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RECEIVED 19 April 2023

ACCEPTED 02 August 2023

PUBLISHED 31 August 2023

## CITATION

Elizalde-Solis O, Zúñiga-Moreno A,  
Camacho-Camacho LE,  
García-Morales R, González-Arias S and  
Verónico-Sánchez FJ (2023), Densities  
and excess molar volumes of the binary  
systems of the ionic liquid  
trihexyl(tetradecyl)phosphonium  
bromide mixed with acetonitrile or  
tetrahydrofuran at temperatures from  
293.15 to 313.15 K.  
*Front. Phys.* 11:1208382.  
doi: 10.3389/fphy.2023.1208382

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# Densities and excess molar volumes of the binary systems of the ionic liquid trihexyl(tetradecyl) phosphonium bromide mixed with acetonitrile or tetrahydrofuran at temperatures from 293.15 to 313.15 K

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Experimental densities and excess molar volumes of two binary mixtures composed of the ionic liquid trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) mixed with acetonitrile (ACN) or tetrahydrofuran (THF) are reported in this work. Measurements were made using a vibrating tube densimeter at temperatures from 293.15 to 323.15 K. Both binary systems were studied in the whole composition range along with the pure compounds. Excess molar volumes were calculated from the experimental densities and were fitted with the Redlich–Kister polynomial equation. Excess molar volumes were negative for the mixtures and became more negative as the temperature increased. In addition, the ERAS model was applied for the modeling of excess molar volumes.

## KEYWORDS

acetonitrile, density, excess molar volume, ionic liquid, trihexyl(tetradecyl)phosphonium bromide, tetrahydrofuran

## 1 Introduction

Room-temperature ionic liquids or simply ionic liquids are generally defined as those ionic liquids with the melting point below or at temperatures of approximately 100°C [1]. Ionic liquids are formed entirely of cations and anions [2] and serve as efficient solvents for inorganic and organic compounds. They consist of non-coordinating ions capable of creating extremely polar solvents. They are immiscible with certain organic solvents, furnish a non-aqueous polar medium suitable for the dual-phase systems, and are non-volatile solvents with low vapor pressure. These properties earned them the status of green solvents [3,4].

TABLE 1 Characteristics of chemicals.

Name	Formula	CAS number	Molar mass	Source	Mass fraction purity	Grade
Trihexyl(tetradecyl)phosphonium bromide	C <sub>32</sub> H <sub>68</sub> BrP	654057-93-3	573.76	Sigma-Aldrich	0.95	
Acetonitrile (ACN)	C <sub>2</sub> H <sub>3</sub> N	75-05-8	41.05	J. T. Baker	0.999	HPLC
Tetrahydrofuran (THF)	C <sub>4</sub> H <sub>8</sub> O	109-99-9	72.11	J. T. Baker	0.999	HPLC
Water	H <sub>2</sub> O	7732-18-5	18.02	Anton Paar		Standard reference fluid

Phosphonium-based ionic liquids have better chemical and thermal stabilities over other ionic liquids. Phosphonium-based ionic liquids have achieved popularity because of their relatively low-cost synthesis, and the rates of phosphonium salt formation are faster than those of nitrogen-based salts, resulting in higher productivity and lower costs in industrial manufacturing of phosphonium-based ionic liquids. Their good thermal stability is suitable or beneficial for high-temperature operation, and phosphonium-based ionic liquids are less dense than water [1,5]. These ionic liquids are hydrophobic [6] and possess properties that can be harnessed in different academic and industrial areas such as reaction media, polymer processing, biological science, electrochemical applications, separation processes, and catalysis [1]. The potential of ionic liquids, especially phosphonium-based ionic liquids, is immense and undeniable. Knowledge of thermophysical and thermodynamic insights about pure ionic liquids and their mixtures with organic solvents is necessary since these are the fundamental basis and starting point of correct design, optimization, and operation of chemical processes [5,6]. Trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) has been reported as a good solvent for carbon dioxide solubilization [7]; in general, the trihexyl(tetradecyl)phosphonium cation has been shown to exhibit very good properties to dissolve carbon dioxide [8–11]. Our interest in the study of excess molar volume of mixtures of [THTDP][Br] with organic solvents aimed to elucidate and understand the molecular interactions between like and unlike molecules, for example, using aprotic solvents, such as ACN and THF.

In this work, the study of densities and excess molar volumes is reported for two binary mixtures composed of [THTDP][Br] + acetonitrile (ACN) and [THTDP][Br] + tetrahydrofuran (THF) in the temperature interval of 293.15–313.15 K. Excess molar volumes were correlated using the Redlich–Kister equation, which is of general use in academics and industry because of its simplicity. Additionally, the ERAS model was applied in the description of excess molar volumes at 298.15 K. To the best of our knowledge, only the previous work by [12] reported a volumetric study involving [THTDP][Br]. Specifically, densities of mixtures of [THTDP][Br] + *N,N*-dimethylformamide were studied. The volumetric and viscosity behaviors of binary mixtures of trihexyl(tetradecyl)phosphonium chloride ionic liquid + methanol were reported by [13]. [14] studied the excess molar volumes and the deviations in molar refraction at 298.15 K for the binary systems diisopropyl ether or tert-amyl methyl ether, methanol, or 1-propanol + trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate. Densities of pure [THTDP][Br] were studied by [5–7,9].

## 2 Experimental

### 2.1 Chemicals

[THTDP][Br] was supplied by Sigma-Aldrich with purity >0.95 in mass fraction, determined by NMR. The water content of the ionic liquid after the vacuum process, determined by Karl Fischer titration (Metrohm, model 915 KF), was 350 ppm. ACN and THF were of HPLC grade with purity >0.999 in mass fraction and were supplied by J. T. Baker. Water of high purity (standard reference fluid) for vibrating tube densimeter calibration was supplied by Anton Paar. Chemicals were used without further purification except for a careful

TABLE 2 Densities ( $\rho$ ) of pure compounds of trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]), acetonitrile (ACN), and tetrahydrofuran (THF) in the temperature interval of 293.15–313.15 K at  $p = 0.78$  bar, along with density literature data.

