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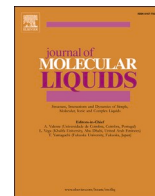
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## Insights on the solvation of toluene by deep eutectic solvents

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### ABSTRACT

Thermodynamic properties including excess volumes, viscosities and excess Gibbs activation energies of viscous flow were measured for two deep eutectic solvents (DESS) mixed with toluene over the entire composition range. Two DESSs were formed by combining tetrabutylphosphonium bromide and levulinic acid (TBPBr:Lev) or tetrabutylammonium bromide and decanoic acid (TBABr:Dec). The DESSs were assumed to behave as a pseudo-pure component. The excess volumes values for TBABr:Dec, were negative throughout the composition range, whereas TBPBr:Lev showed negative values only for DES mole fractions higher than 0.2. The excess Gibbs energies of activation of viscous flow were found to be positive for the TBABr:Dec, and changing from positive to negative for TBPBr:Lev around 0.4 mol fraction. These values remain smaller than RT, the energy of the thermal motion of the components of the mixture. Deviations from the averaged viscosity of the pure components were negative for both mixtures across all compositions. The analysis of the IR and FT-Raman spectra showed minimal influence of the mixture composition on vibration modes. Quantum calculations were used to assign the vibration modes. Our results suggest that the variation in thermodynamic data with composition arises from the packing arrangement of the mixture components.

### 1. Introduction

Deep eutectic solvents (DESSs) are a new generation of green solvents that can be prepared as mixtures of a variety of compounds. These solvents are being weighed up as new solvents for the chemical industry covering a wide range of applications: electrochemistry, electrodeposition, catalysis, reaction media, extraction, absorption of gas and volatile organic compounds and even for the food and pharmaceutical industries [1]. The definition of DES is still controversial, but for an eutectic mixture to be classified as “Deep”, its eutectic temperature should be significantly lower [2] than that of the ideal liquid mixture [3]. The compounds leading to the formation of DES belong to different chemical families such as salts, metal halides, alcohols, carboxylic acids, amino acids, sugars... Therefore, DESSs can be described as designer solvents since specific properties can be achieved based on the choice of the compounds and their relative concentrations in the mixture [4].

The first published DES [5] and the most studied so far is the one based on choline chloride (ChCl) and urea (U) at the molar ratio (1:2) along with its aqueous solutions. The excess properties of ChCl:U/water mixtures were determined under different conditions of temperature

[6–9] and pressure [10]. The effect of organic solvents, with a major focus on the dilution of ChCl:U in methanol [11], ethanol [12] and dimethyl sulfoxide [13], ChCl:glycerol in methanol [14,15], ethanol and *iso*-propanol [15] and ChCl:ethylene glycol in methanol [14,16], ethanol [17] and dimethyl sulfoxide [18] was also investigated. Moreover, Gajardo-Parra *et al.* studied the physicochemical properties of DESSs formed by ChCl and either levulinic acid, ethylene glycol or phenol at a 1:2 M ratio. In the same study, the effect of the addition of 1-butanol as a third component to the DES was followed through the mixtures' density, viscosity and excess properties measurements [19]. For all the above systems, the excess molar volume values were found to be negative, but with a clear discrepancy when comparing the magnitude of the values and the behaviour with the temperature between water and organic solvents. Comparing the deviation when water is added to the DES, the values of the excess molar volumes are small and decrease (less negative) as the temperature increases. In contrast, the excess molar volume values are much larger and show more negative values with temperature when the organic solvents are added.

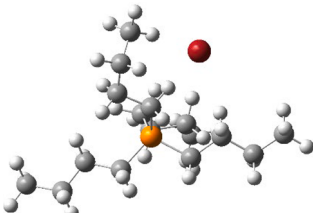
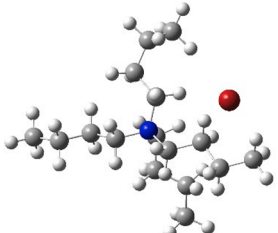
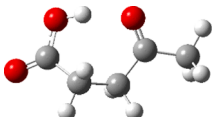
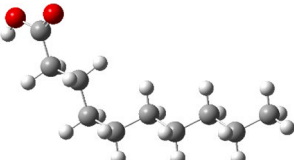
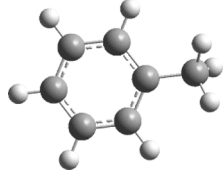
These literature data point towards the influence of the intermolecular interactions between the components forming the eutectic mixtures

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**Table 1**  
List of chemicals used in the study, their purities and suppliers.

Chemical	CAS	M/(g.mol <sup>-1</sup> )	Supplier	Purity
 Tetrabutylphosphonium bromide (TBPBr)	3115-68-2	339.33	Aldrich	98 %
 Tetrabutylammonium bromide (TBABr)	1643-19-2	322.37	Acros Organics	>99 %
 Levulinic acid (Lev)	123-76-2	116.12	Aldrich	98 %
 Decanoic acid (Dec)	334-48-5	172.26	Acros Organics	99 %
 Toluene (Tol)	108-88-3	92.14	Carlo Erba	>99.8 %

on their physical properties, and thus, on their future applications. More interestingly, these literature data also clearly indicate those interactions are altered by the addition of conventional solvents. Recently, Trenzado *et al.* studied experimentally and through molecular modelling the solubilization of toluene in cineole-based NADES, which is explained by effective intermolecular interactions and fitting of toluene in the solvent [20]. The measurements of the physicochemical properties of the ternary mixtures (the two components forming the DES and a third component, *i.e.* an organic solvent or water) allow to access their volumetric and thermodynamic properties. Since the latter can be related to the intermolecular interactions between the components of the mixture, studying the ternary mixture contributes to a better understanding of the different types of interactions that govern their microscopic structure and macroscopic properties.

In a previous study, we evaluated a series of DESs for their ability to absorb and solubilize volatile organic compounds (VOCs), such as toluene [21,22]. We have shown that the tested DESs decrease the vapour/liquid partition coefficient of VOCs, indicating that they are

good absorbents. Moreover, the DESs could be easily regenerated, underling a potential physical absorption of the VOCs. Herein, we investigated the effect of toluene on the properties of two different DESs formed either by tetrabutylphosphonium bromide (TBPBr) and levulinic acid (Lev) at 1:6 M ratio or by tetrabutylammonium bromide (TBABr) and decanoic acid (Dec) at 1:2 M ratio with the aim of a better understanding of the solubilisation process of toluene. These DESs have already been reported in the literature [23,24]. TBPBr:Lev is considered a hydrophilic DES due to its miscibility with water, while TBABr:Dec is the first described hydrophobic, water immiscible DES. In this work, we measured the density and viscosity of these two DESs mixed with toluene over the entire compositional range at temperatures from 288.15 to 303.15 K. The temperature dependency of both the density and the viscosity were correlated by a linear fit or by a Vogel-Fulcher-Tammann (VFT) equation, respectively. The excess molar and partial molar volumes, viscosity deviations and excess molar Gibbs energy of activation for viscous flow were calculated and fitted with Redlich-Kister polynomial fits. In order to get information on the nature of the

**Table 2**

Mole ratio, composition, molar mass ( $M$ ) and water content of the DESs used in this work.

