  | 308.15 | -0.239 | -0.0008 | 0.0002 | -0.0001 | $5.0 \times 10^{-9}$ |
|  | 313.15 | -0.1137 | -0.0055 | 0.0011 | -0.0006 | $1.4 \times 10^{-8}$ |
| $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}\left(10^{-6} \mathrm{~m}^{3} \mathrm{~mol}^{-1}\right)$ |  |  |  |  |  |  |
| $[\mathrm{BMPip}] \mathrm{BF}_{4}(1)+2 \mathrm{P}(2)$ | 303.15 | -64.3707 | -19.0737 | 16.6333 | -7.9954 | 0.5325 |
|  | 308.15 | -58.2339 | -17.2393 | 15.3026 | -6.9341 | 0.5043 |
|  | 313.15 | -52.1925 | -15.4744 | 13.9715 | -5.9113 | 0.4671 |
| $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}\left(10^{-15} \mathrm{~m}^{2} \mathrm{~N}^{-1}\right)$ |  |  |  |  |  |  |
| $\left[\mathrm{BMPip}^{\text {a }} \mathrm{BF}_{4}(1)+2 \mathrm{P}(2)\right.$ | 303.15 | -0.0355 | -0.011 | 0.0023 | -0.0012 | $1.200 \times 10^{-9}$ |
|  | 308.15 | 0.1251 | -0.0551 | 0.0107 | -0.0049 | $1.165 \times 10^{-7}$ |
|  | 313.15 | 0.1343 | -0.1437 | 0.0272 | -0.0116 | $7.689 \times 10^{-7}$ |

$$
\begin{equation*}
\mathrm{Q}_{\mathrm{Y}_{\mathrm{RRK}}^{\mathrm{E}}\left(x_{1}\right)}=\frac{\mathrm{Y}_{\mathrm{RK}}^{\mathrm{E}}\left(x_{1}\right)}{x_{1}\left(1-x_{1}\right)} \tag{10}
\end{equation*}
$$

On applying the reduced function on $\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}$ and $\mathrm{K}_{\mathrm{s}, \mathrm{m}}^{\mathrm{E}}$, the graphs of Fig. 2a-b turn in to Fig. 4a-b, respectively. The abnormality of $\mathrm{Q}_{\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}, \mathrm{T}}\left(x_{1}\right)$ at all temperatures has been shown in Fig. 4 a over an entire concentration for all composites. This evidently distinguishes the hydrophobic interactions are present and stronger in the region of higher concentrations. In addition, hydrophobic interactions are very weak at high concentrations of water, 1-propanol and 2-propanol. The order of interactions are $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}(1)+2 \mathrm{P}(2)>\left[\mathrm{BMPip}^{2}\right]-\mathrm{BF}_{4}(1)+$ $1 \mathrm{P}(2)>\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}(1)+\mathrm{W}(2)\right.$.

For the present scenario, the reduced functions values $\mathrm{Q}_{\mathrm{K}_{s, \mathrm{~m}}^{\mathrm{E}}, \mathrm{T}}\left(x_{1}\right)$ are higher on W/1P/2P side and lower on [BMPip] $\mathrm{BF}_{4}$ side. This clearly visible in Fig. 4b, for the replicated sequence of $\mathrm{Q}_{\mathrm{K}_{\mathrm{S}, \mathrm{m}}^{\mathrm{E}}, \mathrm{T}}\left(x_{1}\right)$. This result indicates composites are less compressible than the corresponding ideal mixtures. This strongly evident that strong interactions occur in these composites. It also clearly indicates that 2-propanol molecules are more sterically hindered in [BMPip] $\mathrm{BF}_{4}$ molecule than the rest of the two binary fluids.