[THTDP][Br]					
$\rho/\text{g}\cdot\text{cm}^{-3}$					
T/K	This work	[5]	[6]	[7]	[9]
293.15	0.9613	0.9565	0.9617	0.9582	0.95995
298.15	0.9582		0.9586	0.9552	
303.15	0.9550	0.9503	0.9555	0.9521	0.95402
308.15	0.9519		0.9524	0.949	
313.15	0.9487	0.9441	0.9493	0.946	0.94800
ACN					
	This work	[20]	[21]	[22]	[23]
293.15	0.7821		0.7820		
298.15	0.7767	0.77693	0.7766	0.7765	0.77669
303.15	0.7713	0.77144			0.77189
308.15	0.7658	0.76597	0.7663	0.7657	0.76546
313.15	0.7603	0.76068			0.76086
THF					
	This work	[24]	[25]	[26]	[27]
293.15	0.8875	0.88741		0.88873	0.888766
298.15	0.8820		0.882209	0.88324	0.883297
303.15	0.8764	0.87647		0.87760	0.877809
308.15	0.8707	0.87096	0.871159	0.87202	0.872279
313.15	0.8649			0.86623	0.866713

**TABLE 3** Densities ( $\rho$ ) of the binary systems trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + acetonitrile (ACN) (2) and [THTDP][Br] (1) + tetrahydrofuran (THF) (2) in the temperature interval of 293.15–313.15 K at 0.78 bar and at different mole fractions of [THTDP][Br] ( $x_1$ ).

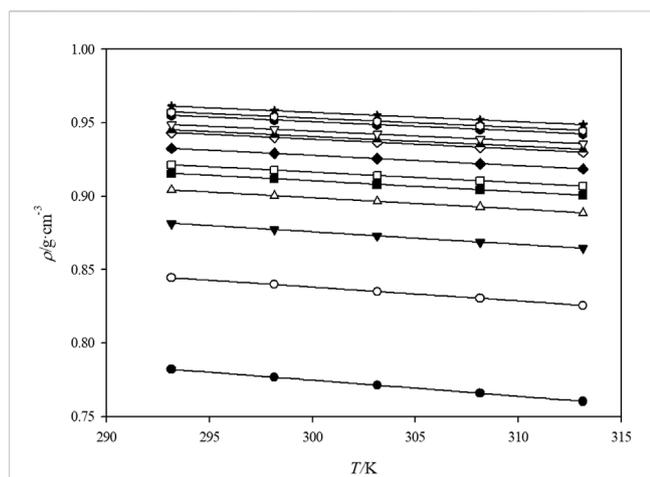
$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$				
	$T = 293.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 308.15 \text{ K}$	$T = 313.15 \text{ K}$
[THTDP][Br] (1) + ACN (2)					
0.0000	0.7821	0.7767	0.7713	0.7658	0.7603
0.0433	0.8444	0.8398	0.8350	0.8304	0.8256
0.0941	0.8815	0.8774	0.8730	0.8688	0.8646
0.1499	0.9042	0.9004	0.8965	0.8927	0.8887
0.1916	0.9156	0.9119	0.9081	0.9044	0.9007
0.2215	0.9214	0.9178	0.9141	0.9105	0.9069
0.2982	0.9326	0.9291	0.9256	0.9221	0.9186
0.4217	0.9433	0.9400	0.9366	0.9333	0.9299
0.4521	0.9452	0.9419	0.9385	0.9353	0.9319
0.5215	0.9488	0.9455	0.9422	0.9390	0.9357
0.6978	0.9551	0.9519	0.9487	0.9456	0.9424
0.7916	0.9574	0.9543	0.9511	0.9480	0.9448
1.0000	0.9613	0.9582	0.9550	0.9519	0.9487
[THTDP][Br] (1) + THF (2)					
0.0000	0.8875	0.882	0.8764	0.8707	0.8649
0.0500	0.9102	0.9055	0.9009	0.8961	0.8914
0.1000	0.9243	0.9200	0.9157	0.9114	0.9071
0.1499	0.9334	0.9294	0.9254	0.9213	0.9173
0.2000	0.9398	0.9360	0.9322	0.9284	0.9246
0.2472	0.9443	0.9406	0.9369	0.9332	0.9295
0.2975	0.9477	0.9441	0.9405	0.9369	0.9333
0.4052	0.9524	0.9490	0.9455	0.9421	0.9386
0.5068	0.9550	0.9517	0.9483	0.9450	0.9416
0.6075	0.9568	0.9535	0.9502	0.9470	0.9436
0.7211	0.9583	0.9551	0.9519	0.9487	0.9454
0.8423	0.9597	0.9566	0.9534	0.9503	0.9471
1.0000	0.9613	0.9582	0.9550	0.9519	0.9487

degassing of samples under vacuum and low temperature (2°C). Characteristics of chemicals used are summarized in Table 1.

## 2.2 Equipment and procedure

Densities of pure compounds and binary mixtures were measured using a vibrating tube densimeter (Anton Paar DMA 4500 M). Measurements were carried out at atmospheric pressure; the laboratory is located in Mexico City where the atmospheric pressure is 0.78 bar; saturation temperatures at this pressure calculated using the Wagner equation are 73.7°C and 58.1°C for

ACN and THF, respectively. Densities are reported for the liquid phase; however, the closer the mixture is to the saturation temperature of the pure compound, the more likely the mixture undergoes partial vaporization, which leads to the formation of bubbles. Indeed, this also depends on the composition of the mixture. To avoid this issue, measurements were restricted to the short range of 293.15–313.15 K. For example, in the case of tetrahydrofuran, instabilities occurred approximately at 50°C, reflected by the presence of bubbles in the cell, so it is impossible to perform measurements. The densimeter performs the function of detecting these bubbles, and it is possible to see them with an internal camera. The volume of a U-shape measuring cell is



**FIGURE 1**

Experimental densities for the binary system trihexyl(tetradecyl) phosphonium bromide ([THTDP][Br]) (1) + acetonitrile (2) as a function of temperature at  $p = 0.78$  bar and at the following mole fractions of [THTDP][Br] ( $x_1$ ):  $x_1 = 0.0000$ , ●;  $x_1 = 0.0433$ , ×;  $x_1 = 0.0941$ , ▼;  $x_1 = 0.1499$ , △;  $x_1 = 0.1926$ , ■;  $x_1 = 0.2215$ , □;  $x_1 = 0.2982$ , ◆;  $x_1 = 0.4217$ , ◇;  $x_1 = 0.4521$ , ▲;  $x_1 = 0.5215$ , ▽;  $x_1 = 0.6978$ , ●;  $x_1 = 0.7916$ , ○; and  $x_1 = 1.0000$ , ★. Lines are used only for guiding purposes.

approximately 1 mL. A volume of 2 mL of the sample was used for the measurements, taking into account cell and hose volumes; however, considering only 1 mL of cell volume, the masses fed varied approximately between 0.76 and 0.96 g at 20°C. The vibrating tube densimeter has an accuracy of  $1 \times 10^{-5}$  g·cm<sup>-3</sup> and uncertainty in the temperature of  $\pm 0.01$  K. Air and water were used as reference fluids for the calibration of the vibrating tube densimeter. Densities of air were taken from the DMA 4500 M instruction manual and from the reference equation CIPM-2007 described by [15]; meanwhile, densities of water were calculated from the reference equation of the state of water reported by [16]. Uncertainty in density measurements was estimated to be better than  $\pm 2 \times 10^{-4}$  g·cm<sup>-3</sup>. The sources of uncertainties are vibration periods of water, air, and sample mixture, uncertainties of density of water and air, and temperature. Binary mixtures were prepared gravimetrically in a room with controlled humidity and temperature. Additionally, a glove box with an argon atmosphere was utilized to avoid any contamination of water [12]. A Metter-Toledo mass balance (model AB204), with an accuracy of  $\pm 0.1$  mg, was used and calibrated periodically by means of a 200 g reference mass. Uncertainty in the mole fraction was estimated to be  $\leq \pm 0.0001$ . The samples were degassed under vacuum in the injection syringe (10 mL) before being injected into the vibrating tube densimeter. The syringe was cooled using a PolyScience recirculation bath (model PD15R-40) at 2°C to avoid evaporation and shifting of the composition in the binary mixtures.

