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Evaluation of Solution Thermodynamic Properties of Mixed Ionic Liquids at Different Temperatures (293.15– 343.15) K

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Additional information is available at the end of the chapter

Abstract

The solution thermodynamic properties of mixed ionic liquids such as density, excess molar volume, partial molar volume and apparent molar volume are highly influential on the design of an effective separation unit and in the optimization of operating parameters like pressure, temperature and concentration for the separation processes. Therefore, it could be better to do a prior experimental study on of the solution thermodynamic properties of mixed ionic liquids at different temperatures for the whole mole fractions rather than doing separation characterization studies like selectivity, efficiency, distribution coefficient and performance index. In addition, the recovery and regeneration of ionic liquids also challenge researchers and separation scientists in several fields of applications. Therefore, in this chapter, density of pure 1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide $\{[BIMIM][NtF_2]\}$, 1-ethyl-3-methylimidazolium ethyl sulfate $\{[EMIM][ESO_4]\}$, 1-ethyl-3-methylimidazolium hydrogen sulfate $\{[EMIM][HSO_4]\}$ and 1-butyl-3-methylimidazolium acetate $\{[BMIM][OAc]\}$ and its binary mixtures have been measured at T (293.15–343.15) K. From the measured densities, isobaric expansivity, excess molar volume, partial molar volume, excess partial molar volume, and apparent molar volume have been calculated. Results were discussed in terms of physical interaction, chemical interaction and structural orientation at molecular level and their temperature and composition dependency.

Keywords: mixed ionic liquid, density, isobaric expansivity and excess property

1. Introduction

Ionic liquid is a green solvent. It is composed of organic cations and inorganic or organic anions; they can have liquid state near ambient temperature. Since this green solvent has unique properties when compared to conventional solvents such as larger temperature range of liquid state [1], high thermal stability, high ionic conductivity negligible vapor pressures, nonflammability and high solvating capacity (i.e., solubility), for polar or nonpolar organic, inorganic and organometallic compounds [2, 3]. It is well known that the solvation capacity of green solvent is influenced by the hydrogen bonded structure and interaction between the individual ions (cation or anion) with other substances. On the other hand, the green solvent is an organic salt and its microscopic structure is usually composed of a large cation with low order of molecular symmetry. Hence, the unstable lattice structure lowers the melting point to well below the room temperature [4]. Therefore, the green solvent has the capabilities as environmental-friendly solvent in many green chemical processes [5] such as, biocatalytical transformation, isomerization, used in multiphase homogeneous catalysis [6], synthesis, catalysis, liquid-liquid extraction and supercritical extraction, and also used as thermal fluids, lubricants, and working fluids in electrochemical devices such as batteries, capacitors and solar cells [7].

But there is no systematic study on application of green solvent at different temperature and compositions. On the other hand, the solution thermodynamic properties of pure ionic liquids and its mixtures are of interest from the point of both basic and applied research [7]. Also, a detailed knowledge of the solution thermodynamic properties of mixed green solvents are important in relating the microscopic and macroscopic behavior. In this context, There is no data generated by experimental or theoretical approach. Moreover, the complete design of new green chemical processes and new green products based on green solvents and mixed green solvents can only be achieved when their solution thermodynamic properties such as molar volume, excess molar volume, partial molar volume, excess partial molar volume, and apparent molar volume are adequately characterized. But there is no data on solution thermodynamic properties of mixed green solvents at different temperature for an entire mole fractions range. Therefore, it is very important to accumulate a sufficiently large data bank not only for green processes and product design but also for the development of correlation for these properties. In addition, a better understanding of the behavior of mixed green solvent demands the knowledge of density and its temperature and composition dependence. Obtaining knowledge on the solution thermodynamic properties is extremely important to improve their selection and performance.

2. Experimental methods

2.1. Chemicals

Green solvents like 1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide {[BIMIM][NtF$_2$]}, 1-ethyl-3-methylimidazolium ethyl sulfate {[EMIM][ESO$_4$]}, 1-ethyl-3-methylimidazolium hydrogen sulfate {[EMIM][HSO$_4$]} and 1-butyl-3-methylimidazolium acetate {[BMIM][OAc]} were supplied by Aldrich Chemistry, Germany with purity greater than 98%. All the green solvents (i.e., ionic liquids) were used without further purifications.

2.2. Sample preparation

The binary mixture was prepared by transferring a known amount of the pure liquids via syringe into stoppered bottles and was properly sealed with parafilm tape to prevent evaporation and addition of moisture to the mixtures, using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g. The estimated uncertainty on the composition measurement was $\pm 10^{-4}$ g mole fraction. The stoppered bottles were placed inside a water-shaker bath set at atmospheric pressure, and allowed to shake for more than 6 h at 300 rpm in thermostatic shaker bath. Spring clamps were used to hold the flasks on the tray. The binary mixture was then allowed to settle for minimum of 12 h so that equilibrium is attained. The sample is taken from vial with a syringe to measure the density at temperature from 293.15 to 343.15 K with 5 K interval.

2.3. Density measurement

Density was measured using an Anton Paar DMA 4100 M with the oscillating U-tube method. In this method, the sample is introduced into a U-shaped borosilicate glass tube that is being excited to vibrate at its characteristic frequency. The characteristic frequency changes depending on the density of the sample. Through a precise determination of the characteristic frequency a mathematical conversion, the density of the sample can be measured. The density is calculated from the quotient of the period of oscillations of the U-tube and the reference oscillator [8]:

$$\rho = K_A * Q^{2*} f_1 - K_B * f_2 \qquad (1)$$

where; K_A and K_B are apparatus constants, respectively, Q is the oscillation period of the reference oscillator. f_1 and f_2 are correction factors for temperature, viscosity, and nonlinearity.

3. Theory

When two liquid chemical species mixed with each other, the total weight of the mixture is equal to the sum of masses of the individual chemical species. But it is not true in case of volume. When two miscible liquids are mixed with each other, volume of the mixtures may not equal to the sum of the volume of the individual chemical species [9]. Ideal binary liquid mixture does not have volume changes. Hence, the binary liquid mixture has deviation from ideality due to the molecular interactions between solute-solvent or two components in the mixtures. In addition, the binary liquid mixture volume either increase or decrease as the function of composition of component i in the mixture. This difference in the volume of the mixture can be taken as a criterion and measure of molecular interactions at molecular level by means of isobaric expansivity, excess molar volume, partial molar volume, excess partial molar volume and apparent molar volume (**Figure 1**).