Partial molar volumes and partial molar isentropic compressibilities: The reduced Redlich-Kister (RRK) functions of $\mathrm{Q}_{\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}, \mathrm{T}}\left(x_{1}\right)$ and $\mathrm{Q}_{\mathrm{K}_{s, \mathrm{~m}}^{\mathrm{E}}, \mathrm{T}}\left(x_{1}\right)$ at infinite dilution over a constant temperature and pressure was an addition tool to represents partial molar volumes and partial isentropic compressibilities at infinite dilutions [43]. The extrapolation expression (8) has modified as:
$\mathrm{Q}_{\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}}\left(x_{1}=0\right)=\mathrm{A}_{0, \mathrm{~T}}-\mathrm{A}_{1, \mathrm{~T}}+\mathrm{A}_{2, \mathrm{~T}}-\mathrm{A}_{3, \mathrm{~T}}=\overline{\mathrm{V}}_{1, \mathrm{p}, \mathrm{m}}^{\mathrm{E}, \infty}=\overline{\mathrm{V}}_{1, \mathrm{p}, \mathrm{m}}^{\infty}-\mathrm{V}_{1, \mathrm{~m}}(11)$
$\mathrm{Q}_{\mathrm{V}_{\mathrm{m}}^{\mathrm{E}}}\left(x_{1}=1\right)=\mathrm{A}_{0, \mathrm{~T}}-\mathrm{A}_{1, \mathrm{~T}}+\mathrm{A}_{2, \mathrm{~T}}-\mathrm{A}_{3, \mathrm{~T}}=\overline{\mathrm{V}}_{2, \mathrm{p}, \mathrm{m}}^{\mathrm{E}, \infty}=\overline{\mathrm{V}}_{2, \mathrm{p}, \mathrm{m}}^{\infty}-\mathrm{V}_{2, \mathrm{~m}}$ $\overline{\mathrm{V}}_{1, \mathrm{p}, \mathrm{m}}^{\mathrm{E}, \infty}$ and $\overline{\mathrm{V}}_{2, \mathrm{p}, \mathrm{m}}^{\mathrm{E}, \infty}$ are excess partial molar volumes two pure components at infinite dilutions. $\overline{\mathrm{V}}_{1, \mathrm{p}, \mathrm{m}}^{\infty}$ and $\overline{\mathrm{V}}_{2, \mathrm{p}, \mathrm{m}}^{\infty}$ are partial molar volumes at infinite dilutions. $\mathrm{V}_{1, \mathrm{~m}}$ and $\mathrm{V}_{2, \mathrm{~m}}$ are pure molar
volumes of two components [BMPip] $\mathrm{BF}_{4}$ and water, 1-propanol and 2-propanol. Similarly, the equation analogy is also true for partial isentropic compressibilities. But, the real-time analysis of partial molar volumes and partial isentropic compressibilities over a molefraction concentration at constant pressure and temperature can be evaluated from the differential equation is

$$
\begin{align*}
& \overline{\mathrm{V}}_{\mathrm{i}, \mathrm{p}, \mathrm{~m}}=\mathrm{V}_{\mathrm{m}}\left(x_{\mathrm{i}}\right)-x_{\mathrm{j}}\left(\frac{\partial \mathrm{~V}_{\mathrm{m}}\left(x_{\mathrm{j}}\right)}{\partial x_{\mathrm{j}}}\right)_{\mathrm{T}, \mathrm{P}}  \tag{13}\\
& \overline{\mathrm{~K}}_{\mathrm{i}, \mathrm{p}, \mathrm{~s}}=\mathrm{K}_{\mathrm{s}}\left(x_{\mathrm{i}}\right)-x_{\mathrm{j}}\left(\frac{\partial \mathrm{~K}_{\mathrm{s}}\left(x_{\mathrm{j}}\right)}{\partial x_{\mathrm{j}}}\right)_{\mathrm{T}, \mathrm{P}} \tag{14}
\end{align*}
$$

Here $x_{\mathrm{i}}$ and $x_{\mathrm{j}}$ are the mole fractions of two components in the composite ( $\mathrm{i}=1,2 \& \mathrm{j}=\mathrm{i}-1$ ). The intermolecular interactions in the composites can be interpreted in terms of packing efficiency of molecules with the help of partial molar volumes and partial isentropic compressibilities. The partial molar volumes of two components $\mathrm{V}_{1, \mathrm{p}, \mathrm{m}}$ and $\mathrm{V}_{2, \mathrm{p}, \mathrm{m}}$ play vital role in the binary fluids [44]. Because the domain influence of the components in the mixture changes with respect to the composition concentration and temperature. In this scenario, the partial molar volumes of components $[\mathrm{BMPip}] \mathrm{BF}_{4}+2 \mathrm{P},[\mathrm{BMPip}]-$ $\mathrm{BF}_{4}+1 \mathrm{P}$ and $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W}$ at all temperatures has been presented in Fig. 5a, b and c, respectively. In each figure, the scaffolded Z symbol graph contains three coloured meshes, which are concerned to red $\left(\mathrm{V}_{1, \mathrm{p}, \mathrm{m}}\right)$, green (total molar volume, V ) and blue $\left(\mathrm{V}_{2, \mathrm{p}, \mathrm{m}}\right)$.