## 3 Results and discussion

### 3.1 Pure compounds

Reliability of the vibrating tube densimeter and procedure used in this work has been tested previously by [12,17–19]. Densities of

[THTDP][Br], ACN, and THF were measured in the temperature interval of 293.15–313.15 K at 0.78 bar and compared with some selected literature data. Experimental data measured in this work along with literature values are reported in Table 2. For comparison purposes, the following average absolute relative deviation (AARD) is defined:

$$AARD = 100 \left( \frac{|\rho_{exp} - \rho_{lit}|}{\rho_{lit}} \right) / n_p, \quad (1)$$

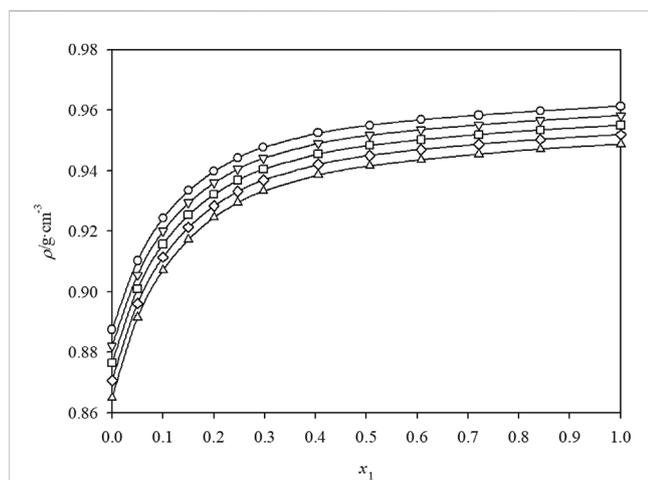
where  $\rho_{exp}$  and  $\rho_{lit}$  are experimental densities derived from this work and literature, respectively. Meanwhile,  $n_p$  is the number of data points of every dataset compared. Comparisons of densities for the ionic liquid [THTDP][Br] were as follows: good agreement was found with the data from [7], with an AARD of 0.05%. Larger deviations were observed with the datasets reported by [5,6,9], with AARD values of 0.49, 0.31, and 0.11%, respectively. Deviations among datasets can be explained from the purities of the samples used in each work. [7] used a sample of the same purity of that used in this work; meanwhile, [5,6] used a sample with higher purities of 0.98 and 0.96 mass fractions, respectively. For ACN, excellent agreement was found when data were compared with those from [20] (sample purity was not reported), [21] (sample purity: 0.998 mass fraction), and [22] (sample purity: 0.999 mass fraction), with AARD values of 0.03, 0.03, and 0.02%, respectively. An AARD value of 0.05% was obtained for the comparison with the dataset described by [23] (sample purity: 0.999 mass fraction), which is in good agreement. Regarding THF, excellent agreement was observed with the dataset reported by [24] with an AARD of 0.01% (puriss p. a. reagent by Sigma-Aldrich, 107 ppm of water content). A good agreement was observed with the data reported by [25] (sample purity: 0.993 mass fraction) with an AARD of 0.04%. Larger deviations were observed when compared with datasets reported by [26] (sample purity: 0.995 mass fraction) and [27] (sample purity: 0.993 mass fraction), with AARD values of 0.14% and 0.16%, respectively. These comparisons validated the experimental procedure used in this work. The increasing order of densities of the pure compounds used in this study is given as follows:  $\rho_{ACN} < \rho_{THF} < \rho_{[THTDP][Br]}$ .

### 3.2 Binary mixtures

Binary mixtures were studied covering the complete interval of compositions. The [THTDP][Br] (1) + ACN (2) mixture was studied at the following compositions in [THTDP][Br] mole fraction:  $x_1 = 0.0433, 0.0941, 0.1499, 0.1916, 0.2215, 0.2982, 0.4217, 0.4521, 0.5215, 0.6978, \text{ and } 0.7916$ ; meanwhile, for the [THTDP][Br] (1) + THF (2) binary system, the following compositions were studied:  $x_1 = 0.0500, 0.1499, 0.2000, 0.2472, 0.2973, 0.4052, 0.5068, 0.5068, 0.6075, 0.7211, \text{ and } 0.8423$ . Experimental densities of the two binary systems along with pure compound densities in the temperature interval of 293.15–313.15 K at  $p = 0.78$  bar are reported in Table 3. Figures 1, 2 show the behavior of densities of the [THTDP][Br] (1) + ACN (2) system as a function of temperature and composition ( $x_1$ ), respectively. Density decreased with the increase in temperature,

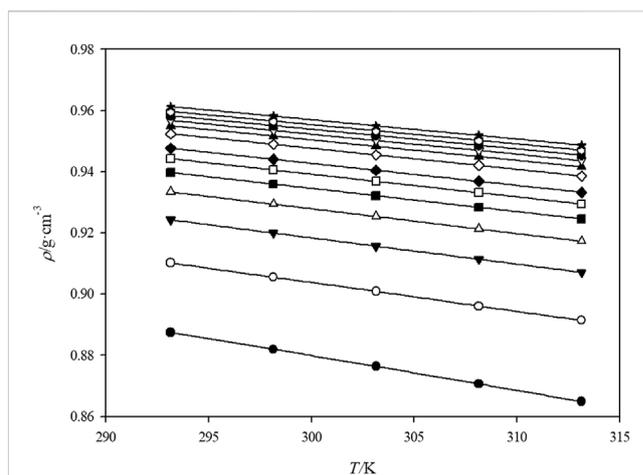
**TABLE 4** Values of the derivative of density ( $\rho$ ) with respect to temperature ( $T$ ) at constant pressure  $(\frac{\partial \rho}{\partial T})_p$ , as described in Eq. 2, for the binary systems trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + acetonitrile (ACN) (2) and [THTDP][Br] (1) + tetrahydrofuran (THF) (2) at 0.78 bar and at different mole fractions of [THTDP][Br] ( $x_1$ ).