Isobaric expansivity is inversely proportional to the volume of component "i" in the mixture and its product with the rate of change of volume with respect to temperature at constant pressure. Hence the isobaric expansivity is defined as;
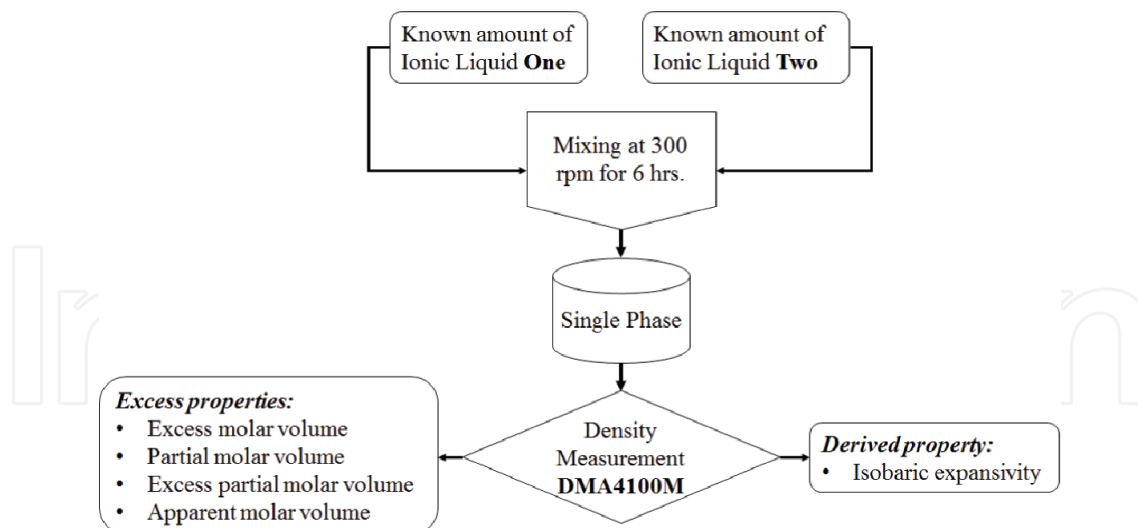
Figure 1. Illustrating the density measurement of binary mixtures using Anton Paar DMA 4100 M.

$$\alpha \;=\; \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P \;=\; -\frac{1}{\rho}\left[\frac{\partial \rho}{\partial T}\right]_P \;=\; -\left[\frac{\partial \ln\rho}{\partial T}\right]_P \tag{2}$$

where; α is the isobaric expansivity, v is the volume of the fluid, ϱ is the density of the fluid, T is the temperature, P is the pressure.

The excess molar volume is the good estimator of unlike interaction in the binary mixture as a function of concentration of component "i" at constant temperature and pressure. The excess molar volume (cm^3/mole) is defined as [1, 13];

$$V_m^E \;=\; V_m^{real} - \sum_{i=1,2} V_m^{ideal} \tag{3}$$

$$= V_m^{real} - x_1\,V_1^0 - x_2\,V_2^0 \tag{4}$$

$$= \frac{x_1 M_1 + x_2 M_2}{\rho_{mix}} - \left[\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right] \tag{5}$$

where; V_m^E is the excess molar volume, V_m^{real} is the molar volume of real fluid, V_m^{ideal} is the molar volume of ideal, V_1^0 and V_2^0 are the molar volume of component 1 and 2, respectively. x_1 and x_2 are the mole fraction of component 1 and 2 in the binary mixture. M_1 and M_2 are the molecular weight of component 1 & 2. ρ_{mix}, ρ_1 & ρ_2 are the densities of binary mixture, component 1 and component 2, respectively.

Partial molar volume is the thermodynamic quantity and it is used to measure the change s in extensive properties of the binary mixture as the function of composition at constant temperature and pressure. In addition, the partial molar volume is a potential tool to esti-mate the solute-solvent interaction in the binary mixture at molecular level. The partial molar volume is used to measure the incremental volume by addition of co-solvent in the binary

mixtures. Hence, the partial molar volume is not necessarily the same as the molar volume of the pure component as it depends on how the molecules interact, structural rearrangement, and the geometrical fitting of the molecules [13]. The partial molar volume (cm^3/mole) can be evaluated using the following equations;

$$\bar{V}_1 = V_m^E + V_1^0 + x_2 \left(\frac{\partial V_m^E}{\partial x_1} \right)_{P,T} \tag{6}$$

$$\bar{V}_2 = V_m^E + V_2^0 - x_1 \left(\frac{\partial V_m^E}{\partial x_1} \right)_{P,T} \tag{7}$$

where; $\bar{v}_i$ and $\bar{v}_2$ are the partial molar volume of component 1 and 2, respectively.

Excess partial molar volume is the property of binary mixtures which is useful to characterize the non-ideal behavior of real mixtures. Excess partial molar volume is the different between the partial molar volume of a component "i" in a real mixture and the molar volume of the component in an ideal mixture (cm^3/mole). It can be defined as;

$$\bar{V_1^E} = \bar{V}_1 - V_1^0 \tag{8}$$

$$\bar{V_2^E} = \bar{V}_2 - V_2^0 \tag{9}$$

where; $\bar{v}_1^E$ and $\bar{v}_2^E$ are the excess partial molar volume of component 1 and 2, respectively.

Apparent molar volume is one of the solution thermodynamic properties which can measure the amount of solute is required to bring the solvent volume up to the solution volume. Hence, the apparent molar volume (cm^3/mole) is defined as;

$$V_{\varphi,1} = V_1^0 - \frac{V_m^E}{x_1} \tag{10}$$

$$V_{\varphi,2} = V_1^0 - \frac{V_m^E}{x_1} \tag{11}$$

where; $V_{\varphi,1}$ and $V_{\varphi,2}$ are the apparent molar volume of component 1 and 2, respectively.

