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MEASUREMENT OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR ALCOHOLS IN [BMIM][CH_3SO_4] USING HS-SPME/GC-FID

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ABSTRACT - The activity coefficient at infinite dilution(γ_i^∞)and distribution ratios at infinite dilution (K_i^∞) were determined for alkanols (methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, and 2-methyl-2-propanol) in the ionic liquid (IL) 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][CH_3SO_4]) by HS-SPME (Headspace - Solid Phase Micro Extraction) at four temperatures (298.15, 313.15, 333.15, and 353.15K) using headspace - solid phase microextraction (SPME-HS). The results showed significant agreement with literature data. In addition, partial molar excess enthalpies at infinite dilution $\left(\Delta H_i^{E,\infty}\right)$, excess Gibbs energies $\left(\Delta G_i^{E,\infty}\right)$, and excess entropies $\left(\Delta S_i^{E,\infty}\right)$ were calculated from the γ_i^∞ values.

Keywords: Solid-phase microextraction, 1-butyl-3-methylimidazolium methyl sulfate, ionic liquid.

INTRODUCTION

The separation of pure components from mixtures is one of the most widespread processes in the chemical industry (Banat et al., 1999). Selective solvents have an important role in the separation of solutions, with the potential of allowing separation of azeotropes (Elias et al., 2014; Krummen et al., 2002), which occur in large numbers in diverse industrial processes (Wlazło et al., 2014). Therefore, the solvent choice is one of the most important steps in the separation processes.

The use of ionic liquids (ILs) as mass separating agents is one of the fastest growing fields in recent years and is especially conducive to useon an industrial scale (Domanska et al., 2012). New methods using ILs have been proposed for extraction, extractive distillation, and separation (Domanska and Lukoshko, 2013). These solvents are described in the literature as bulky organic cations with low symmetry (Greaves and Drummond, 2008); imidazolium and pyridinium are the main cations (Dobryakov and Maurer, 2008) and the main anions are usually polyatomic and inorganic such as CH_3SO_4- and BF4- (Huang et al., 2008). However, various combinations of cations and anions can be synthesized to adjust the liquid properties required for specific applications (Bahadur et al., 2013).

Ionic liquidsare an attractive research area because they are considered to be more environmentally friendly than conventional volatile organic solvents (Krummen et al., 2002; Dobryakov and Maurer, 2008).In addition, they alsodisplay thermal stability and good solubility (Dobryakov and Maurer, 2008; Greaves and Drummond, 2008), and have low vapor pressures, which may result in less complex processesand simpler solvent regeneration, thereby decreasing energy consumption in comparison to volatile solvents (Bahadur et al., 2013).

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The utility of the limiting values of activity coefficients at infinite dilution in evaluating the parameters of correlations has been amply illustrated. The determination of interactions between solute and solvent is of extreme importance in separation processes. Activity coefficient at infinite dilution and liquid-gas partition coefficient provide a quantitative measure of interactions between unlike molecules and provide information on the intermolecular energy between ILs and organic solutes (Ge et al., 2014). This coefficient is also useful in calculating selectivity, which is the ratio between two activity coefficients of solutes at infinite dilution in the same solvent and ata fixed temperature. The selectivity ratio is useful for determining the best solvent for extracting the component of interest from a mixture (Krummen et al., 2000A; Krummen et al., 2002; Dobryakov and Maurer, 2008), including specific azeotropic mixtures (Wlazło et al., 2014).

The activity coefficients at infinite dilution can be determined by various methods such as gas-liquid chromatography (Krummen et al., 2000B), dilutor technique (Krummen et al., 2000A; Krummen et al., 2002; Dobryakov and Maurer, 2008), and SPME(Fonseca and Coelho, 2007; Furtado and Coelho, 2010; Furtado and Coelho 2012; Elias et al., 2014). Zhang and Pawliszyn (1996) proposed an easy-to-implement, alternative method for the determination of activity coefficients using chromatography coupled with SPME.

Solid Phase Microextraction is a technique for extracting and concentrating analytes for subsequent analysis on analytical equipment such as gas chromatography (GC) or high-performance liquid chromatography (HPLC). SPME uses a polymer-coated fine silica rod, 100 mm long, to extract and concentrate target analytes that are present in a matrix. The critical component of SPME fibers is the coating material. These coatings have specific characteristics, such as thickness and polarity that directly influence extraction kinetics (Pawliszyn, 1997). The thermodynamic modeling related to this method allowed the determination of these coefficients by headspace analysis (Fonseca and Coelho, 2007; Furtado and Coelho, 2010; Furtado and Coelho 2012; Elias et al., 2014).