[THTDP][Br] (1) + ACN (2)		[THTDP][Br] (1) + THF (2)	
$x_1$	$(\frac{\partial \rho}{\partial T})_p / g \cdot cm^{-3} \cdot K^{-1}$	$x_1$	$(\frac{\partial \rho}{\partial T})_p / g \cdot cm^{-3} \cdot K^{-1}$
0.0000	- 0.0011	0.0000	- 0.0011
0.0433	- 0.0009	0.0500	- 0.0009
0.0941	- 0.0008	0.1000	- 0.0009
0.1499	- 0.0008	0.1499	- 0.0008
0.1916	- 0.0007	0.2000	- 0.0008
0.2215	- 0.0007	0.2472	- 0.0007
0.2982	- 0.0007	0.2975	- 0.0007
0.4217	- 0.0007	0.4052	- 0.0007
0.4521	- 0.0007	0.5068	- 0.0007
0.5215	- 0.0007	0.6075	- 0.0007
0.6978	- 0.0006	0.7211	- 0.0006
0.7916	- 0.0006	0.8423	- 0.0006
1.0000	- 0.0006	1.0000	- 0.0006

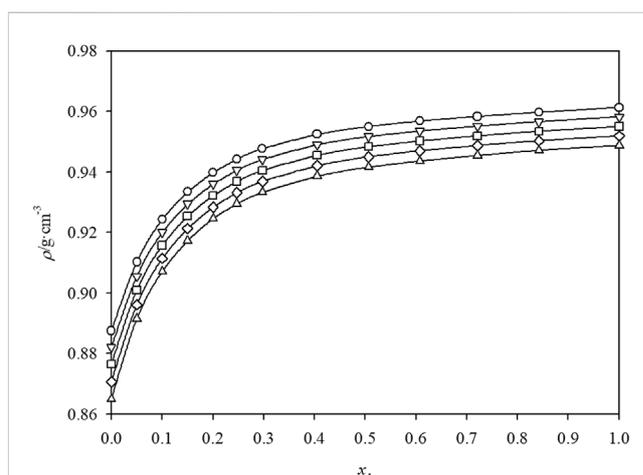


**FIGURE 2** Experimental densities at  $p = 0.78$  bar for the binary system trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + acetonitrile (2) as a function of the mole fraction of [THTDP][Br] ( $x_1$ ) at the following temperatures:  $T = 293.15$  K,  $\circ$ ;  $T = 298.15$  K,  $\square$ ;  $T = 303.15$  K,  $\triangle$ ;  $T = 308.15$  K,  $\diamond$ ; and  $T = 313.15$  K,  $\nabla$ . Lines are used only for guiding purposes.

as shown in Figure 1, for different compositions of the mixture. Once the behavior of density as a function of temperature is known at constant pressure, the thermal expansion ( $\alpha$ ) can be estimated according to the following thermodynamic definition:



**FIGURE 3** Experimental densities for the binary system trihexyl(tetradecyl) phosphonium bromide ([THTDP][Br]) (1) + tetrahydrofuran (2) as a function of temperature at 0.78 bar and at the following mole fractions of [THTDP][Br] ( $x_1$ ):  $x_1 = 0.0000$ ,  $\bullet$ ;  $x_1 = 0.0500$ ,  $\times$ ;  $x_1 = 0.1000$ ,  $\nabla$ ;  $x_1 = 0.1499$ ,  $\triangle$ ;  $x_1 = 0.2000$ ,  $\square$ ;  $x_1 = 0.2472$ ,  $\blacksquare$ ;  $x_1 = 0.2975$ ,  $\blacklozenge$ ;  $x_1 = 0.4052$ ,  $\diamond$ ;  $x_1 = 0.5068$ ,  $\blacktriangle$ ;  $x_1 = 0.6075$ ,  $\nabla$ ;  $x_1 = 0.7211$ ,  $\bullet$ ;  $x_1 = 0.8423$ ,  $\circ$ ; and  $x_1 = 1.0000$ ,  $\star$ . Lines are used only for guiding purposes.



**FIGURE 4** Experimental densities at  $p = 0.78$  bar for the binary system trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + tetrahydrofuran (2) as a function of the mole fraction of [THTDP][Br] ( $x_1$ ) at the following temperatures:  $T = 293.15$  K,  $\circ$ ;  $T = 298.15$  K,  $\square$ ;  $T = 303.15$  K,  $\triangle$ ;  $T = 308.15$  K,  $\diamond$ ; and  $T = 313.15$  K,  $\nabla$ . Lines are used only for guiding purposes.

$$\alpha = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p \quad (2)$$

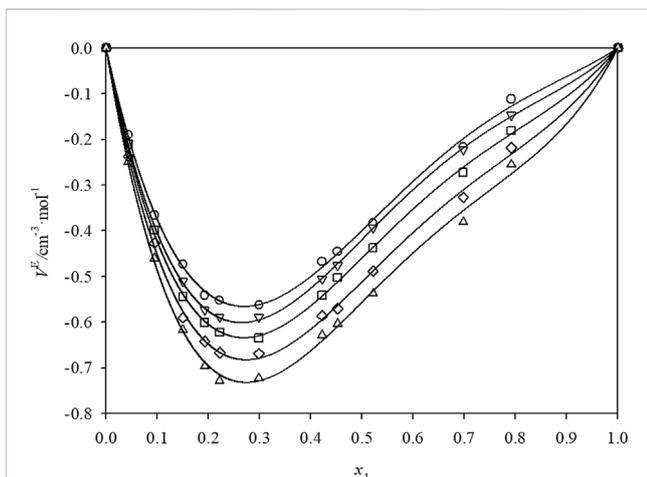
This property is also known as volume expansivity. A linear trend was observed for density as a function of temperature (Figure 1) for all compositions studied; therefore,  $\alpha$ -values highly depend on the slopes of lines presented in Figure 1, and  $\alpha$ -values showed very little change with change in temperature. Slopes presented in Eq. 2 are reported in

**TABLE 5** Excess molar volumes ( $V^E$ ) of the binary systems trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) + acetonitrile (ACN) (2) and [THTDP][Br] (1) + tetrahydrofuran (THF) (2) in the temperature interval of 293.15–313.15 K at  $p = 0.78$  bar and at different mole fractions of [THTDP][Br] ( $x_1$ ).