For all binary, the partial molar volumes of both components $\mathrm{V}_{1, \mathrm{p}, \mathrm{m}}$ and $\mathrm{V}_{2, \mathrm{p}, \mathrm{m}}$ are lower than of their individual values in the pure state, which reveals the domain influence of the individual components decreasing with their respective lower concentration regions. The abnormality is examined for all constant interval of temperatures. This clearly suggests presence of solute-solvent interactions in between unlike molecules. It is clear from Fig. 5a-c, the effect of domain influence of volume is low for $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}+2 \mathrm{P}$ than compared to the other composites of $[\mathrm{BMPip}] \mathrm{BF}_{4}+1 \mathrm{P}$ and $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W}$,


Fig. 4. Plot of reduced excess thermo physical-features versus mole fraction (a) reduced excess molar volume and (b) reduced excess molar isentropic compressibility


Fig. 5. Plot of partial molar volume against mole fraction and temperature for the solution (a) [BMPip]BF4 (1) + W (2); (b) [BMPip]BF $\mathrm{B}_{4}$ (1) $+1 \mathrm{P}(2) ;$ (c) $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}(1)+2 \mathrm{P}(2)$
respectively. This suggests about the solute-solvent interactions between molecules is high for $[\mathrm{BMPip}] \mathrm{BF}_{4}+2 \mathrm{P}$ than compared to the other composites of $[\mathrm{BMPip}] \mathrm{BF}_{4}+1 \mathrm{P}$ and $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}$ +W . The partial isentropic compressibilities of two components $\mathrm{K}_{1, \mathrm{p}, \mathrm{s}}$ and $\mathrm{K}_{2, \mathrm{p}, \mathrm{s}}$ also play crucial role in binary mixtures [45]. Because the geometrical influence of the components in the mixture changes with respect to the composition concentration and temperature. In this scenario, the partial isentropic compressibilities of components [BMPip]BF $4+\mathrm{W},\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}+1 \mathrm{P}$ and [BMPip] $\mathrm{BF}_{4}+2 \mathrm{P}$ at all temper-atures has been illustrated in Fig. 6. The partial isentropic compressibilities $\mathrm{K}_{1, \mathrm{p}, \mathrm{s}}$ and $\mathrm{K}_{2, \mathrm{p}, \mathrm{s}}$ are more for the binary $[\mathrm{BMPip}] \mathrm{BF}_{4}+2 \mathrm{P}$ than compared to $[\mathrm{BMPip}] \mathrm{BF}_{4}+1 \mathrm{P}$ and $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}+\mathrm{W}$. This clearly suggests the breaking of dipole inclusions between has more in [BMPip]$\mathrm{BF}_{4}+2 \mathrm{P}$ than compared to the other binary of $[\mathrm{BMPip}] \mathrm{BF}_{4}+$ 1 P and $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W}$. Hence, the effect of geometrical influence is low for $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W}$ than compared to the other composites of $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}+1 \mathrm{P}$ and $[\mathrm{BMPip}] \mathrm{BF}_{4}+2 \mathrm{P}$ (Fig. 6).

FT-IR analysis: The FT-IR spectrum of components $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W},[\mathrm{BMPip}] \mathrm{BF}_{4}+1 \mathrm{P}$ and $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}+2 \mathrm{P}$ and their pure components are carried at room temperature (303.15 K)
and the key IR data is given in Table-4 [22]. The peaks of intensity N -H strong for secondary amine, C-H medium stretching, $\mathrm{N}-\mathrm{H}$ bending and $\mathrm{C}=\mathrm{O}$ strong stretching are observed. As shown in Fig.7, the binary [BMPip] $\mathrm{BF}_{4}+1 \mathrm{P}$ is stronger than $[\mathrm{BMPip}] \mathrm{BF}_{4}+\mathrm{W}$. This contention was supported by the formation of inter and intra molecular strong bonds between binary fluids.