In the present study, the headspace-SPME technique (HS-SPME) was applied to determine activity coefficients at infinite dilution for six alcohols in the ionic liquid1-butyl-3-methylimidazolium methyl sulfate ([BMIM][CH_3SO_4]). The main objective of the work is to evaluate the SPME methodology. The results are presented and compared with literature data obtained using the dilutor technique or inert gas stripping method.

EXPERIMENTAL METHOD

Materials

The ionic liquid 1-butyl-3-methyllimidazolium methyl sulfate [BMIM][CH_3SO_4] (mass fraction ≥ 0.9800, M=0.2503 kg) was purchased from BASF. The IL was further purified by vacuum evaporation (2 mbar) for five days at 323.15K in order to remove any volatile chemicals and water. Purity (> 0.9995 mass fraction) was verified by headspace microextraction with PDMS coating. The water mass fraction was analyzed byKarl Fisher analysis and was less than 8.10-3mass fraction.

Methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol (solutes), and o-xylene (solvent for calibration curves)were purchased from Sigma Aldrich. Their purities were analyzed by gas chromatography and were greater than 0.9922 (Table 1). SPME fibers with 100 µm PDMS coating and holders were purchased from Supelco. These fibers were conditioned for 2 hours at 523.15K before use. Gasesused in the experiments were obtained from Linde AG.

Table 1. The mass fraction purities of chemicals used.

Chemicals	Purities in massfraction	
	Provided by producer	GC analysis
methanol	0.9900	0.9968
ethanol	0.9900	0.9959
1-propanol	0.9950	0.9980
1-butanol	0.9900	0.9977
2-butanol	0.9950	0.9961
2-methyl-2-propanol	0.9950	0.9974
o-xylene	0.9800	0.9922

Gas chromatography conditions for SPME and liquid injections

The experiments were performed using a GC-2010 Shimadzu gas chromatograph with a FID (Flame Ionization Detector) and an HP-INNO wax column (60 m x 0.32 mm x 0.25 µm). Both injector and detector were kept at 523.15 K; the injector operated in the constant pressure mode. Helium was used as the carrier gas (mass fraction 0.99999) at a column flow of 2.0 mL/min in all experiments. The column was maintained at 323.15 K for 5 min, ramped up to 363.15 K at a rate of 10 K/min, and maintained at this temperature for 2 min. The conditions were determined to optimize the determination of chromatographic peaks of the pure solutes.

Construction of calibration curves

Stock solutions of alkanols were prepared by dissolving 50.0 µL of alkanol in 2.0 mL of o-xylene. Standard solutions were prepared by successive dilution of stock solutions in o-xylene. The eight-point calibration curve for each alkanol was obtained by injecting 5 to 8 replicates of 1.4 µL of standard solutions. The chromatographic conditions applied during these experiments were the same as described above.

Determination of extraction time and fiber-gas partition coefficients

Solid phase microextraction is a multiphase equilibration process. The extraction system is frequently complex. In order to simplify the system, only three phases were initially considered: the fiber coating, gas phase or headspace, and liquid phase. When the three-phase system is at equilibrium, the chemical potentials of the analyte must be equal in all three phases.

Gas samples were prepared by injecting1.0 µL of o-xylene stock solution into 44 mL amber vials capped with a PTFE/silicone septum. Fibers wereexposed to single solute gas samples at times ranging from 1 to 60 min. Extraction times were determined by exposing fibers to a single solute gas sample at t times between 1 and 60 min. Extracted material was quantified in the gas chromatograph. Temperature inside the vials was maintained at 298.15 K by a thermostatic bath with a precision of 0.1 K. Fiber-gas partition coefficients K_{fg} were determined as described above and at temperatures of 298.15, 313.15, 333.15, and 353.15 K using previously defined extraction times. The complete theory and equations used to calculate the fiber-gas partition coefficients are presented in Furtado and Coelho (2012).

Determination of infinity dilution activity coefficients by SPME

A closed system containing a liquid, gaseous, and polymeric phase of the SPME fiber is necessary for the determination of infinite dilution activity coefficients by headspace SPME (HS-SPME); a schematic representation is presented in Furtado and Coelho (2012). A closed system implies that the total amount of solute will be distributed between the gas, liquid, and polymeric phases.