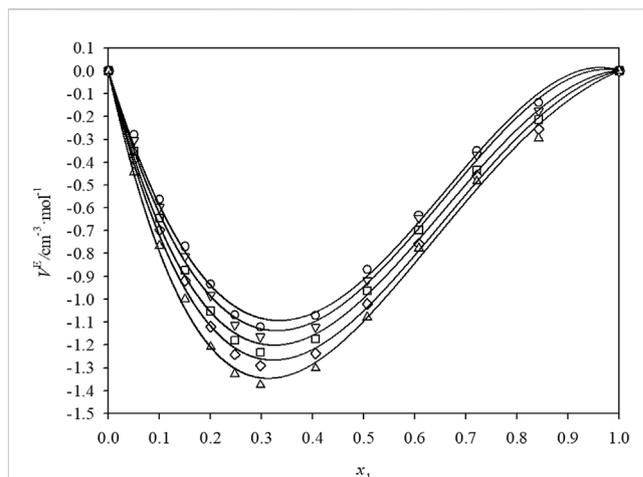
$x_1$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
[THTDP][Br] (1) + ACN (2)					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0433	– 0.1893	– 0.2075	– 0.2109	– 0.2374	– 0.2490
0.0941	– 0.3658	–0.3966	–0.3989	– 0.4264	– 0.4611
0.1499	– 0.4737	– 0.5110	– 0.5442	– 0.5904	– 0.6174
0.1926	– 0.5413	– 0.5733	– 0.6014	– 0.6418	– 0.6959
0.2215	– 0.5523	– 0.5891	– 0.6221	– 0.6672	– 0.7278
0.2982	– 0.5625	– 0.5890	– 0.6351	– 0.6691	– 0.7233
0.4217	– 0.4679	– 0.5059	– 0.5415	– 0.5861	– 0.6284
0.4521	– 0.4461	– 0.4757	– 0.5029	– 0.5703	– 0.6040
0.5215	– 0.3833	– 0.3936	– 0.4370	– 0.4880	– 0.5373
0.6978	– 0.2166	– 0.2225	– 0.2720	– 0.3268	– 0.3808
0.7916	– 0.1117	– 0.1464	– 0.1806	– 0.2183	– 0.2555
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
[THTDP][Br] (1) + THF (2)					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0500	– 0.2788	– 0.3036	– 0.35333	– 0.3862	– 0.4448
0.1000	– 0.5639	– 0.5963	– 0.6446	– 0.6968	– 0.7657
0.1499	–0.7689	– 0.8118	– 0.8733	– 0.9181	– 0.9996
0.2000	– 0.9340	– 0.9826	– 1.0525	– 1.1195	– 1.2089
0.2472	– 1.0693	– 1.1131	– 1.1806	– 1.2419	– 1.3278
0.2975	– 1.1221	– 1.1638	– 1.2319	– 1.2901	– 1.3755
0.4052	– 1.0727	– 1.1221	– 1.1733	– 1.2371	– 1.3029
0.5068	– 0.8717	– 0.9167	– 0.9631	– 1.0200	– 1.0787
0.6075	– 0.6342	– 0.6445	– 0.6967	– 0.7574	– 0.7782
0.7211	– 0.3503	– 0.3682	– 0.4338	– 0.4586	– 0.4842
0.8423	– 0.1404	– 0.1766	– 0.2135	– 0.2541	– 0.2956
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4 for the different compositions studied. Slopes became almost constant after the composition of  $x_1 = 0.1916$  and can be ascribed to the predominant effect of the ionic liquid in the mixture. This effect is better illustrated in Figure 2. Densities of the mixtures increased with the increase in the ionic liquid content in the mixture; this effect can be seen in Figure 1 but is better described in Figure 2. After the composition of  $x_1 = 0.1916$ , changes in density are less significant and tend toward the values of pure ionic liquid density. Figures 3, 4 show the behavior of densities of the [THTDP][Br] (1) + THF (2) system as a function of temperature and composition ( $x_1$ ), respectively. Similar behavior was found for this binary

system. As expected, density decreased as the temperature increased. A linear dependency of density on temperature was found, as depicted in Figure 3 and was used to calculate slopes presented in Eq. 2 and are reported in Table 4. After the composition of  $x_1 = 0.2472$ , slopes are almost constant, reflecting the effect of the presence of the increasing content of the ionic liquid. This effect is also better illustrated in Figure 4. Similar to the aforementioned binary system, the influence of the ionic liquid on the density of the mixture is more noticeable after the composition of  $x_1 = 0.2472$ , and after this point, densities tend toward the values of the pure ionic liquid density. A dominant effect of the ionic liquid on the



**FIGURE 5**  
Excess molar volumes ( $V^E$ ) of the binary system trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + acetonitrile (2) as a function of the mole fraction of [THTDP][Br] ( $x_1$ ) at  $p = 0.78$  bar at the following temperatures:  $T = 293.15$  K,  $\times$ ;  $T = 298.15$  K,  $\nabla$ ;  $T = 303.15$  K,  $\square$ ;  $T = 308.15$  K,  $\diamond$ ; and  $T = 313.15$  K,  $\triangle$ . Lines represent values obtained using the Redlich–Kister equation.



**FIGURE 6**  
Excess molar volumes ( $V^E$ ) of the binary system trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + tetrahydrofuran (2) as a function of the mole fraction of [THTDP][Br] ( $x_1$ ) at  $p = 0.78$  bar at the following temperatures:  $T = 293.15$  K,  $\times$ ;  $T = 298.15$  K,  $\nabla$ ;  $T = 303.15$  K,  $\square$ ;  $T = 308.15$  K,  $\diamond$ ; and  $T = 313.15$  K,  $\triangle$ . Lines represent values obtained using the Redlich–Kister equation.

**TABLE 6** Adjusted parameters ( $A_i$ ) for the Redlich–Kister equation along with standard deviations ( $\sigma$ ) for the correlation of excess molar volumes ( $V^E$ ) of the binary systems trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + acetonitrile (ACN) (2) and [THTDP][Br] (1) + tetrahydrofuran (THF) (3) in the temperature interval of 293.15–313.15 K at  $p = 0.78$  bar.

$T/K$	$A_0/\text{cm}^{-3}\cdot\text{mol}^{-1}$	$A_1/\text{cm}^{-3}\cdot\text{mol}^{-1}$	$A_2/\text{cm}^{-3}\cdot\text{mol}^{-1}$	$\sigma$
[THTDP][Br] (1) + ACN (2)				
293.15	– 1.597	– 2.171	– 1.301	0.0098
298.15	– 1.677	– 2.249	– 1.599	0.0043
303.15	– 1.841	– 2.205	– 1.719	0.0067
308.15	– 2.047	– 2.203	– 1.905	0.0098
313.15	– 2.227	– 2.229	– 2.188	0.0124
[THTDP][Br] (1) + THF (2)				
293.15	– 3.649	– 3.964	0.427	0.0319
298.15	– 3.778	– 4.082	0.160	0.0349
303.15	– 3.978	– 4.165	– 0.340	0.0305
308.15	– 4.199	– 4.294	– 0.584	0.0299
313.15	– 4.381	– 4.600	– 1.162	0.0336

densities of the binary systems was observed, and this effect can be ascribed to the higher density of the ionic liquid and the asymmetric nature of the binary mixtures.