DES (Salt:HBD)	Mole ratio (Salt:HBD)	Mole fraction of HBD ( $x_{HBD}$ )	$M/(g \cdot mol^{-1})$	Water content (wt%)
TBPBr:Lev	1:6.001	0.8572	148.00	0.43
TBABr:Dec	1:2.000	0.6667	222.29	0.14

interactions between the components of the mixture, a spectroscopic study by infrared (IR) and Fourier transform Raman spectroscopy (FT-Raman) was performed on the DES/toluene over the entire mixture composition.

## 2. Experimental

### 2.1. Materials

All the chemicals used in this study are listed in Table 1. The chemicals were used without any further purification.

### 2.2. Preparation of DESs and DES/toluene mixtures

DESs were prepared gravimetrically using an analytic balance Ohaus, Switzerland. The balance was calibrated before the preparation of the DESs and the mixtures, to ensure a precision of  $10^{-4}$  g. After weighing the salt and the hydrogen bond donor (HBD) into a round-bottomed flask, the content of the flask was kept under stirring, at room temperature, until the formation of the liquid mixture. No heat was used in the preparation of the DES in order to prevent any undesirable chemical reaction or product degradation. The water content of the prepared DESs was determined using a coulometric Karl Fisher titrator (Mettler Toledo C20S). The composition and water content of DESs are listed in Table 2. Mixtures of DES and toluene (DES/toluene) were also prepared gravimetrically. Each sample was prepared by weighing the DES first followed by the toluene, and ensuring that the mixture occupied the volume available in the vial to prevent any composition errors due to differential evaporation. All the samples were directly weighed and sealed in septum-capped vials to prevent any contact with atmosphere.

DESs are by definition a mixture [25], so the molar mass is calculated from the concentration of the DES components in mole fraction:

$$M_{DES} = x_{salt} \cdot M_{salt} + x_{HBD} \cdot M_{HBD} \quad (1)$$

where  $M$  and  $x$  are the molar mass and the mole fraction for each component, respectively.

The mixtures of DESs and toluene are ternary systems with a precise

cut in the ternary phase diagram at the DES composition 1:6 and 1:2 for TBPBr:Lev and TBABr:Dec, respectively. Therefore, it is appropriate to represent the composition of the DES/toluene mixture along this cut with the fixed DES mole fraction and thus considered as a pseudo-binary mixture. Subsequently, the mole fraction of the DES can be calculated as follows:

$$x_{DES} = \frac{m_{DES}/M_{DES}}{m_{DES}/M_{DES} + m_{toluene}/M_{toluene}} \quad (2)$$

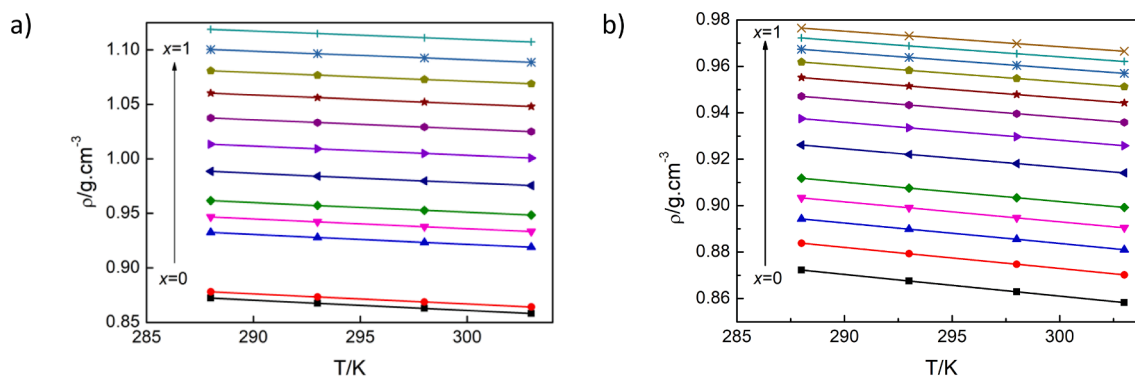
The mixtures TBABr:Dec/toluene are miscible in all compositions tested at temperatures ranging from 288.15 K to 333.15 K, whereas, the mixtures TBPBr:Lev/toluene showed partial immiscibility at  $x_{DES}$  of 0.05, 0.10 and 0.15 at 288.15 K. By progressively increasing the temperature, to 333.15 K, the system TBPBr:Lev/toluene becomes miscible in the whole composition range.

### 2.3. Density and viscosity measurements

Density and viscosity measurements were carried out on a U-shaped vibrating-tube densimeter (Anton Paar, model SVN 3001) operating in static mode. All measurements were performed at atmospheric pressure and temperatures ranging between 288.15 and 303.15 K. Factory calibration was used and checks were performed before and after each measurement with air and deionized water. A check of the densimeter was carried out before each set of measurements, using the oil of standard viscosity (APS3, APN7.5, APN26 and APN415), covering the whole range of viscosities measured. The SVM 3001 performs an analysis with an estimated uncertainty in density and temperature of  $\pm 0.1 \text{ kg m}^{-3}$  and  $\pm 0.001 \text{ }^\circ\text{C}$ , respectively. The device has a built-in correction for liquids with a viscosity higher than 700 mPa s, as in the present case.

### 2.4. Vibration spectroscopy and quantum calculations

Vibration spectroscopy (both IR and Raman) has been proven to be an efficient tool for investigating the interactions between the components of the mixture through the changes in the shape of specific vibration modes (changes of frequency, intensity and peak width). These interactions and then their contribution to the vibration spectra are modulated by the change of the mixture and allow in principle to get information on the local environment of atoms involved in these vibration modes. The mixtures compositions are the same as those used for the thermodynamic analysis. We recorded the ATR-FTIR spectra of the mixtures using a BRUKER Vertex 70 FT-IR instrument. In every case, 64 spectra were averaged from scans made between 4000 and 400  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ . FT-Raman spectra were recorded with a Bruker IFS 66 V spectrometer. Radiation of 1064 nm from a Nd:YAG laser was used for the excitation with a laser power of 1040 mW. The spectral resolution was set to 4  $\text{cm}^{-1}$ , with a number of scans equal to 1000. Furthermore, in order to have a clear assignment of the IR and FT-



**Fig. 1.** Density of (a) TBPBr:Lev/toluene and (b) TBABr:Dec/toluene mixture as function of temperature, at different DES' mole fractions (Error < 1%).

**Table 3**

Densities of TBPBr:Lev/toluene and TBABr:Dec/toluene mixtures as function of temperature at 0.1 MPa.