To determine activity coefficients at infinite dilutions, alkanol solutions were prepared by the addition of 1.0 µL of solute to 3 ml of ionic liquid in a 40 mL amber vial, capped with a PTFE/silicone septum. A stainless steel base was built to house the vial and resistances. Temperaturewas controlled by a PID controller equipped with a PT-100 thermocouple (precision of 0.1 K). The system was magnetically stirred at rotations above 1500 rpm. Figure 1 shows the experimental scheme. Equilibration times were measured by headspace extractions with PDMS fiber after 20, 30, 40, and 90 min of agitation; the system was kept at a constant temperature for 30 min after these times. The fiber was exposed in the gas chromatograph's injector for the quantification of extracted material. Activity coefficients at infinite dilution were determined using equation 1. Molar volumes of solutes were calculated using the Rackett equation (Reid, 1987); second virial coefficients were calculated by the Tsonopoulos correlation (Gmehling and Kolbe, 1988). Vapor pressures were determined by the Wagner equation (Reid, 1987).

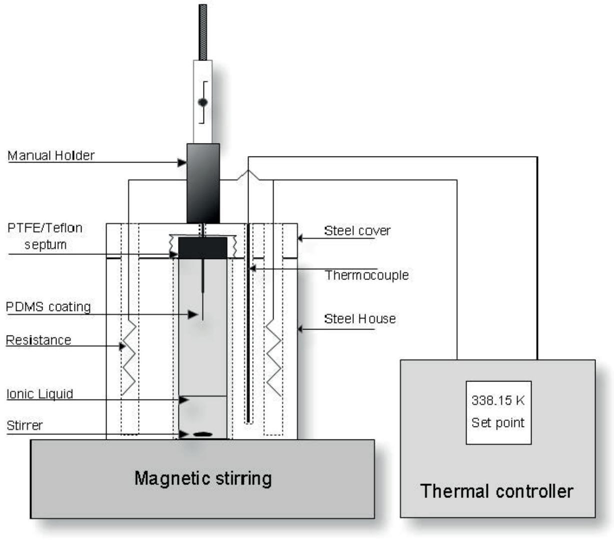

Figure 1. Scheme of the experimental unit used.

The equation used for the calculation of activity coefficients at infinite dilution is a modified Everett (1965) and Cruickshank et al. (1969) equation, expressed here as Equation 1.

$$\ln\left(\gamma_i^{\infty}\right) = ln\left(\frac{\rho_s RT}{K_i^{\infty} P_i^{sat} M_s}\right) - \frac{P_i^{sat}\left(B_{11} - v_i^{0}\right)}{RT} \tag{1}$$

where γ_i^{∞} is the activity coefficient at infinite dilution of solute i, ρ_s is the solvent density, R is the gas constant, T is the system temperature, K_i^{∞} is the partition coefficient liquid-gas at infinite dilution, P_i^{sat} is the saturation pressure of solute at temperature T, M_s is the molar mass of solvent, B_{11} is the second virial coefficient(coefficients with repeated subscripts, Bii, are those of pure components and correspond to interaction of pairs of like molecules), and v_i^{0} is the molar volume of solute as liquid.

Limiting distribution ratios (K_i^{∞}) were determined by the first approach presented in Furtado and Coelho (2012), which is shown in equation 2.

$$K_i^{\infty} = \left[K_{fg} V_f\left(\frac{n_i^{0}}{n_i^{f}} - 1\right) - V_g\right]\frac{1}{V_L} \tag{2}$$

where V_f is the volume of the polymeric coating of the SPME fiber, n_i^{0} is the initial mass of solute i in the system, n_i^{f} is the mass of solute i on the fiber, and V_g and V_L are volumes of gas and liquid phases, respectively.

RESULTS AND DISCUSSION

Calibration curves were constructed for each alkanol and correlation coefficients (R²) for all calibration curves were greater than 0.9999. Extraction time for the 100 µm PDMS fibers was determined for each alkanol, and the longest time observed was 20 min. However, an extraction time of 30 minutes was assumed to ensure that equilibrium in the fibersystem had been achieved. After each extraction, the PDMS fibers were re-exposed to the chromatograph's injector and no non-desorbed material was detected.

The values of B11, v_i^{0}, and P_i^{sat} were calculated for each solute for the determination of activity coefficients at infinite dilution (Table 2).

Table 2. Summary of values of solute properties at different temperatures.