4. Results and discussion

4.1. Density of pure ionic liquids

The density of pure [EMIM][ESO$_4$], [EMIM][HSO$_4$], [BMIM][OAc] and [BMIM][NtF$_2$] ionic liquid at the temperature range from 293.15 to 343.15 K are presented in **Table 1**. Densities of IL's used in this work and commonly used ILs are given in **Figure 2**. Density of all IL's decreases as in the order of; [BMIM][NTF$_2$] (this work) < [EMIM][TOS] < [BMIM][PF$_6$] < [EMIM][HSO$_4$]

S. No	Name	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
1	[EMIM][SCN] [10]	NA	1.1168	NA	1.1107	NA	1.1047	NA	1.0927	NA	NA	NA
2	[BMIM][BF$_4$] [5]	NA	1.2076	1.2041	1.2005	1.1970	1.1934	1.1899	NA	1.1754	NA	NA
3	[HMIM][BF$_4$] [5, 10]	NA	1.1488	1.1453	1.1418	1.1384	1.1350	1.1316	NA	NA	NA	NA
4	[OMIM][BF$_4$] [11]	NA	1.1018	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	[BMIM][PF$_6$] [12]	NA	1.3697	1.3635	1.3592	1.3555	1.3520	1.3474	NA	NA	NA	NA
6	[EMIM][TOS] [13]	NA	1.3895	1.3853	1.3811	1.3769	1.3727	1.3686	NA	NA	NA	NA
7	[BMIM][TOS] [13]	NA	1.3016	1.2976	1.2937	1.2897	1.2858	1.2819	NA	1.14997	1.14667	1.14347
8	[MMIM][MSO$_4$] [14]	NA	1.3415	1.3341	1.3248	1.3206	NA	NA	NA	NA	NA	NA
9	[EMIM][EtSO$_4$] [15]	1.2424	1.2394	1.2363	1.2333	1.2302	1.2272	1.2241	1.2211	1.2181	1.2151	1.2120
		1.2402*	1.2368*	1.2334*	1.2300*	1.2266*	1.2232*	1.2199*	1.2165*	1.2132*	1.2099*	1.2066*
10	[BMIM][MSO$_4$] [5]	NA	1.2107	1.2074	1.2041	1.2008	1.1975	1.1942	NA	NA	NA	NA
11	[EMIM][HSO$_4$]*	1.3691	1.3660	1.3629	1.3599	1.3567	1.3537	1.3508	1.3477	1.3448	1.3418	1.3388
12	[EMIM][OAc]*	1.0555	1.0525	1.0495	1.0465	1.0435	1.0405	1.0375	1.0346	1.0316	1.0287	1.0257
13	[BMIM][NtF2]*	1.4406	1.4358	1.4310	1.4262	1.4215	1.4167	1.4120	1.4073	1.4026	1.3979	1.3933

Table 1. Density as function of temperature for pure ionic liquids.

(this work) < [MMIM][MSO$_4$] < [BMIM][TOS] < [HMIM][PF$_6$] < [OMIM][PF$_6$] < [EMIM][ESO$_4$] (this work) < [BMIM][BF$_4$] < [HMIM][BF$_4$] < [EMIM][SCN] < [BMIM][OAc] (this work) < Water at 298.15 K. Densities of all the studied ionic liquids slightly decreases with increasing temperatures from 293.15 to 343.15 K. It is observed that temperature effect on densities of studied ionic liquids are very small and it may be neglected. The density of ILs' decrease as in the order of; [BMIM][NtF$_2$] < [EMIM][HSO$_4$] < [EMIM][ESO$_4$] < [BMIM][OAc] (**Figure 1**). Since the densities of pure ionic liquids play an important role to estimate the volumetric behavior of individual IL's with other IL's in the binary mixtures for the whole composition at different temperatures. It is noted that the length of alkyl-chain in cation as well as the variety of
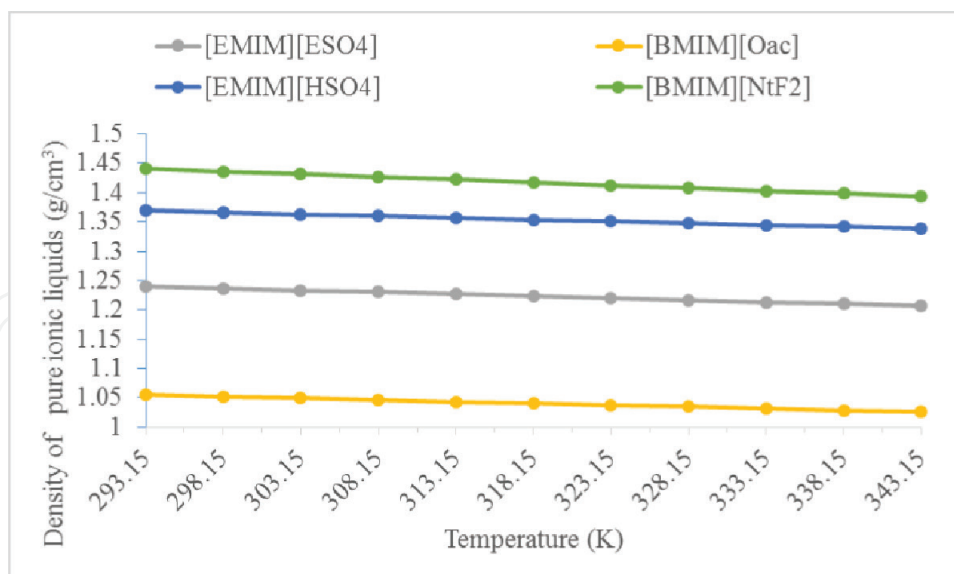
Figure 2. Density of investigated ionic liquids in this work at different temperature.

anion has great impact on density of IL's. Generally, density of pure IL's decreases due to the following reasons; (i) increasing length of the alkyl chain and (ii) increasing volume of the anions [1].