$x_{DES}$	$\rho/\text{g}\cdot\text{cm}^{-3}$			
	288.15 K	293.15 K	298.15 K	303.15 K
TBPBr:Lev/toluene				
0.0000	0.8723	0.8676	0.8629	0.8582
0.0200	0.8781	0.8734	0.8688	0.8642
0.1999	0.9325	0.9279	0.9234	0.9190
0.2489	0.9467	0.9422	0.9377	0.9333
0.3001	0.9617	0.9572	0.9528	0.9484
0.4000	0.9886	0.9842	0.9799	0.9756
0.4988	1.0135	1.0092	1.0050	1.0008
0.5995	1.0375	1.0333	1.0292	1.0251
0.6997	1.0603	1.0562	1.0521	1.0481
0.8004	1.0808	1.0768	1.0729	1.0689
0.8996	1.1003	1.0964	1.0925	1.0887
1.0000	1.1188	1.1149	1.1111	1.1073
TBABr:Dec/toluene				
0.0000	0.8723	0.8676	0.8629	0.8582
0.0498	0.8838	0.8793	0.8748	0.8702
0.0999	0.8943	0.8899	0.8855	0.8811
0.1500	0.9033	0.8990	0.8947	0.8904
0.1998	0.9118	0.9076	0.9034	0.8992
0.3001	0.9262	0.9221	0.9181	0.9141
0.4000	0.9375	0.9336	0.9297	0.9259
0.5004	0.9471	0.9434	0.9396	0.9359
0.6001	0.9552	0.9515	0.9479	0.9443
0.7000	0.9619	0.9583	0.9548	0.9513
0.7999	0.9673	0.9639	0.9604	0.9570
0.8993	0.9723	0.9688	0.9655	0.9621
1.0000	0.9765	0.9731	0.9698	0.9665

Raman spectra of the pure components, we carried out quantum calculations. As dispersion plays an important role in describing the interionic and ions with the molecular components (Lev, Dec and Tol) interactions, we used the M06-2X functional to better take into account the medium-range dispersion effect. This functional was coupled with 6-311 + g(d,p) basis set [26]. The geometry optimizations were followed by harmonic frequency analysis to ensure that the obtained structure was true minima by the absence of imaginary wavenumber and to rationalize the experimental results in terms of the obtained optimized configurations (see Figure 1). Density functional theory calculation was conducted using the Gaussian 16 software package [27]. Visualization was performed with Gaussview 6.

### 3. Results and discussion

#### 3.1. Volumetric properties

The density of the two pseudo-binary mixtures (TBPBr:Lev/toluene and TBABr:Dec/toluene) was measured at different temperatures and

over all the composition range. The experimental values are reported in Table 3. The density variation for the two systems with the temperature at different molar compositions is illustrated in figure 1. For the pure DES and their mixtures, the densities decrease linearly with the increase of the temperature. This is a common behavior found in both DES [28] and ionic liquids (ILs) [29], as the thermal expansion accompanies the increase of temperature and the mixture becomes less dense. The values were adjusted to appropriate polynomial functions. The parameters of the fits are listed in Table S1 of the Supporting Information (SI). With a density of  $1.1188 \text{ g}\cdot\text{cm}^{-3}$  TBPBr:Lev is more dense than TBABr:Dec with a density of  $0.9765 \text{ g}\cdot\text{cm}^{-3}$  at 288.15 K. As expected, increasing the mole fraction of toluene led to a decrease in the density of the mixture, as shown in figure S1 of the SI.

In order to investigate the nonideality of the solutions, the excess molar volume of the mixture ( $V^E$ ) was calculated using the following equation:

$$V^E = \frac{x_{DES} \cdot M_{DES} + x_{Tol} \cdot M_{Tol}}{\rho} - \left( \frac{x_{DES} \cdot M_{DES}}{\rho_{DES}} + \frac{x_{Tol} \cdot M_{Tol}}{\rho_{Tol}} \right) \quad (3)$$

where  $\rho$ ,  $\rho_{DES}$  and  $\rho_{Tol}$  are the densities of the mixture, the DES and the pure toluene, respectively.

The calculated  $V^E$  values were fitted as function of the mixture's composition using a Redlich-Kister (RK) polynomial equation (4) at each temperature. The fit parameters for each system are regrouped in Table S2 of the SI.

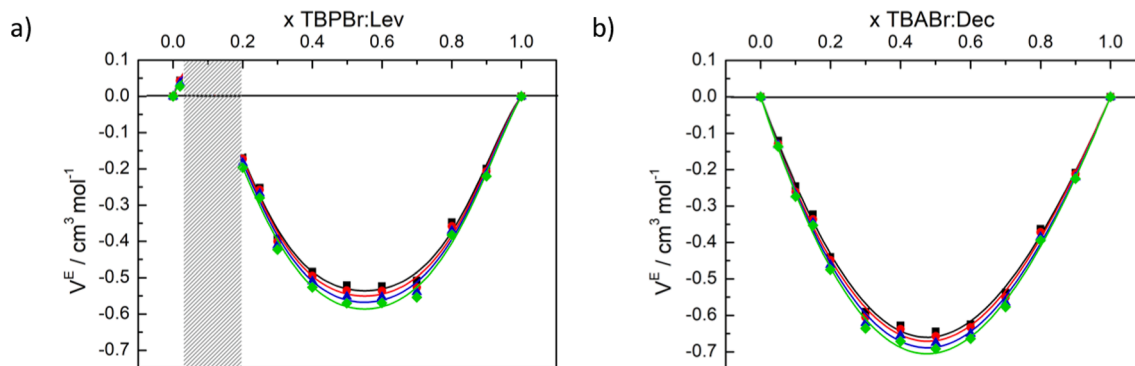
$$V^E = x_{DES} x_{Tol} \sum_{j=0}^k A_j (x_{DES} - x_{Tol})^j \quad (4)$$

where  $A_j$  is the RK polynomial coefficient and the  $k$  is the order of the polynomial fit, which was set to be 4 for the system TBPBr:Lev/toluene and 3 for TBABr:Dec/toluene, to ensure the best fit.

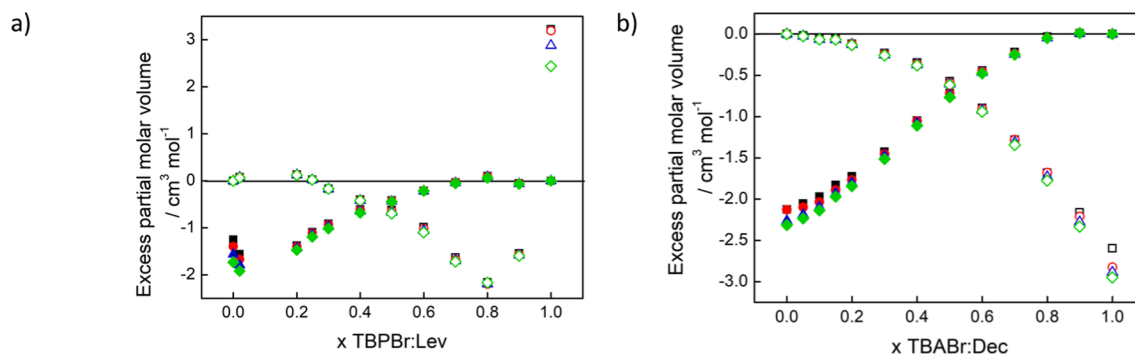
The  $V^E$  at the different compositions are presented in Fig. 2 at the temperatures studied. As seen for TBPBr:Lev/toluene,  $V^E$  follows a sinusoidal (S-shape) variation with respect to the mole fraction of the DES. At a low mole fraction of TBPBr:Lev ( $x_{DES} = 0.02$ ), the system shows a slight positive  $V^E$ . Between  $0.02 < x_{DES} < 0.2$  TBPBr:Lev/toluene forms a heterogeneous mixture at 288.15 K. Above a TBPBr:Lev mole fraction of 0.2, the DES is miscible with toluene from 288.15 K and shows a negative  $V^E$  with the largest negative value of  $-0.54 \text{ cm}^3 \text{ mol}^{-1}$  at  $x_{DES} \approx 0.5$  at 288.15 K.