Excess molar volumes ( $V^E$ ) are defined as follows:

$$V^E = V - V^{id}, \tag{3}$$

where  $V$  is the molar volume of the mixture and  $V^{id}$  represents the ideal molar volume of the mixture. Eq. 3 can be rewritten in terms of density as expressed in the following equation:

$$V^E = \frac{x_1 M_1 + (1 - x_1) M_2}{\rho} - \left( \frac{x_1 M_1}{\rho_1} + \frac{(1 - x_1) M_2}{\rho_2} \right), \tag{4}$$

where  $\rho$  is the density of the mixture,  $x_1$  is the mole fraction of the ionic liquid [THTDP][Br],  $M_1$  and  $M_2$  are the molar masses, and  $\rho_1$  and  $\rho_2$  are the densities of pure compounds [THTDP][Br] (1) and ACN or THF (2), respectively. Excess molar volumes were calculated using the densities reported in Table 3 and the molar masses listed in Table 1. These results are presented in Table 5 for the two binary mixtures studied and are plotted in

**TABLE 7** Pure compound parameters for the ERAS model at  $T = 298.15$  K. Thermal expansion ( $\alpha$ ), isothermal compressibility ( $\beta$ ), molar volume ( $V$ ), characteristic molar volume ( $V^*$ ), characteristic pressure ( $P^*$ ), and surface-to-volume ratio ( $S$ ).

Component	$\alpha \cdot 10^4 / \text{K}^{-1}$	$\beta \cdot 10^4 / \text{MPa}^{-1}$	$V / \text{cm}^3 \cdot \text{mol}^{-1}$	$V^* / \text{cm}^3 \cdot \text{mol}^{-1}$	$P^* / \text{MPa}$	$S / \text{nm}^{-1}$
Trihexyl(tetradecyl)phosphonium bromide	6.572	4.615 <sup>a</sup>	588.35	501.60	584.11	91.46 <sup>a</sup>
Acetonitrile	13.945	10.998 <sup>b</sup>	52.85	39.94	662.07	15.19 <sup>d</sup>
Tetrahydrofuran	12.585	9.97 <sup>c</sup>	81.76	62.97	634.48	13.31 <sup>c</sup>

<sup>a</sup>Estimated from experimental data from this work.

<sup>b</sup>Obtained from [36].

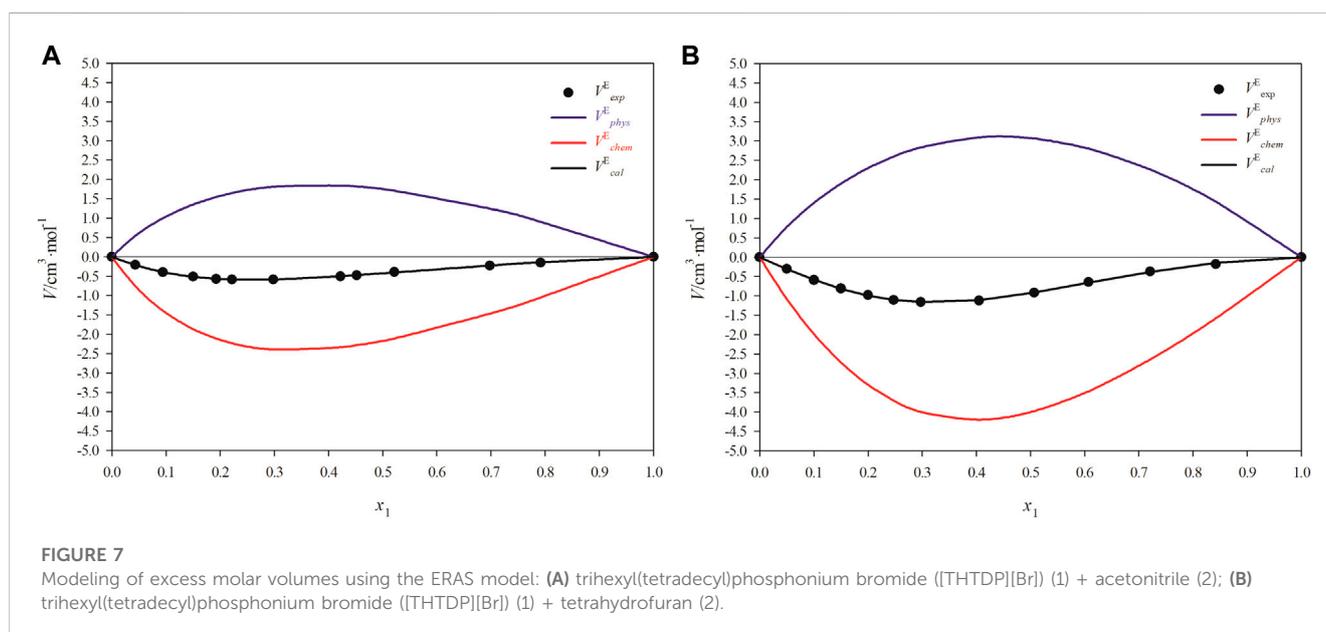
<sup>c</sup>Obtained from [33].

<sup>d</sup>Obtained from [34].

<sup>e</sup>Obtained from [35].

**TABLE 8** Interaction parameters for the ERAS model at  $T = 298.15$  K along with standard deviation of the fit for the binary mixtures.

System	$K_{AB} / -\zeta$	$\Delta V_{AB}^* / \text{cm}^3 \cdot \text{mol}^{-1}$	$\chi_{AB} / \text{MPa}$	$\sigma / \text{cm}^3 \cdot \text{mol}^{-1}$
[THTDP][Br] (1) + acetonitrile (2)	4.11	-16.84	56.27	0.005
[THTDP][Br] (1) + tetrahydrofuran (2)	6.53	-18.87	64.64	0.017