4.2. Isobaric expansivity

The study of temperature and pressure dependence of isobaric expansivity of [EMIM][ESO$_4$], [EMIM][HSO$_4$], [BMIM][OAc] and [BMIM][NtF$_2$] ionic liquids. The ILs do not expanded appreciably at the temperature range from 293.15 to 343.15 K. Isothermal expansivity of all studied ILs are presented in **Table 2**. [BMIM][OAc] gave 5.77 × 10^{-4}, 4.94 × 10^{-4} for [BMIM][NtF$_2$], 4.09 × 10^{-4} for [EMIM][ESO$_4$] and 2.95 × 10^{-4} for [EMIM][HSO$_4$].

4.3. Excess molar volume

Experimental densities for different binary mixtures of [EMIM][ESO$_4$] + [BMIM][OAc], [EMIM][ESO$_4$] + [BMIM][NtF$_2$] and [EMIM][ESO$_4$] + [BMIM][HSO$_4$] as a function of composition at T = 293.15–343.15 K were used to estimate excess molar volume. Excess molar volumes for the binary mixtures of [EMIM][ESO$_4$] + [BMIM][OAc], [EMIM][ESO$_4$] + [BMIM][NtF$_2$] and [EMIM][ESO$_4$] + [BMIM][HSO$_4$] from 293.15 to 343.15 K versus the mole fraction of [EMIM][ESO$_4$] are shown in **Figures 3–5**.

Generally, V^E can be considered arising from three types of interactions between two components in the mixtures: (i) physical interaction mainly consisting of dispersion forces or weak dipole-dipole interactions and making a positive contribution. (ii) Chemical or specific interactions which include charge transfer, formation of hydrogen bonds and other complex forming interactions resulting in negative contribution, and (iii) the structural contributions arising from geometrical fitting of one component into another due to difference in molar volumes resulting in negative excess molar volume [16].

S. no	Name	α (1/K)	
		This work	Literature
1	[EMIM][SCN] [8]	NA	7.23×10^{-4}
2	[BMIM][BF$_4$] [5]	NA	5.84×10^{-4}
3	[HMIM][BF$_4$] [5, 8]	NA	6.14×10^{-4}
4	[BMIM][PF$_6$] [10]	NA	6.63×10^{-4}
5	[EMIM][TOS] [11]	NA	5.80×10^{-4}
6	[BMIM][TOS] [11]	NA	6.19×10^{-4}
7	[MMIM][MSO$_4$] [12]	NA	10.52×10^{-4}
8	[BMIM][MSO$_4$]	2.95×10^{-4}	NA
9	[EMIM][EtSO$_4$] [13]	4.09×10^{-4}	4.88×10^{-4}
10	[BMIM][OAc]	5.77×10^{-4}	NA
11	[EMIM][NtF$_2$]	4.94×10^{-4}	NA

Table 2. Observed and literature values of isobaric thermal expansivities.
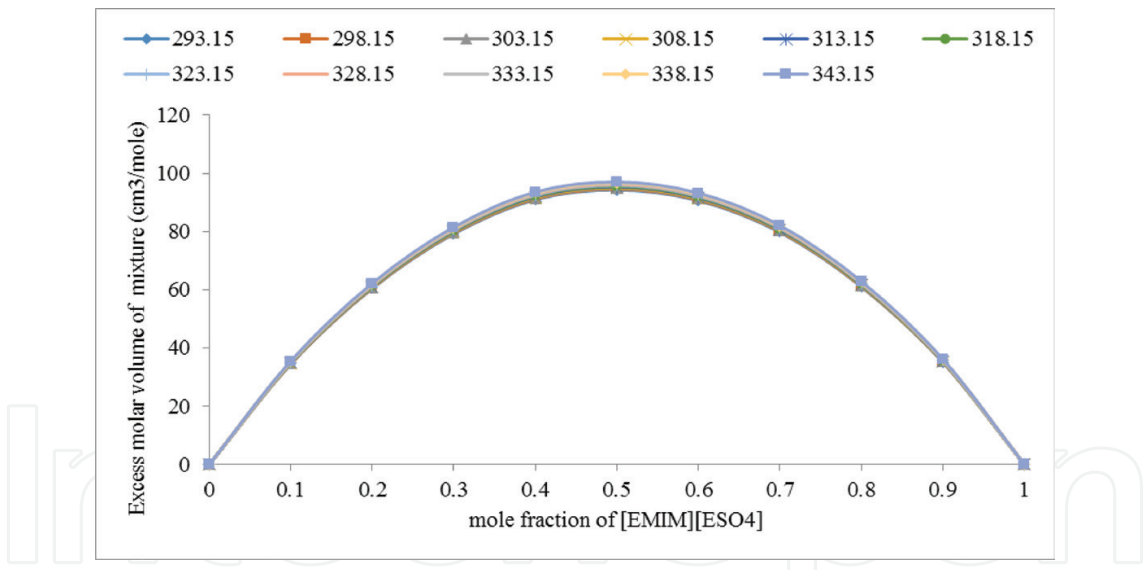
Figure 3. Excess molar volume of binary mixture of [EMIM][ESO$_4$] + [BMIM][OAc] at different temperature.