For the mixture TBABr:Dec/toluene,  $V^E$  are negative over the whole concentration range. Similar trends for the  $V^E$  were found in other DES/liquid mixtures reported in the literature [15,16]. The minimum value of  $V^E$  was  $-0.66 \text{ cm}^3 \text{ mol}^{-1}$  at 288.15 K, representing a maximum deviation from the ideality at  $x_{DES} \approx 0.5$  and leading to a quasi-symmetric curve with composition.

The negative values of  $V^E$  can result from numerous contributions



**Fig. 2.** Excess molar volume of (a) TBPBr:Lev/toluene and (b) TBABr:Dec/toluene mixture as a function of  $x_{DES}$ , (the lines correspond to RK fits). The grey area delimits the range of immiscibility observed at these temperatures for the TBPBr:Lev/toluene system. ■, 288 K; ●, 293 K; ▲, 298 K; ◆, 303 K.



**Fig. 3.** Variation of the excess partial molar volumes of DES and toluene; (a)TBPBr:Lev and (b)TBABr:Dec; as a function of  $x_{DES}$  at different temperatures.  $\square$ , Toluene 288 K;  $\circ$ , Toluene 293 K;  $\triangle$ , Toluene 298 K;  $\diamond$ , Toluene 303 K; (b)  $\blacksquare$ , DES 288 K;  $\bullet$ , DES 293 K;  $\blacktriangle$ , DES 298 K;  $\blacklozenge$ , DES 303 K.

that can involve specific interactions such as strong H-bonding or strong dipole–dipole interactions between the components of the mixture (or between toluene and at least one component of the DES). These different contributions can lead to volume contraction and therefore negative  $V^E$  values. On the other hand, negative values of  $V^E$  can simply be due to an efficient structural packing of the constituents of the mixture.

Besides  $V^E$ , we have calculated the partial molar volumes,  $\bar{V}_i$ , and the excess partial molar volumes,  $\bar{V}_i^E$  for the components of the mixture:

$$\bar{V}_{DES} = V^E + V_{DES} + (1 - x_{DES}) \left( \frac{\partial V^E}{\partial x_{DES}} \right)_{T,p} \quad (5)$$

$$\bar{V}_{Tol} = V^E + V_{Tol} - x_{DES} \left( \frac{\partial V^E}{\partial x_{DES}} \right)_{T,p} \quad (6)$$

where  $V_{DES}$  and  $V_{Tol}$  are the pure molar volumes of DES and toluene, respectively.

Then, the values of the excess partial volumes are calculated using Eq. (7) at each temperature.

$$\bar{V}_i^E = \bar{V}_i - V_i \quad (7)$$

To obtain the partial molar volumes for the DES and toluene at infinite dilution in the mixture, we use Eqs. (5) and (6) with the composition of each species tending to zero at each temperature,

$$\bar{V}_i^\infty = V^E + \left( \frac{\partial V^E}{\partial x_i} \right)_{T,p,x_i \rightarrow 0} \quad (8)$$

where  $\bar{V}_i^\infty$  is the partial molar volumes of DES and toluene at infinite dilution, respectively.

Then, the excess partial molar volumes for DES and toluene at infinite dilution,  $\bar{V}_i^{E,\infty}$  of each component at each temperature could be calculated using Eq. (9)

$$\bar{V}_i^{E,\infty} = \bar{V}_i^\infty - V_i \quad (9)$$

The excess partial molar volumes for each species of the two mixtures are presented in Fig. 3 and the values are summarized in tables S3 and S4 in SI for TBPBr:Lev/toluene and TBABr:Dec/toluene, respectively.

As illustrated in Fig. 3, the TBPBr:Lev/toluene mixture shows some positive and negative excess partial molar volumes, while TBABr:Dec/toluene shows only negative ones. Negative values of excess partial molar volume suggest that the molar volume of each component in the mixture is lower than its pure molar volume. The negative values of excess partial molar volume and their decrease with increasing temperature are similar to those obtained for excess molar volumes.

Further insight was gained by examining the excess partial molar volumes at infinite dilution. For TBPBr:Lev/toluene (Table 4 and Fig. 3a), they were shown to be positive for toluene ( $x_{TBPBr:Lev} \rightarrow 1$ ), indicating that toluene prefers not to be solvated by the DES. To the best of our knowledge, this is the first time that this behavior has been reported for a mixture of DES and solvent. These values are consistent with the observation of partial miscibility and positive values of  $V^E$  encountered at low concentrations of toluene. Moreover, the decrease of these values with the increase of the temperature shows that the increase of the temperature favors the solubilization of the toluene. On the other hand, the DES has a negative value of the excess partial molar volumes at infinite dilution ( $x_{TBPBr:Lev} \rightarrow 0$ ), showing the tendency of the DES to be solvated by toluene. For TBABr:Dec/toluene (Table 4 and Fig. 3b), the excess partial molar volume values at infinite dilution are all negative. This suggests that DES-toluene interactions are much stronger than DES-DES or toluene-toluene interactions. These results point towards different toluene solvation mechanisms in the two studied DES.

### 3.2. Dynamic properties

The viscosities of the two mixtures (TBPBr:Lev/toluene and TBABr:Dec/toluene) were measured at different temperatures and over the whole range of compositions (Table 5). The viscosity values of the different mixtures were fitted to Vogel-Fulcher-Tammann (VFT) equations with parameters given in Table S5 of SI. For both systems, the viscosity decreased with increasing temperature and the toluene content as represented in Fig. 4. We observe that the effect of increasing the temperature by 10 K for the pure DES is the same as adding 6.5 wt% or 4.4 wt% of toluene (corresponding to  $x_{tol} \simeq 0.1$ ) in TBPBr:Lev or TBABr:Dec, respectively.

The deviations of the viscosity  $\Delta\eta$  from the averaged values at each composition of the DES and pure toluene were calculated as:

$$\Delta\eta = \eta - (x_{DES}\eta_{DES} - x_{Tol}\eta_{Tol}) \quad (10)$$

where  $\eta$ ,  $\eta_{DES}$  and  $\eta_{Tol}$  are the viscosities of the mixture, the pure DES and toluene, respectively.

**Table 4**

Values of pure molar volumes, partial molar volumes and excess partial molar volumes at infinite dilution of DES and toluene for the DES/toluene mixtures as a function of temperature at 0.1 MPa.

