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# Volumetric properties of ternary (IL + 2-propanol or 1-butanol or 2-butanol + ethyl acetate) systems and binary (IL + 2-propanol or 1-butanol or 2-butanol) and (1-butanol or 2-butanol + ethyl acetate) systems

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ABSTRACT

The experimental densities for the binary or ternary systems were determined at $T$ = (298.15, 303.15, and 313.15) K. The ionic liquid methyl trioctylammonium bis(trifluoromethylsulfonyl)imide ($[MOA]^+[Tf_2N]^-$) was used for three of the five binary systems studied. The binary systems were ($[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol) and (1-butanol or 2-butanol + ethyl acetate). The ternary systems were {methyl trioctylammonium bis(trifluoromethylsulfonyl)imide + 2-propanol or 1-butanol or 2-butanol + ethyl acetate}. The binary and ternary excess molar volumes for the above systems were calculated from the experimental density values for each temperature. The Redlich–Kister smoothing polynomial was fitted to the binary excess molar volume data. Virial-Based Mixing Rules were used to correlate the binary excess molar volume data. The binary excess molar volume results showed both negative and positive values over the entire composition range for all the temperatures.

The ternary excess molar volume data were successfully correlated with the Cibulka equation using the Redlich–Kister binary parameters.



## 1. Introduction

An ionic liquid (IL) is a material containing only ionic species and is a liquid at temperatures <373 K. Most ionic liquids are a combination of an alkylimidazolium, pyridinium or pyrrolidinium cation and a charge diffuse inorganic or organic anion [1]. ILs are also called "designer solvents" [2,3] because of the wide range of possible anion/cation combinations. Ionic liquids are a viable reaction media for numerous types of reactions [4]. ILs have also received attention from both industrial and academic research in diverse areas such as electrochemistry, catalysis, organic synthesis, biotechnology, and material separation [5–10]. They are also used as "green chemistry" solvents because of their negligible vapor pressure and recyclability [11–13]. Literature data on physicochemical and thermodynamic properties of ternary ionic liquid mixtures are minimal [14–17].

Binary excess molar volume, $V^E_{12}$, ternary excess molar volume, $V^E_{123}$, and binary partial molar volume at infinite dilution, $V^\infty_{m,i}$, data can be used for understanding the molecular interactions (such as dispersion forces, hydrogen-bonding interactions) in mixtures [18]. The excess molar volume is a useful parameter in the design of technological processes of a reaction [19]. The $V^\infty_{m,i}$ of a substance in a binary mixture is the change in volume per mole of substance added to a large volume of the first component [20]. Studies on the thermodynamic properties of complex mixtures are helpful in characterizing the structure and properties of the solutions [21].

In this work, three of the five binary systems studied contained the ionic liquid methyl trioctylammonium bis(trifluoromethylsulfonyl) imide. The binary systems were ($[MOA]^+[Tf_2N]^-$ + 2-propanol or 1-butanol or 2-butanol), (1-butanol + ethyl acetate), and (2-butanol + ethyl acetate). The binary excess molar volume data were fitted by the Redlich–Kister polynomial and correlated by Virial Based Mixing Rules (VBMR). The partial molar volumes were calculated using both the Redlich–Kister and VBMR correlation coefficients.

The ternary systems were {methyl trioctylammonium bis(trifluoromethylsulfonyl)imide + 2-propanol or 1-butanol or 2-butanol + ethyl acetate}. All ternary excess molar volume data were determined over the entire composition range at $T$ = (298.15, 303.15, and 313.15) K. The Cibulka equation was used to correlate the ternary excess molar volume data. The binary and ternary excess molar volume results are discussed in terms of intermolecular forces.

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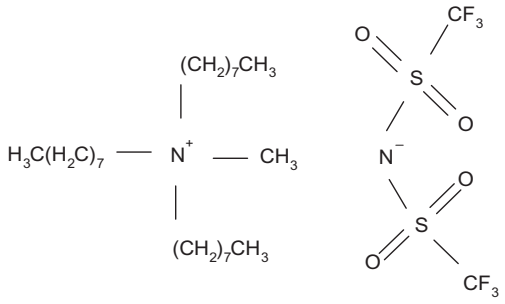

**FIGURE 1.** Structure of the IL, {methyl trioctylammonium bis(trifluoromethylsulfonyl)imide}.

This work is a continuation of our research group's work on thermodynamic properties of ILs [22–26]. The structure of the ionic liquid used in this work is presented in figure 1.