Excess molar volumes are positive over the whole composition range for [EMIM][ESO$_4$] + [BMIM][OAc] and [EMIM][ESO$_4$] + [BMIM][NtF$_2$]. [EMIM][ESO$_4$] + [BMIM][HSO$_4$] also has positive values at temperature from 293.15 to 343.15 K. But, [EMIM][ESO$_4$] + [BMIM][HSO$_4$] has a negative values at 308.15 and 313.15 K which is indicated that alkyl group substitution at anions has a significant role in the formation of hydrogen bond with other IL's at different temperature. The rise in temperature does not show any considerable effect on the excess molar volume of all the studied mixed IL's systems. But [EMIM][ESO$_4$] + [EMIM][HOS$_4$] system has shown negative deviation from 0 to 3.5 at 308.15 K and 0 to 6.5 mole fraction of [EMIM][ESO$_4$]
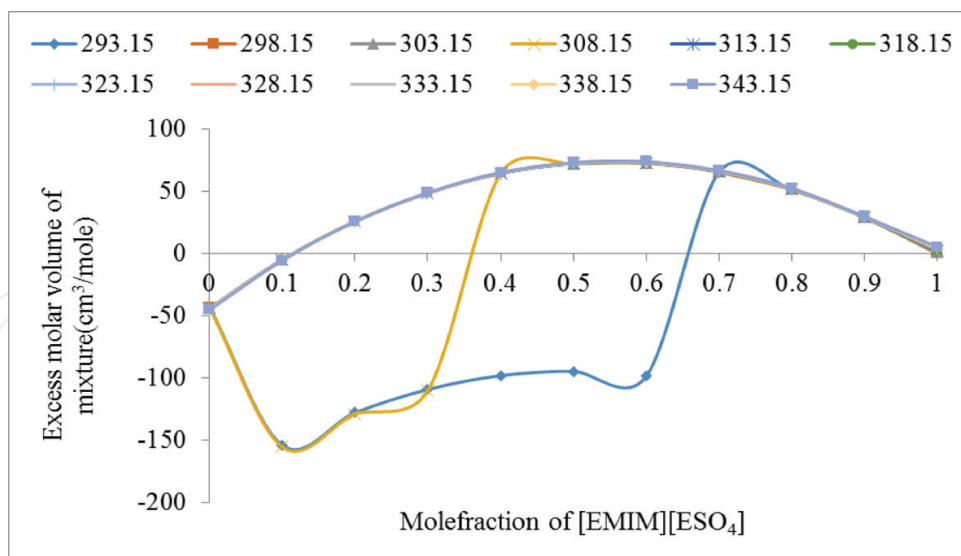
Figure 4. Excess molar volume of binary mixture of [EMIM][ESO$_4$] + [EMIM][HSO$_4$] at different temperature.
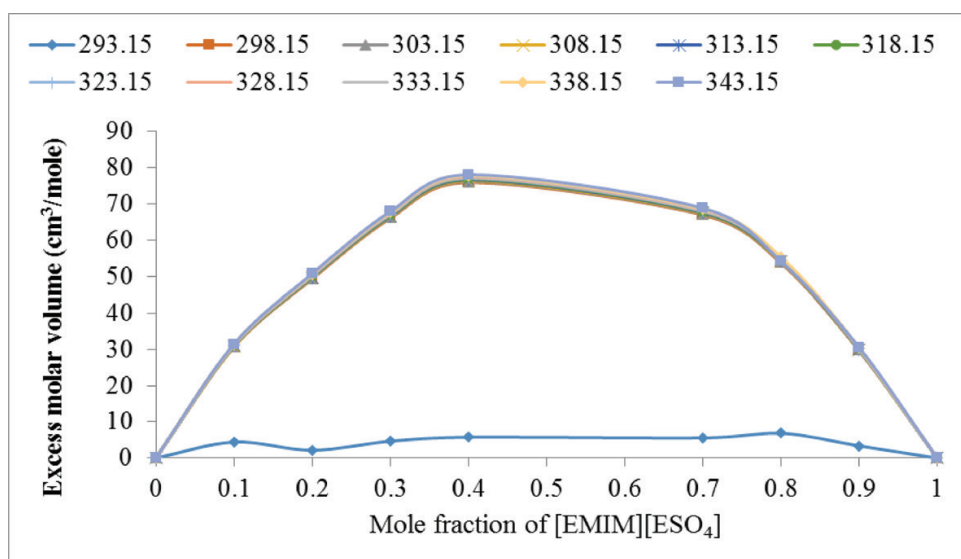
Figure 5. Excess molar volume of binary mixture of [EMIM][ESO$_4$] + [BMIM][NtF$_2$] at different temperature.

in [EMIM][HSO$_4$]. It may be due to the formation of hydrogen bond and also because of inter-actions. It is also observed that the sign of the excess molar volume and shape of the curve of excess molar volume as a function of [EMIM][ESO$_4$] is mainly depends on nature and changes of ion's in IL's.

4.4. Partial molar volume

Figures 6–8 shows the partial molar volume of [EMIM][ESO$_4$] in [EMIM][HSO$_4$], [BMIM][OAc] and [BMIM][NtF$_2$] at T (293.15–343.15) K. The values of partial molar volume of all studied system shows negative deviation for the mole fractions of [EMIM][ESO$_4$] at different temperatures, except [EMIM][ESO$_4$] + [EMIM][HSO$_4$] system. [EMIM][ESO$_4$] + [EMIM][HSO$_4$]
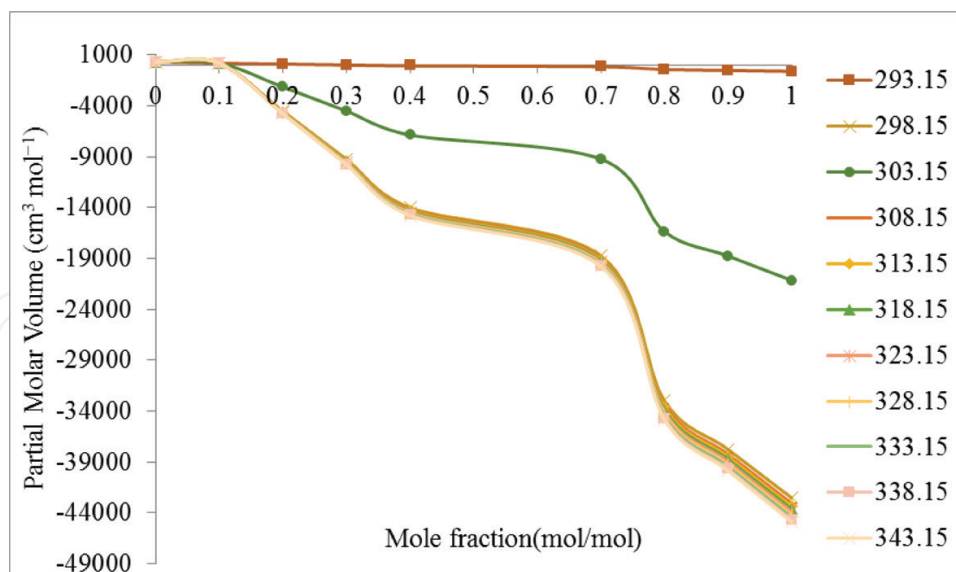
Figure 6. Partial molar volume of [EMIM][ESO₄] in [BMIM][NtF₂] at different temperature.
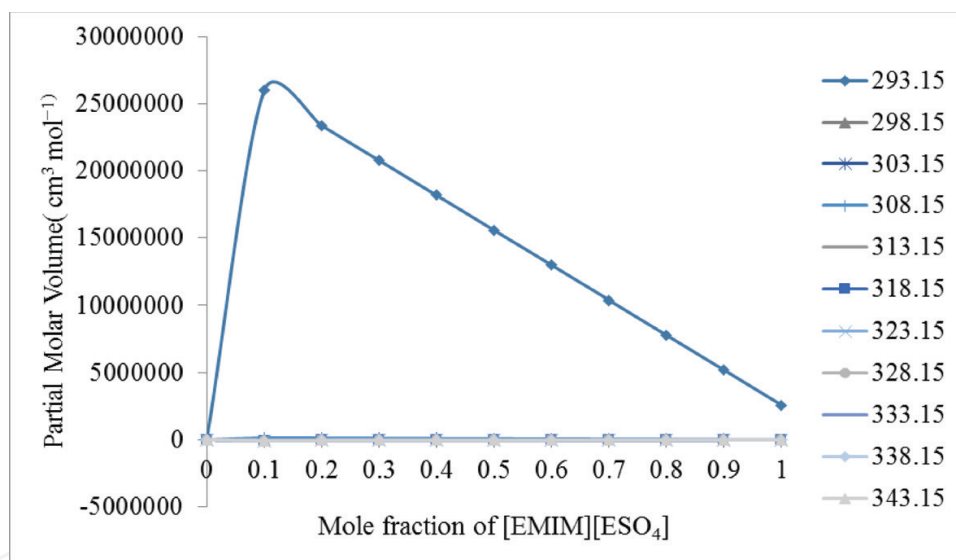