## Conclusion

In this framework, the values of excess thermodynamic parameters have been calibrated for an entire composition of $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}+\mathrm{W},[\mathrm{BMPip}] \mathrm{BF}_{4}+1 \mathrm{P}$ and $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}+2 \mathrm{P}$ with accustomed levels of temperatures. This is clearly elucidating a strong hydrogen bonding, dipole-inclusion interactions present in the component molecules. Moreover, the reduced excess thermodynamic parameters have been executed by using contemporary reduced Redlich-Kister polynomial over an entire composition with accustomed levels of temperatures. This revealed more specific features about the smaller molar mass of water,1propanol and 2-propanol molecules sterically hindered in larger molar mass of [ BMPip$] \mathrm{BF}_{4}$ in their respective compositions.


Fig. 6. Plot of partial molar isentropic compressibilities against mole fraction and temperature for the solution (a) [BMPip]BF ${ }_{4}$ (1) +W (2); (b) $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}$ (1) $+1 \mathrm{P}(2)$; and (c) $\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}(1)+2 \mathrm{P}(2)\right.$

| TABLE-4 FT-IR ANALYSIS |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Name of the component | $\begin{gathered} \mathrm{N}-\mathrm{H} \mathrm{str} \mathrm{~cm}^{-1} \\ \text { (secondary amine) } \end{gathered}$ | C-H med ( $\mathrm{cm}^{-1}$ ) | $\begin{gathered} \text { N-H bending } \\ \left(\mathrm{cm}^{-1}\right) \end{gathered}$ | $\begin{aligned} & \begin{array}{l} \mathrm{O}-\mathrm{H} \operatorname{str}\left(\mathrm{H}_{-}^{-1}\right. \\ \text { bonded })\left(\mathrm{cm}^{-1}\right) \end{array} \end{aligned}$ | O-H bending alcohol ( $\mathrm{cm}^{-1}$ ) | $\begin{gathered} \text { C-O stretching } \\ \left(\mathrm{cm}^{-1}\right) \text { pri. alcohol } \end{gathered}$ |
| [BMPip] $\mathrm{BF}_{4}+\mathrm{W}$ | 3362.10 | - | 1632.10 | - | - | 1063.00 |
| W | - | - | - | 3327.30 | - | - |
| $\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}+1 \mathrm{P}\right.$ | 3371.00 | 2964.10 | 1639.20 | - | 1466.00 | 1053.90 |
| 1P | - | 2936.36 | - | 3327.82 | 1457.78 | 1053.63 |



Fig. 7. Normalized FT-IR spectra analysis for the binary mixtures over the range 4000 to $400 \mathrm{~cm}^{-1}$ for the combination (a) [BMPip]BF $\mathrm{B}_{4}$ (1) + 1P (2); and (b) $\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}(1)+\mathrm{W}(2)\right.$

The reduced excess parameters value decreases for increases of temperatures in their compositions due to their thermal agitations. The reactive of composites are in the order $\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}(1)+\right.$ $\mathrm{W}(2)<\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}(1)+1 \mathrm{P}(2)<\left[\mathrm{BMPip}^{2}-\mathrm{BF}_{4}(1)+2 \mathrm{P}(2)\right.\right.$. Further, an addition tool partial molar volume was extracted from reduced Redlich-Kister polynomial. In this connection, the partial molar volumes of both components have been plotted in 3D graphs. This discloses the intermolecular interactions are strong in $\left[\mathrm{BMPip}^{2} \mathrm{BF}_{4}(1)+2 \mathrm{P}(2)\right.$ as compared to [BMPip]$\mathrm{BF}_{4}(1)+1 \mathrm{P}(2)$ and $\left[\mathrm{BMPip}^{2}\right] \mathrm{BF}_{4}(1)+\mathrm{W}(2)$. The results of these intermolecular interaction behaviour were also supported by FT-IR analysis.

## ACKNOWLEDGEMENTS

One of the authors (Shaik Babu) is thankful to Department of Science and Technology (DST), Government of India, New Delhi for the award of DST-FIST Level-1 Scheme (SR/FST/ PS-1/2018/35) to Department of Physics, Koneru Lakshmaiah Education Foundation, Vaddeswaram, India.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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