## 2. Experimental

### 2.1. Materials

The chemicals, suppliers, purity, literature and experimental densities ($\rho$) are given in table 1. The density of the pure liquids were determined at $T = (298.15, 303.15, \text{and } 313.15)$ K and at atmospheric pressure. The molar mass of the IL is 648.85 g · mol$^{-1}$. The ionic liquid {methyl trioctylammonium bis (trifluoromethylsulfonyl)imide [MOA] + [$Tf_2N$]$^-$}, 2-propanol, 1-butanol, 2-butanol and ethyl acetate were used without any further purification. The water content in the IL was obtained with a Karl–Fischer Coulometer [Metrohm 831] and the mass per cent water content was found to be 0.04.

### 2.2. Experimental procedure and apparatus

The densities were measured using an Anton Paar DMA 38 vibrating U-tube densimeter. The densimeter consists of a built-in thermostat controller capable of maintaining temperature precisely to ±0.01 K and measuring density to ±0.0001 g · cm$^{-3}$. The mixtures were prepared by transferring via syringe the pure liquids into stoppered bottles to prevent evaporation, using an OHAUS mass balance for the exact masses of each component. The mass balance has a precision of 0.0001 g. The uncertainty in the mole fraction is 0.0006. The mixtures were shaken in order to ensure complete homogeneity of the compounds, since the ionic liquid is slightly viscous. To avoid formation of bubbles inside the vibrating tube of the densimeter, injections were done slowly. For a different temperature, the instrument had to be switched off and reset to the required temperature with the solution in

**TABLE 1**
Pure compound specifications for supplier, purity, literature, and experimental densities at $T = (298.15, 303.15, \text{and } 313.15)$ K.

| Compound | Supplier | Mole fraction purity | $\rho$/(g · cm$^{-3}$) | | | |
|---|---|---|---|---|---|---|
| | | | Temperature/K | | | |
| | | | Literature | | Experimental | |
| | | | 298.15 | 298.15 | 303.15 | 313.15 |
| 2-Propanol | BDH | 0.997 | 0.78087[a] | 0.7812 | 0.7772 | 0.7694 |
| 1-Butanol | BDH | 0.998 | 0.80575[b] | 0.8070 | 0.8037 | 0.7967 |
| 2-Butanol | Fulka | 0.995 | 0.8024[a] | 0.8028 | 0.7988 | 0.7911 |
| [MOA]$^+$[$Tf_2N$]$^-$ | Solvent innovation | 0.980 | 1.1093[c] | 1.1069 | 1.1032 | 1.09577 |
| Ethyl acetate | Fluka | 0.997 | 0.8948[d] | 0.8948 | 0.8886 | 0.8752 |

[a] Reference [30].
[b] Reference [29].
[c] Reference [26].
[d] Reference [38].

**TABLE 2**
Binary densities and excess molar volumes for the {ionic liquid ($x_1$) + 2-propanol ($x_2$)} at $T = (298.15, 303.15, \text{and } 313.15)$ K.

| $x_1$ | $\rho$/(g · cm$^{-3}$) | $V^E_{12}$/(cm$^3$ · mol$^{-1}$) | $x_1$ | $\rho$/(g · cm$^{-3}$) | $V^E_{12}$/(cm$^3$ · mol$^{-1}$) |
|---|---|---|---|---|---|
| *{[MOA]$^+$[$Tf_2N$]$^-$ ($x_1$) + 2-propanol ($x_2$)}* | | | | | |
| *T = 298.15 K* | | | | | |
| 0.0530 | 0.8769 | 0.191 | 0.4824 | 1.0676 | −0.271 |
| 0.1000 | 0.9326 | −0.279 | 0.5896 | 1.0789 | 0.257 |
| 0.2045 | 1.0049 | −1.456 | 0.7066 | 1.0890 | 0.429 |
| 0.2841 | 1.0338 | −1.681 | 0.7967 | 1.0952 | 0.505 |
| 0.3934 | 1.0562 | −1.079 | 0.8960 | 1.1005 | 0.734 |
| *T = 303.15 K* | | | | | |
| 0.0530 | 0.8730 | 0.177 | 0.4824 | 1.0639 | −0.304 |
| 0.1000 | 0.9289 | −0.324 | 0.5896 | 1.0752 | 0.234 |
| 0.2045 | 1.0015 | −1.564 | 0.7066 | 1.0854 | 0.374 |
| 0.2841 | 1.0303 | −1.776 | 0.7967 | 1.0916 | 0.452 |
| 0.3934 | 1.0526 | −1.148 | 0.8960 | 1.0969 | 0.683 |
| *T = 313.15 K* | | | | | |
| 0.0530 | 0.8651 | | 0.4824 | 1.0566 | −0.417 |
| 0.1000 | 0.9213 | −0.376 | 0.5896 | 1.0681 | 0.056 |
| 0.2045 | 0.9947 | −1.778 | 0.7066 | 1.0783 | 0.188 |
| 0.2841 | 1.0233 | −1.971 | 0.7967 | 1.0844 | 0.304 |
| 0.3934 | 1.0451 | −1.218 | 0.8960 | 1.0895 | 0.633 |