Figure 7. Partial molar volume of [EMIM][ESO₄] in [EMIM][HSO₄] at different temperature.

has positive deviation due to very strong physical interaction between [EMIM][ESO₄] and [BMIM][OAc]/[BMIM][NtF₂]. Physical interaction mainly consisting of dispersion forces or weak dipole-dipole interaction, and weak ion-dipole interaction make a positive deviation. The partial molar volume of [EMIM][ESO₄] with [EMIM][OAc] and [BMIM][NtF₂] mixtures are more negative than [EMIM][ESO₄] + [EMIM][HSO4] mixtures, which imply that there are stronger ion-dipole interactions. On the other hand, packing effect, charge transfer, hydrogen bond formation, other complex interaction, geometrical fitting one component into other due to difference in molar volume make a negative deviation. [EMIM][ESO₄] + [EMIM][HSO₄]
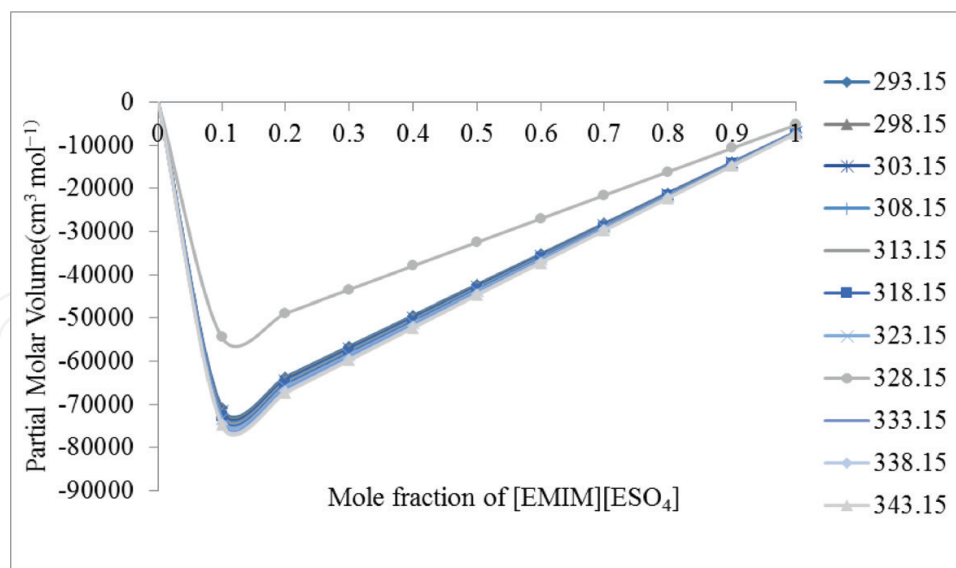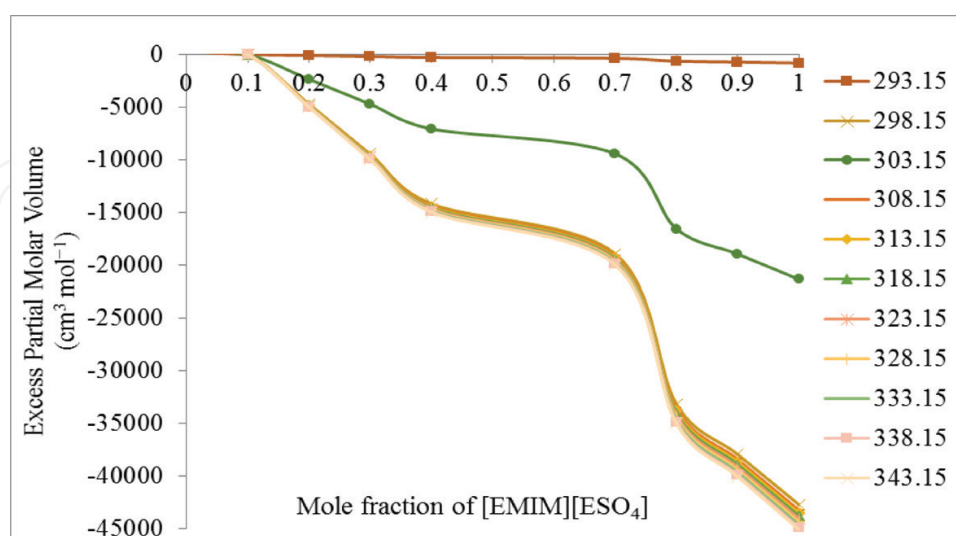
Figure 8. Partial molar volume of [EMIM][ESO$_4$] in [BMIM][OAc] at different temperature.

system has positive deviation due to very strong physical interaction between these two IL's at molecular level. Usually, physical interaction is dispersion forces or weak dipole-dipole interaction.