T/K	$V_{DES}$	$\bar{V}_{DES}^\infty$	$\bar{V}_{DES}^{E,\infty}$	$V_{Tol}$	$\bar{V}_{Tol}^\infty$	$\bar{V}_{Tol}^{E,\infty}$
TBPBr:Lev/toluene						
288.15	132.291	131.040	-1.251	105.631	108.853	3.222
293.15	132.751	131.355	-1.396	106.205	109.397	3.192
298.15	133.207	131.644	-1.563	106.778	109.657	2.879
303.15	133.664	131.931	-1.733	107.359	109.797	2.437
TBABr:Dec/toluene						
288.15	227.658	225.532	-2.126	105.631	103.036	-2.595
293.15	228.442	226.314	-2.128	106.205	103.381	-2.824
298.15	229.224	226.961	-2.263	106.778	103.892	-2.886
303.15	230.006	227.692	-2.315	107.359	104.412	-2.948

**Table 5**

Viscosities of TBPBr:Lev/toluene and TBABr:Dec/toluene mixtures as a function of temperature at 0.1 MPa.

$x_{DES}$	$\eta$ / mPa.s			
	288.15 K	293.15 K	298.15 K	303.15 K
TBPBr:Lev/toluene				
0.0000	0.495	0.468	0.443	0.419
0.0200	0.558	0.525	0.496	0.470
0.1999	1.957	1.710	1.521	1.372
0.2489	2.328	2.082	1.870	1.692
0.3001	2.936	2.609	2.332	2.097
0.4000	4.751	4.142	3.637	3.217
0.4988	7.792	6.635	5.701	4.946
0.5995	13.31	11.02	9.226	7.823
0.6997	23.65	18.95	15.41	12.72
0.8004	42.61	32.70	25.90	20.75
0.8996	78.39	57.87	44.30	34.42
1.0000	144.5	103.0	76.21	57.42
TBABr:Dec/toluene				
0.0000	0.495	0.468	0.443	0.419
0.0498	1.245	1.132	1.035	0.951
0.0999	2.319	2.079	1.875	1.702
0.1500	3.493	3.108	2.777	2.497
0.1998	5.029	4.442	3.945	3.520
0.3001	9.671	8.358	7.267	6.365
0.4000	18.05	15.18	12.87	11.00
0.5004	34.19	27.73	23.00	19.17
0.6001	65.10	51.20	41.26	33.46
0.7000	122.0	92.69	72.47	57.15
0.7999	226.2	166.9	126.8	97.33
0.8993	416.8	299.8	219.7	164.0
1.0000	744.9	521.1	371.2	270.4

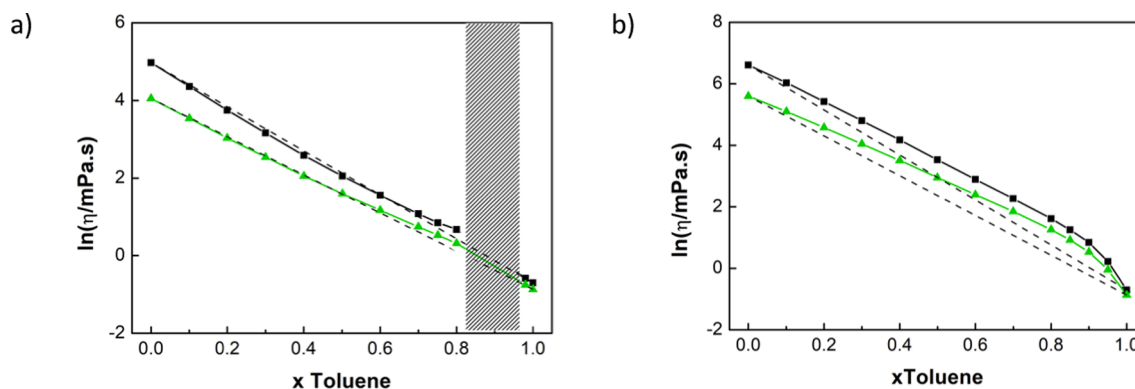
The calculated  $\Delta\eta$  values are shown in Fig. 5 and the fitting parameters are gathered in Table S6 in SI. These values are negative throughout the composition and temperature ranges studied. The absolute values of  $\Delta\eta$  decrease with increasing temperature. The absolute maximum  $\Delta\eta$  values (most negative) appear at  $x_{DES} = 0.7$  for both systems implying that toluene has a greater effect on the viscosity in this region compared to that in toluene-rich compositions. At  $t = 288.15$  K, the maximum absolute value of  $\Delta\eta$  for TBABr:Dec/toluene was 5 times higher than for TBPBr:Lev/toluene, which may be simply due to the difference in viscosities of the pure DES (TBABr:Dec is 5 times more viscous than TBPBr:Lev).

The excess Gibbs free energy of activation of the viscous flow ( $\Delta G^{*E}$ ) was calculated using Eyring's absolute rate theory [30]:

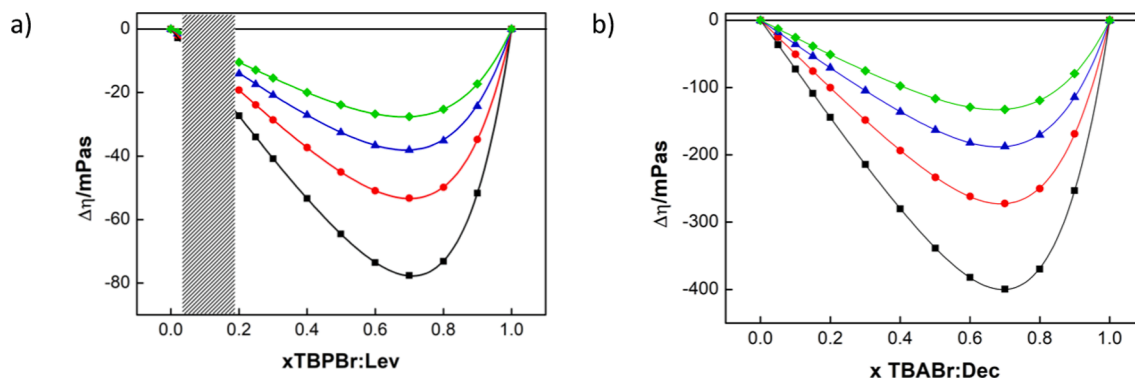
$$\Delta G^{*E} = RT[\ln(\eta V) - x_{DES}\ln(\eta_{DES}V_{DES}) - x_{Tol}\ln(\eta_{Tol}V_{Tol})] \quad (11)$$

where  $R$  is the gas constant,  $T$  is the temperature,  $\eta$ ,  $\eta_{DES}$  and  $\eta_{Tol}$  are the viscosities of the DES/toluene mixture, the pure DES and toluene, respectively.  $V$ ,  $V_{DES}$  and  $V_{Tol}$  are the molar volumes of the DES/toluene mixture, the pure DES and toluene, respectively.