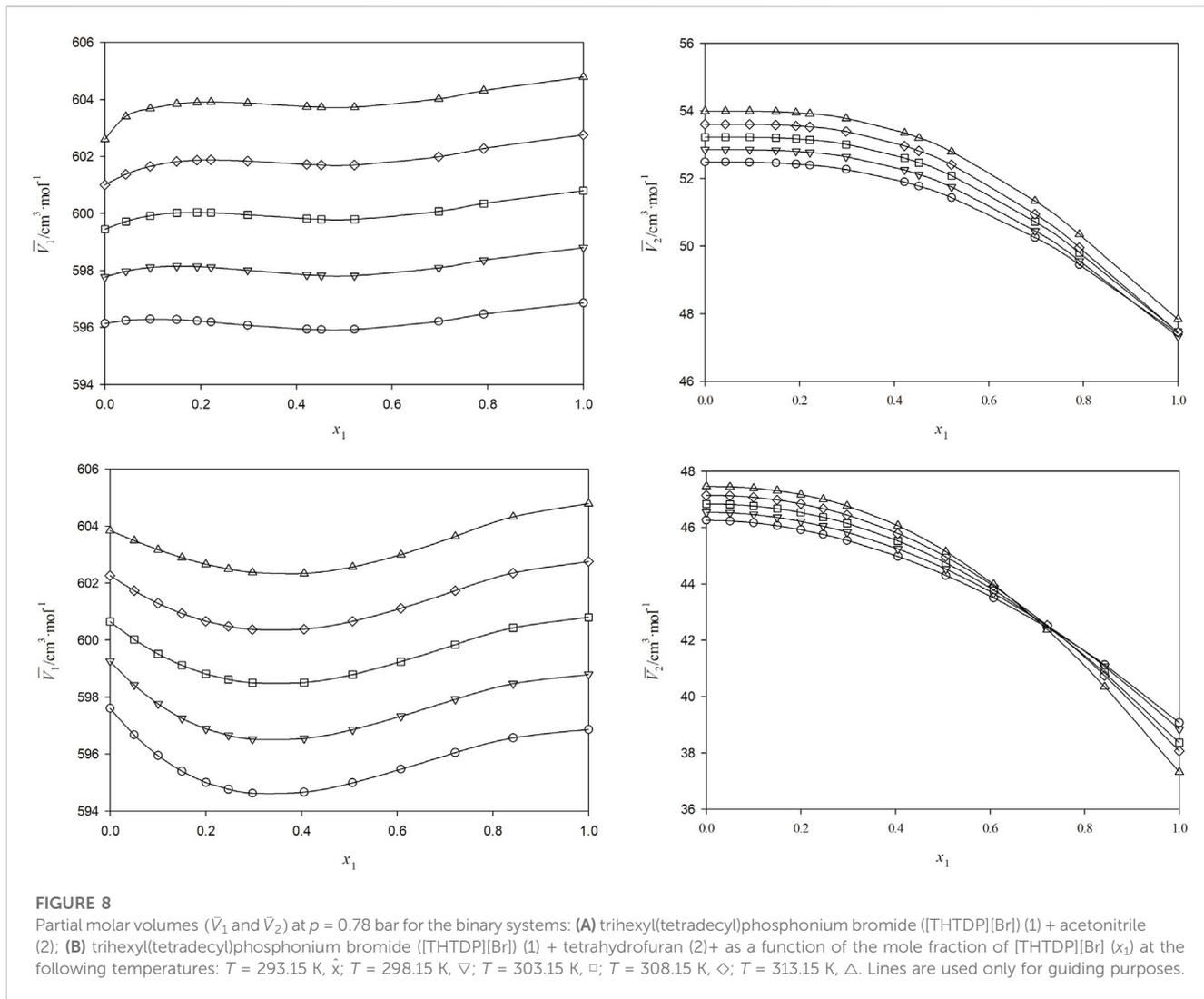
**FIGURE 7**

Modeling of excess molar volumes using the ERAS model: (A) trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + acetonitrile (2); (B) trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) (1) + tetrahydrofuran (2).

Figures 5, 6 as a function of  $x_1$  at different temperatures. Excess molar volumes exhibited negative deviations from ideality, and these became more negative for both binary systems as the temperature increased. Excess molar volumes for the [THTDP][Br] (1) + ACN (2) binary system were smaller than those obtained for the [THTDP][Br] (1) + t THF (2) binary system. Negative values of the excess molar volumes imply that a more effective arrangement and/or attractive interactions happened when the ionic and the organic molecular liquids were mixed. Negative values of excess molar volumes can also be ascribed to the large differences in molar volume between the ionic liquid and ACN or THF molecules. For example, at 293.15 K, the molar volumes are 596.85, 52.48, and

81.25  $\text{cm}^3 \cdot \text{mol}^{-1}$  for pure [THTDP][Br], ACN, and THF, respectively. These large differences between the molar volumes of [THTDP][Br] and ACN or THF suggest a high probability for the relatively small organic molecules of ACN or THF to fit into the interstices of the ionic liquid upon mixing. Therefore, the filling effect of organic molecular liquids in the interstices of the ionic liquid and the ion-dipole interactions between organic molecular liquid and the ionic liquid contributed to the negative values of excess molar volumes [28,29].

A Redlich-Kister-type equation was used to fit the excess molar volumes [30]. This equation can be expressed as a generalized equation as follows:



$$V^E = x_1(1 - x_1) \sum_{i=0}^{i=n} A_i(2x_1 - 1)^i, \tag{5}$$

where  $A_i$  is an adjustable parameter,  $x_1$  denotes the mole fraction of the ionic liquid [THTDP][Br], and  $n$  is the order of the expansion. The order of the expansion used in this work was determined by fitting the excess molar volumes for different values of  $n$  ( $n = 0, 1, 2$ , and  $3$ ). Because of the asymmetric shape of the parabolic curves of  $V^E$  as a function of  $x_1$ , as depicted in Figures 5, 6, the use of expansions of  $n = 0$  and  $1$  for one- and two-parameter equations, respectively, failed to represent the excess molar volumes accurately. Using expansions of  $n = 2$  and  $3$ , three- and four-parameter equations, respectively, represented the excess molar volumes with almost the same accuracy; therefore, parameters  $A_0, A_1$ , and  $A_2$  for the expansion of  $n = 2$  are reported in Table 6 along with the standard deviation of the fits ( $\sigma$ ). Solid lines in Figures 5, 6 represent values obtained using the Redlich–Kister equation.

The ERAS model was applied for modeling the excess molar volumes reported in this study at 298.15 K [31–36]. Only data at 298.15 K were modeled due to some restrictions in isothermal compressibility availability. Parameters of the model are reported in

Tables 7, 8. Physical and chemical contributions are plotted in Figures 7A, B for both systems. Chemical contributions have higher magnitude than physical contributions for both systems, and for the [THTDP][Br] + THF system, these contributions have higher magnitude than those for the [THTDP][Br] + ACN system (Figure 7).