4.5. Excess partial molar volume

The excess partial molar volume of [EMIM][ESO$_4$] in [EMIM][HSO$_4$],[BMIM][OAc] and [BMIM][NtF$_2$] at T (293.15–343.15) K are presented in **Figures 9–11**. [EMIM][ESO$_4$] + [BMIM][NtF$_2$] and [EMIM][ESO$_4$] + [BMIM][OAc] shows negative deviation which indicates that

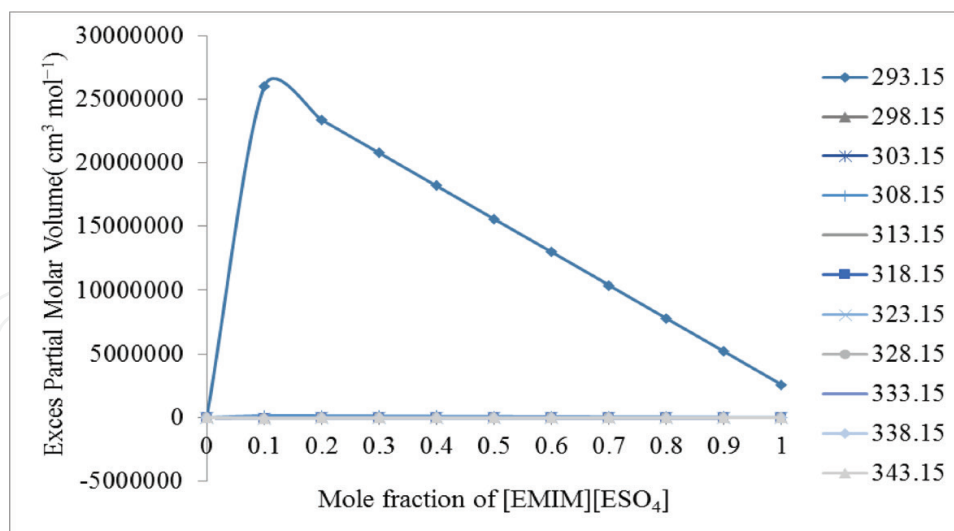**Figure 9.** Excess partial molar volume of [EMIM][ESO$_4$] in [BMIM][NtF$_2$] at different temperature.

Figure 10. Excess partial molar volume of [EMIM][ESO$_4$] in [EMIM][HSO$_4$] at different temperature.

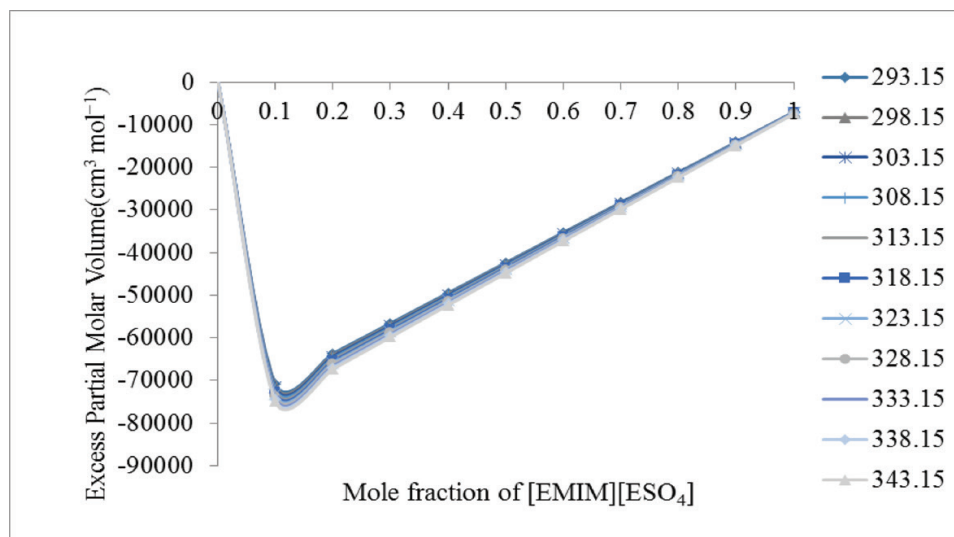**Figure 11.** Excess partial molar volume of [EMIM][ESO$_4$] in [EMIM][OAc] at different temperature.

there is very strong packing effect. The packing effect caused by a large difference in molecular size and configuration between two IL's, charge transfer, hydrogen bond formation and the ion-dipole attractions are even more dominant in IL's mixtures as function of compositions at T (293.15–343.15) K.

4.6. Apparent molar volume

[EMIM][ESO$_4$] in [BMIM][NtF$_2$] has positive deviation up to 0.7 mole fraction of [EMIM][ESO$_4$] due to strong dipole-dipole interaction, dispersion, induction and dipolar forces acting in between these two IL's for entire temperature range (**Figure 12**). The apparent