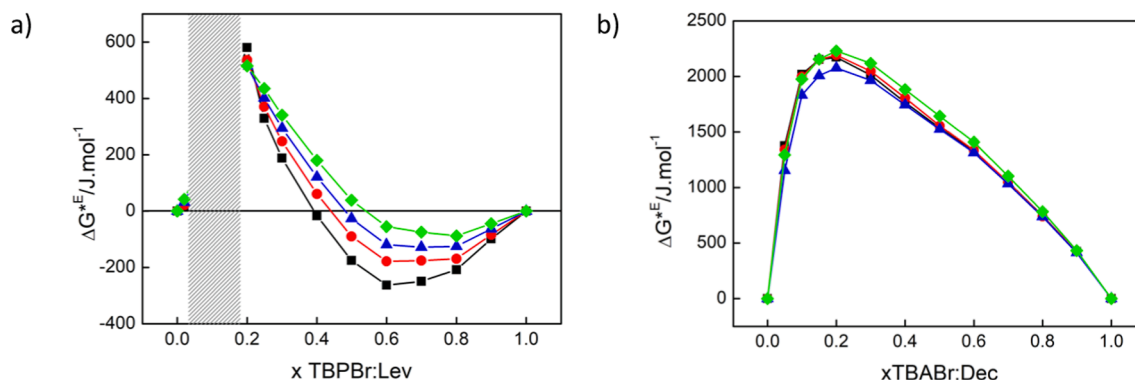
The  $\Delta G^{*E}$  are listed in Table S7 in the SI, and shown in Fig. 6. Positive  $\Delta G^{*E}$  values are usually attributed to the existence of strong interactions, as mentioned in the literature [7,14,31,32]. As shown in Fig. 6, the values of  $\Delta G^{*E}$  TBABr:Dec/toluene are positive in the whole mixture composition while they are negative only in the range  $x_{DES}$  between 1 and 0.2 for the TBPBr:Lev/toluene mixtures. The obtained values of  $\Delta G^{*E}$  are rather small, being always clearly smaller than  $RT$ , the energy of the thermal motion of the components of the mixture (*i.e.* 2.5 kJ. mol<sup>-1</sup>).



**Fig. 4.** Logarithm of viscosity of (a) TBPBr:Lev/toluene and (b) TBABr:Dec/toluene mixtures as a function of toluene molar fraction, at two temperatures. The grey area delimits the range of immiscibility found at these temperatures for the system TBPBr:Lev/toluene. ■, 288 K; ◆, 303 K. The lines were obtained using the VFT fitting parameters, and the dashed straight lines join the viscosities of the DES and pure toluene.



**Fig. 5.** Viscosity deviation of (a) TBPBr:Lev/toluene and (b) TBABr:Dec/toluene mixtures as a function of  $x_{DES}$ . (lines are fourth-order RK fits). The grey area delimits the range of immiscibility found at these temperatures for the system TBPBr:Lev/toluene. ■, 288 K; ●, 293 K; ▲, 298 K; ◆, 303 K.



**Fig. 6.** Excess molar Gibbs energy of activation of (a) TBPBr:Lev/toluene and (b) TBABr:Dec/toluene mixtures as a function of  $x_{DES}$ . The lines are a guide of experimental values. The grey area delimits the range of immiscibility found at these temperatures for the system TBPBr:Lev/toluene. ■, 288 K; ●, 293 K; ▲, 298 K; ◆, 303 K.

### 3.3. Vibration spectroscopy

The thermodynamic data described so far can be summarized as follows: The  $V^E$  are negative in the whole mixture composition of TBABr:Dec/toluene while in the mixture with TBPBr:Lev, they are negative only for  $x_{DES} > 0.2$ . The viscosity deviation values are negative for both mixtures. Finally, the sign of the  $\Delta G^E$  values as a function of  $x_{DES}$  is similar to that of the  $V^E$ , although the range where these values are positive is around  $x_{TBABr:Lev} = 0.35$ . The sign of the excess properties calculated in this paper carries information about the intermolecular interactions and molecular structure of the molecules in a mixture. While in the literature, negative values of  $V^E$  are attributed to specific interactions between the components of the mixture [33–36], they can just be attributed to efficient packing [37]. Furthermore, positive values of  $\Delta \eta$  are consistent with strong interactions between dissimilar molecules of the mixtures, while negative values indicate weaker intermolecular interactions [38–41].

Vibrational spectroscopy is a powerful tool for investigating the interactions between the components of the mixture through the changes in the shape of specific vibrational modes (changes in frequency, intensity and peak width). Our quantum calculations allow us to point out the main vibrational modes that can be used as observables to study the effect of the mixture composition on the intermolecular interactions. The nature of these vibrational modes as well as their corresponding wave number are given in Table 6, namely the C=O, O–H, C–H stretching vibration modes as well as the deformation vibration modes  $\delta C-H$  and  $\delta O-H$ . The corresponding values are given in Table 6 as well as those of the experimental values.

The effect of the DES/toluene mixture composition on the FT-IR and FT-Raman spectra is shown in Figs. 7 and 8.

It is noteworthy that the presence of carbon chains of different lengths (methyl, butyl and nonane) results in an overlap of the vibrational modes involving the C–H bonds of the mixture components. Our calculations show that the C–H closest to the Br anion has the lowest stretching vibration mode among all the possible ones (the corresponding values are given in Table 6). Unfortunately, its overlap with either the C–H vibrational modes of the levulinic acid, decanoic acid or the toluene makes it impossible to assess about the weakening or the strengthening of the cation and anion interactions as a result of variation in the DES/toluene composition.

The analysis of the effect of the mixture composition of TBPBr:Lev/toluene and TBABr:Dec/toluene on the FT-IR and the FT-Raman spectra in particular on the position of the C–H...Br, O–H or C=O vibrational modes clearly shows that they undergo almost no shift. These results are in agreement with those obtained for the mixture composition dependence of the Raman spectra of cineole-decanoic acid [20]. This indicates that the local environment of these moieties is not affected by changing

the mixture composition and concludes that the interactions between the components of the mixtures are weak. This suggests that the behavior of the thermodynamic data at least for the  $V^E$  and the  $\Delta \eta$  is mainly determined by the progressive packing of the two components. The physical picture that may emerge is that the toluene molecules are incorporated into the voids between the flexible carbon chains of the DES to form non-polar domains. These domains are associated with the correlated position of the neutral alkyl side chains of the cations and of the levulinic acid, and decanoic acid moieties, which self-associate or entangle with each other (despite the expected repulsive forces) to form spatially heterogeneous domains. This heterogeneity creates inherent interfaces that should influence the solvation process in such media.

This interpretation is also compatible with the effect of temperature on the  $V^E$  values. In fact, the increase in temperature, at the different mole fractions, results in larger negative values of  $V^E$ . The temperature coefficient  $(\partial V^E / \partial T)_p$  is negative. This effect excludes the hypothesis of interpreting the negative values, as an indication of the formation of hydrogen bonds between the components of the mixture, since an increase in temperature would lead to a decrease in these interactions, resulting in less negative values of the  $V^E$ . The effect of the temperature can then be rationalized as promoting the packing effect by making the carbon chains more flexible allowing their entanglement and then the mutual incorporation of the components of the mixtures. In the case of a NADES formed by cineole:decanoic acid (1:1) has shown that the solvation of toluene occurs without a major perturbation of the structure of the DES, at least for moderate toluene content, where the DES is able to fit toluene into the liquid structure and no specific interactions occur [20].

**Table 6**

Vibration modes selected for pure components, obtained by DFT calculations on the optimized geometries shown in Table 1. The corresponding experimental values are also given in brackets.