Partial molar volumes ( $\bar{V}_1$  and  $\bar{V}_2$ ) were calculated using the Redlich equation with the parameters reported in Table 6, in accordance with the following equations:

$$\bar{V}_1 = V^E + V_1 + (1 - x_1) \left( \frac{dV^E}{dx_1} \right)_{T,p}, \tag{6}$$

$$\bar{V}_2 = V^E + V_2 - x_1 \left( \frac{dV^E}{dx_1} \right)_{T,p}, \tag{7}$$

by differentiation of  $V^E$  (Eq. 5) with respect to  $x_1$ , and using Eqs 6, 7, the following expressions are obtained:

$$\begin{aligned} \bar{V}_1 = & V_1 \\ & + (1 - x_1)^2 \sum_{i=0}^{i=n} A_i(2x_1 - 1)^i + 2x_1(1 - x_1)^2 \sum_{i=0}^{i=n} (i)A_i(2x_1 - 1)^{i-1}, \end{aligned} \tag{8}$$

**TABLE 9** Partial molar volumes ( $\bar{V}_1$  and  $\bar{V}_2$ ) of the binary systems trihexyl(tetradecyl)phosphonium bromide ([THTDP][Br]) + acetonitrile (ACN) (2) and [THTDP][Br] (1) + tetrahydrofuran (THF) (2) in the temperature interval of 293.15–313.15 K at  $p = 0.78$  bar and at different mole fractions of [THTDP][Br] ( $x_1$ ).

$x_1$	$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K	
	$\frac{\bar{V}_1}{\text{cm}^3 \cdot \text{mol}^{-1}}$	$\frac{\bar{V}_2}{\text{cm}^3 \cdot \text{mol}^{-1}}$								
[THTDP][Br] (1) + ACN (2)										
0.0000	596.13	52.49	597.76	52.85	599.44	53.22	601.00	53.60	602.60	53.99
0.0433	596.23	52.49	597.97	52.85	599.72	53.22	601.37	53.61	603.40	53.99
0.0941	596.28	52.48	598.10	52.85	599.92	53.22	601.65	53.60	603.68	53.99
0.1499	596.27	52.46	598.15	52.83	600.02	53.20	601.81	53.59	603.85	53.98
0.1926	596.22	52.42	598.13	52.80	600.03	53.17	601.87	53.56	603.90	53.95
0.2215	596.18	52.39	598.11	52.77	600.02	53.14	601.88	53.53	603.91	53.92
0.2982	596.07	52.26	598.00	52.64	599.95	53.01	601.83	53.39	603.87	53.78
0.4217	595.93	51.89	597.84	52.25	599.81	52.61	601.71	52.96	603.75	53.35
0.4521	595.92	51.77	597.82	52.11	599.79	52.47	601.70	52.81	603.73	53.20
0.5215	595.93	51.43	597.81	51.75	599.79	52.08	601.70	52.40	603.73	52.79
0.6978	596.21	50.25	598.08	50.45	600.07	50.72	601.99	50.95	604.02	51.33
0.7916	596.46	49.45	598.35	49.56	600.35	49.80	602.28	49.95	604.31	50.34
1.0000	596.86	47.42	598.79	47.33	600.80	47.46	602.75	47.45	604.79	47.84
[THTDP][Br] (1) + THF (2)										
0.0000	597.60	46.25	599.25	46.54	600.64	46.84	602.26	47.15	603.84	47.46
0.0500	596.67	46.23	598.42	46.52	600.02	46.82	601.73	47.13	603.49	47.45
0.1000	595.94	46.17	597.75	46.46	599.51	46.77	601.29	47.07	603.17	47.40
0.1499	595.39	46.06	597.25	46.36	599.11	46.67	600.93	46.98	602.89	47.31
0.2000	595.00	45.92	596.88	46.22	598.81	46.53	600.66	46.84	602.66	47.18
0.2472	594.76	45.76	596.65	46.05	598.61	46.37	600.48	46.67	602.49	47.00
0.2975	594.62	45.54	596.52	45.83	598.50	46.15	600.37	46.44	602.37	46.77
0.4052	594.66	44.97	596.54	45.24	598.51	45.53	600.38	45.79	602.34	46.07
0.5068	594.98	44.30	596.85	44.52	598.79	44.75	600.65	44.96	602.56	45.15
0.6075	595.46	43.50	597.32	43.66	599.24	43.79	601.11	43.93	603.00	43.98
0.7211	596.04	42.45	597.92	42.51	599.84	42.48	601.73	42.52	603.64	42.38
0.8423	596.56	41.13	598.47	41.07	600.43	40.84	602.35	40.75	604.33	40.35
1.0000	596.86	39.07	598.79	38.84	600.80	38.36	602.75	38.07	604.79	37.32

$$\bar{V}_2 = V_2 + x_1^2 \sum_{i=0}^{i=n} A_i (2x_1 - 1)^i + 2x_1^2 (1 - x_1) \sum_{i=0}^{i=n} (i) A_i (2x_1 - 1)^{i-1}. \tag{9}$$

Partial molar volumes of the two binary systems studied are reported in Table 9 and plotted as a function of the mole fraction of the ionic liquid in Figures 8A, B for the [THTDP][Br] (1) + ACN (2) system and in Figures 8C, D for the [THTDP][Br] (1) + THF (2) system. These plots show that  $\bar{V}_1$  values did not change significantly, reflecting the influence of the denser ionic liquid.  $\bar{V}_2$  decreases continuously with the increase in the mole fraction of the ionic liquid. Both partial

molar volumes change consistently within the temperature range.

### 4 Conclusion

Densities of two binary systems formed using the ionic liquid trihexyl(tetradecyl)phosphonium bromide mixed with acetonitrile or tetrahydrofuran in the temperature interval of 293.15 to 313.15 K, covering the whole composition interval. Excess molar volumes were calculated from the experimental densities and fitted to a Redlich–Kister equation expansion using

three parameters. Excess molar volumes had negative deviations from ideality and became more negative as the temperature increased. These negative values can be ascribed to different effects: a more effective arrangement and/or attractive interactions, the filling effect of organic molecular liquids in the interstices of the ionic liquid, and the ion–dipole interactions between organic molecular liquid and the ionic liquid. The ERAS model was applied to model the excess molar volumes. The results imply that chemical contributions have higher magnitude than physical contributions

## Data availability statement

The original contributions presented in the study are included in the article/supplementary material; further inquiries can be directed to the corresponding author.

## Author contributions

LC-C and SG-A: methodology, experiment, and validation; RG-M: data analysis and processing, preparation of relevant diagrams, and resources; AZ-M and OE-S: writing—review and editing; AZ-M: funding acquisition, project administration, and supervision; FV-S: review, editing and modeling. All authors contributed to the article and approved the submitted version.

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## Funding

This research was supported by Instituto Politécnico Nacional (IPN) and the National Council of Science and Technology (CONACyT) of Mexico under grant project numbers 20140947 and 83458, respectively.

## Acknowledgments

All authors acknowledge financial support from Instituto Politécnico Nacional (IPN) and the National Council of Science and Technology (CONACyT) of Mexico.

## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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