molar volume of [EMIM][ESO$_4$] in [EMIM][HSO$_4$] shows positive deviation as function of the composition from 293.15 to 333.15 K which implies that there is strong packing effect due to similar size of cation in both IL's (**Figure 13**). [EMIM][ESO4] + [BMIM][OAc] gave negative apparent molar volume which means that there is very strong hydrogen bond formation and charge-charge interaction between one and another at molecular level (**Figure 14**).
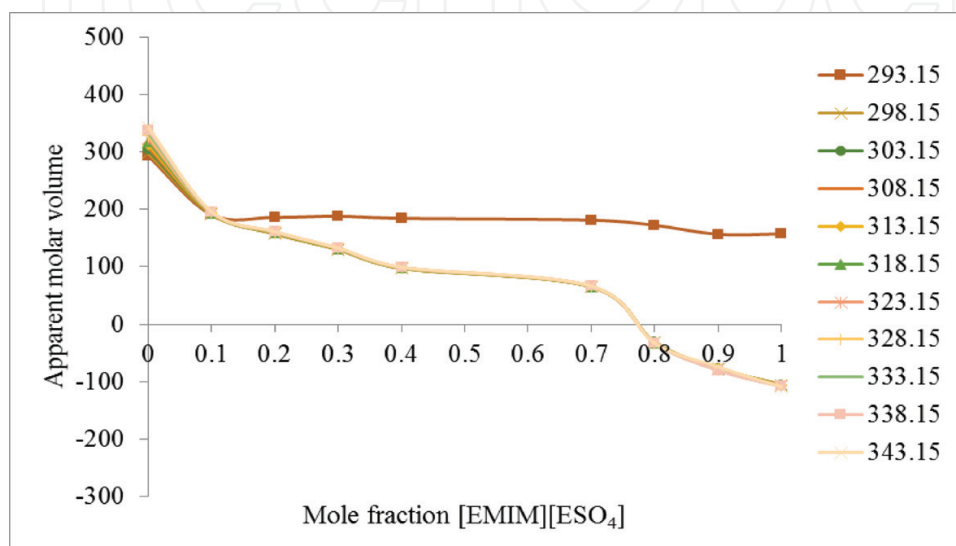

Figure 12. Apparent molar volume of [EMIM][ESO$_4$] in [BMIM][NtF$_2$] at different temperature.
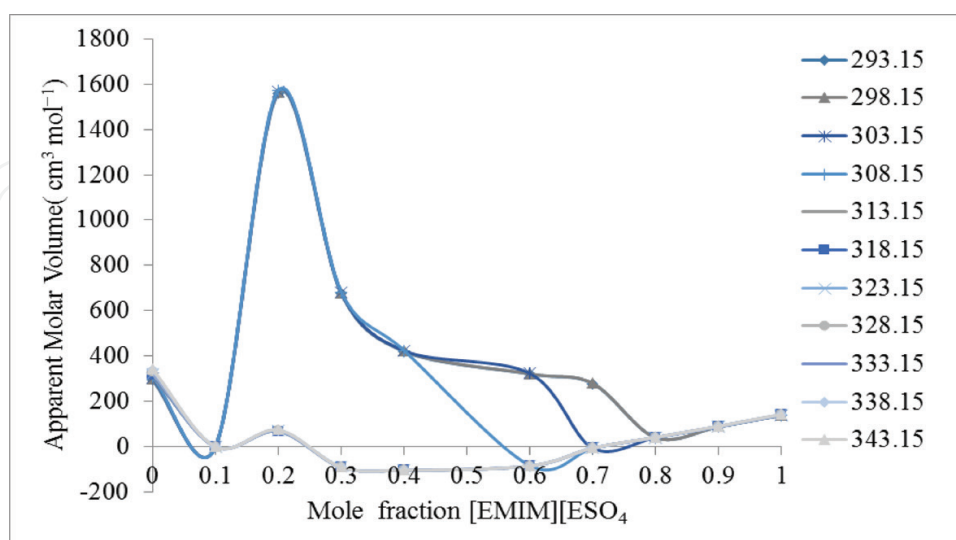

Figure 13. Apparent molar volume of [EMIM][ESO$_4$] in [EMIM][HSO$_4$] at different temperature.
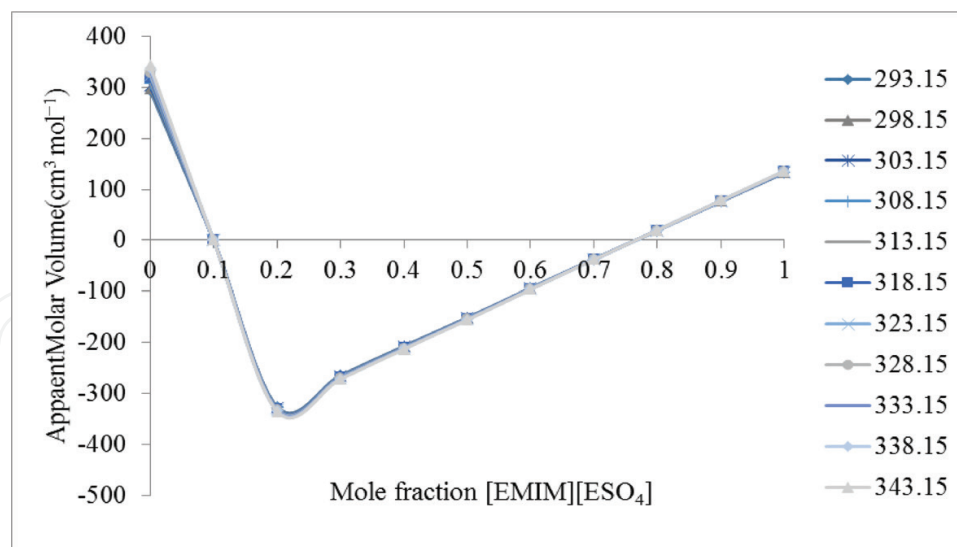
Figure 14. Apparent molar volume of [EMIM][ESO₄] in [EMIM][OAc] at different temperature.

5. Conclusions

Densities for the binary mixtures of [EMIM][ESO$_4$] + [EMIM][HSO$_4$], [EMIM][ESO$_4$] + [BMIM][OAc], [EMIM][ESO$_4$] + [BMIM][NtF$_2$] has been measured at 293.15–343.15 K with an interval of 5 K. Isobaric expansivity of all studied IL's have been calculated for temperature ranges from 293.15 to 343.15 K. The corresponding excess molar volume, partial molar volume; excess partial molar volumes; and apparent molar volume have also been calculated. The volumetric behavior of this binary system have been discussed in terms of ion-dipole interaction, packing effect, dipole-dipole interaction, hydrogen bond formation, geometrical fitting of one component into other, charge transfer, electron-electron interaction, and other complex forming interactions. In these mixtures, the forces (that is: dispersion, induction and dipolar forces) between pairs of unlike molecules are less than the forces between like molecules due to the difference in shape and size of the constituent molecules.

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