Vibration mode / $\text{cm}^{-1}$	TBPBr	TBABr	Lev	Dec	Toluene
C = O			1807 (1720)	1897 (1737)	
O – H			3416 (3290)		
C – H ... Br	2965 (2875)	3021 (2928)			
$\delta C-H \dots Br$	1492 (1408)	1551 (1452)			
$\delta O-H$			1457	1287 (1214)	
C – H					3064 (3057)



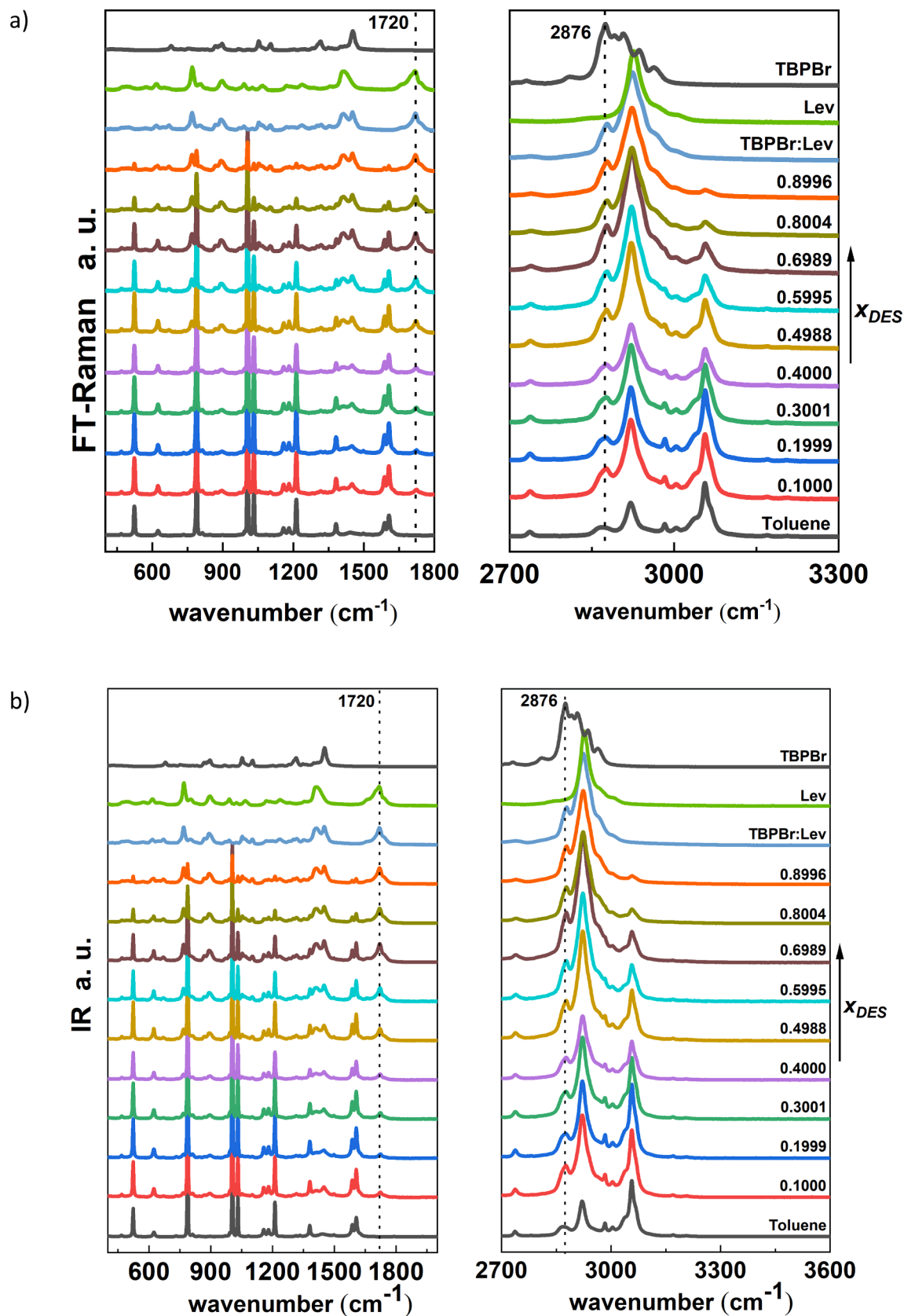
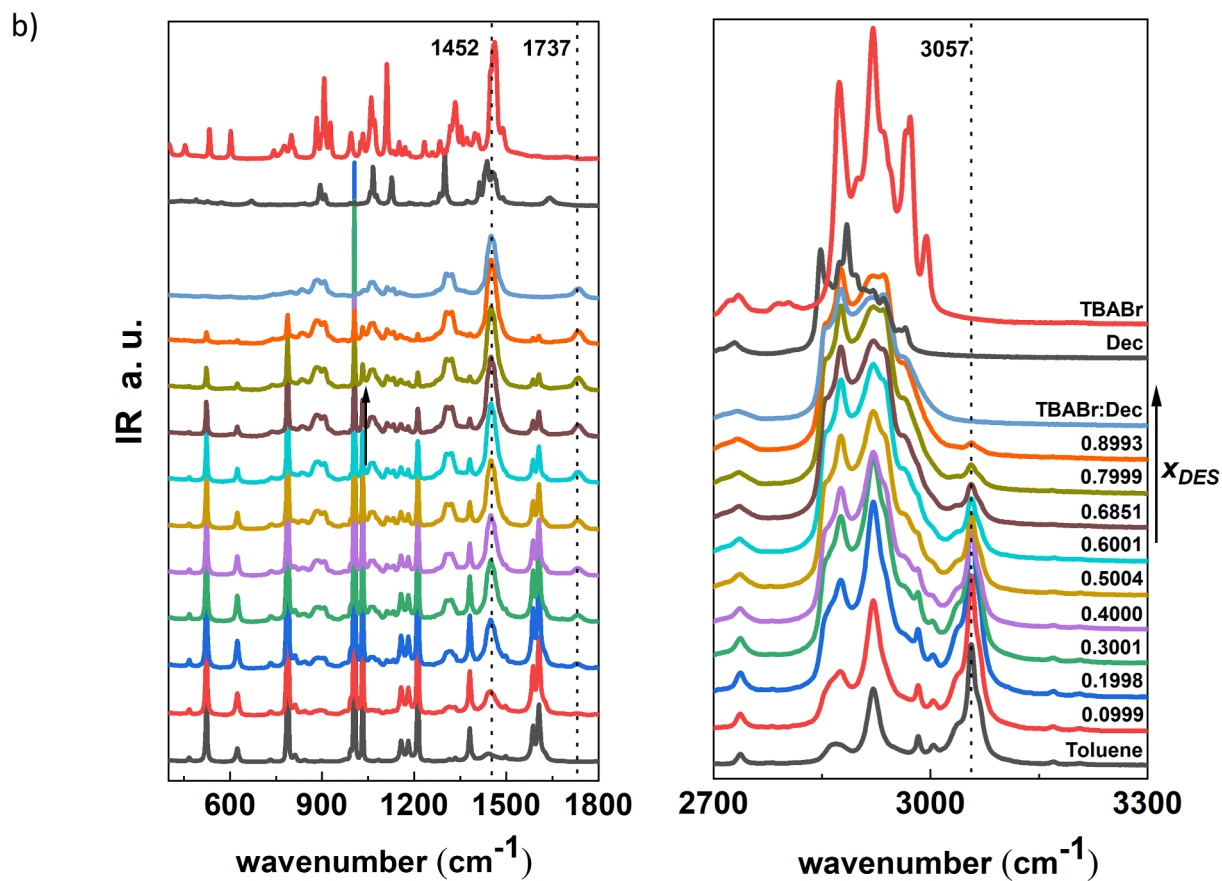
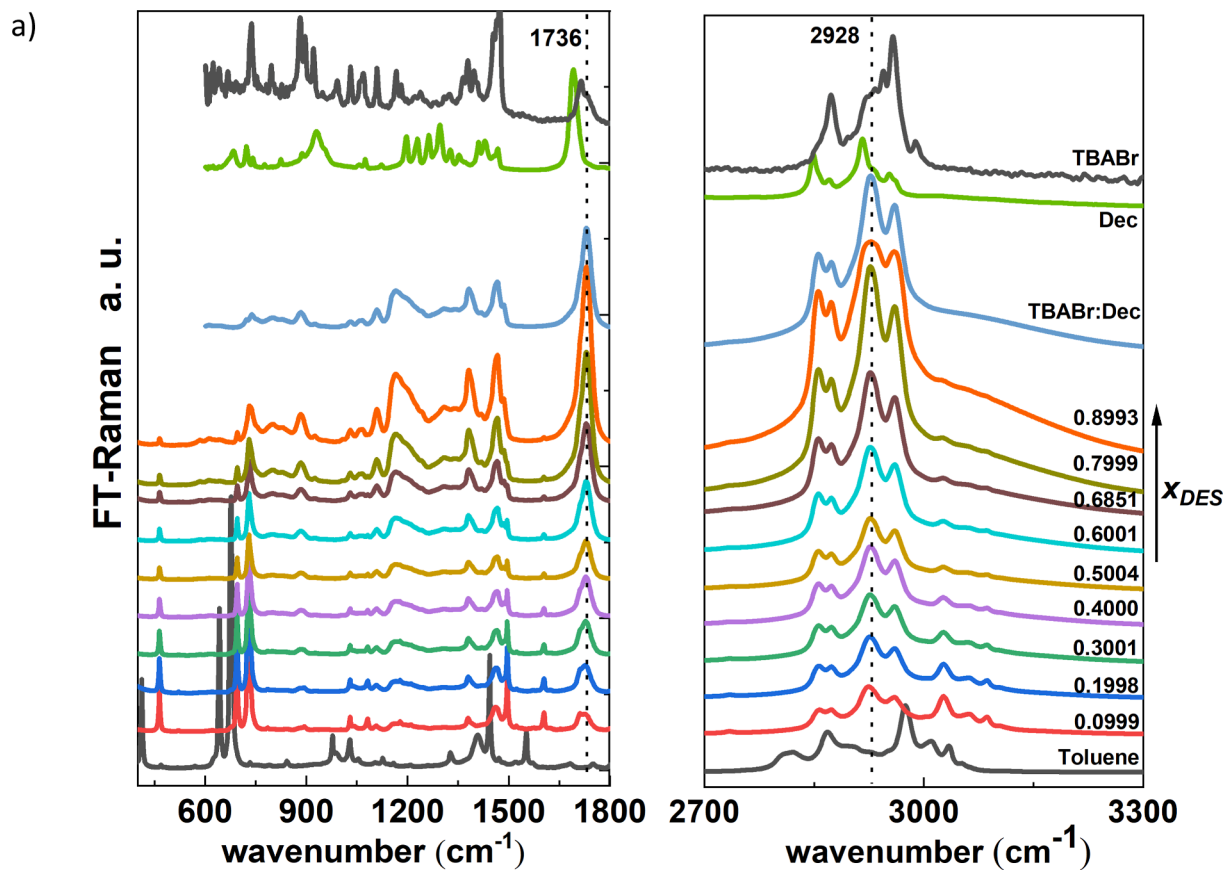


Fig. 7. FT-Raman (a) and IR spectra (b) of the effect of the mole fraction,  $x_{DES}$ , of the DESs formed by tetrabutylphosphonium bromide TBPBr and levulinic acid at 1:6 ratio with toluene. The neat spectra of TBPBr, Lev and toluene are also added. The arrow indicates the increase of the DES mole fraction as indicated in Table 5 and the dashed lines are associated with the vibration modes that are indicated in Table 6. Each spectrum is split into two spectral regions to highlight the changes in its shape.



(caption on next page)

**Fig. 8.** FT-Raman (a) and IR spectra (b) of the effect of the mole fraction,  $x_{DES}$ , the DESs formed by tetrabutylammonium bromide (TBABr) and decanoic acid (Dec) at 1:2 ratio with toluene (Tol). The neat spectra of TBABr, Dec and Tol also are added. The arrow indicates the increase of the DES mole fraction as indicated in Table 5 and the dashed lines are associated with the vibration modes that are indicated in Table 6. Each spectrum is split into two spectral regions to highlight the changes in its shape.

#### 4. Conclusion

The experimental densities and viscosities for the pseudo-binary mixtures of TBPBr:Lev/toluene and TBABr:Dec/toluene were reported in the temperature range of 288.15–303.15 K and at atmospheric pressure. The DESs were prepared at room temperature to ensure that no degradation reactions occurred. The various volumetric and viscometric properties, such as excess molar volume, viscosity deviation and excess Gibbs activation energy for viscous flow, were calculated. The parameters of the Redlich-Kister polynomial equation have been adjusted to these properties with satisfactory results. In addition, partial molar volumes at infinite dilution and excess partial molar volumes at infinite dilution of DES and toluene in their pseudo-binary systems were calculated to gain more insight into the intermolecular interactions governing the mixtures. FT-IR and FT-Raman spectroscopic analyses were also performed to gain a clearer picture of the nature of the established interactions. Analysis of the effect of the mixture composition on the FT-IR and FT-Raman spectra shows that there is no change in the position of some specific vibrational modes involving the C–H (involved in the interaction with Br anion), the C=O and the O–H bonds. We interpret this behavior as an indicator of the packing effect between the components of the mixture, as the main driver of toluene incorporation into the DES rather than to the hydrogen bond interactions, which may play a less important role. This interpretation is compatible with the negative values of both the experimental excess volume and the viscosity deviation, which indicate that the packing efficiency of toluene in the DES networks dominates over the interactions between the toluene and the individual DES components. We didn't interpret the behavior of the Gibbs energy values of the mixture, since the corresponding values are within RT, the energy of the thermal motion of the components of the mixture.

#### CRediT authorship contribution statement

**Tarek Moufawad:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Abdenacer Idrissi:** Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Margarida Costa Gomes:** Writing – review & editing, Validation, Resources. **Sophie Fourmentin:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Methodology.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Editorial board member: Abdenacer Idrissi If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.124753>.

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