Solute	B_{11} **m3·mol-1·103**	v_i^{0} **m3. mol-1·108**	P_i^{sat} **Pa**
		T= 298.15 K	
Methanol	-0.9	4182.8	16953.5
Ethanol	-1.3	5258.8	7894.6
1-Propanol	-1.9	6451.5	2806.2
1-Butanol	-2.6	7965.4	894.9
2-Butanol	-2.2	8267.4	2270.1
2-Methyl-2-propanol	-1.9	8204.2	5596.2
		T= 313.15 K	
Methanol	-0.8	4279.0	35462.1
Ethanol	-1.1	5381.4	17950.8
1-Propanol	-1.6	6589.0	6989.2
1-Butanol	-2.2	8118.8	2468.3
2-Butanol	-1.9	8441.6	5967.9
2-Methyl-2-propanol	-1.6	8400.4	13774.8
		T= 333.15 K	
Methanol	-0.7	4.4195	84583.9
Ethanol	-0.9	5.5605	47052.9
1-Propanol	-1.3	6.7880	20279.9
1-Butanol	-1.8	8.3389	7990.6

Table 2. Cont.

Solute	B_{11} m3·mol-1·103	v_i^0 m3. mol-1·108	P_i^{sat} Pa
2-Butanol	-1.6	8.6936	18057.5
2-Methyl-2-propanol	-1.3	8.6879	38621.8
	T= 353.15 K		
Methanol	-0.6	4576.9	180867.8
Ethanol	-0.8	5761.1	108659.3
1-Propanol	-1.1	7008.2	50836.6
1-Butanol	-1.5	8579.6	21834.2
2-Butanol	-1.3	8972.4	46104.6
2-Methyl-2-propanol	-1.1	9011.3	92300.9

Solvent density was calculated using equation 3. Values of coefficients a and b reported by Dobryakov and Maurer (2008) were used .It was verified that, as usual, the ionic liquid density ρ_s decreased with increasing temperatures (Table 3).

$$\rho_s = a + bT \tag{3}$$

Table 3. Ionic liquid [BMIM][CH_3SO_4] density at different temperatures.

Temperature K	*a* g·cm^{-3}	*b* g·cm^{-3}·K^{-1}	ρ_s g·cm^{-3}
298.15	1.4119	-6.772·10^{-4}	1.2100
313.15			1.1998
333.15			1.1863
353.15			1.1727

The ratio of the mass absorbed/adsorbed by the fiber could be correlated to the total available mass in the vapor phase in the equilibrium state using the gas-fiber partition coefficient K_{fg} (Pawliszyn, 1997). This coefficient is important in determining the liquid-gas partition coefficient and subsequent determination of the activity coefficient. Table 4 shows the K_{fg} values determined at the studied temperatures.

Table 4. Fiber-gas partition coefficient K_{fg} for all studied compounds at po = 101.27 kPa and temperatures from 298.15 to 353.15 K[a].

Solute i	$K_{fg} \pm SD^b$	
	T = 298.15 K	**T = 313.15 K**
Methanol	48.4 ±2.6	29.1 ±0.8
Ethanol	107.3 ±4.3	51.7±0.9
1-Propanol	249.5 ±2.4	117.3 ±0.9
1-Butanol	634.4 ± 31.7	244.4 ± 17.6
2-Butanol	246.0 ± 10.3	126.1 ±3.0
2-Methyl-2-propanol	141.7 ±8.5	77.5 ±1.8
	T = 333.15 K	**T = 353.15 K**
Methanol	14.5 ±0.9	8.5 ±0.6
Ethanol	26.7 ±0.3	15.4 ±0.2
1-Propanol	55.8 ±2.6	31.9 ±1.7
1-Butanol	98.6 ±8.3	51.8 ±1.5
2-Butanol	57.6 ±2.8	30.5 ±1.8
2-Methyl-2-propanol	37.9 ±1.9	20.8 ±1.9

[a] Standard uncertainty u(T) = 0.1 K.

[b] SD - Standard Deviation.

The linearization of fiber gas partition coefficients facilitates the analysis of temperature dependence (Pawliszyn, 1997). A decrease in K_{fg} values with increasing temperature was observed in the alcohol-IL systems. The fiber-gas partition coefficients showed low values for molecules with the highest polarities. Molecules with the highest polarities interact less with the polymer (PDMS is a non-polar polymer), which explains the low values obtained for methanol (Martos and Pawliszyn, 1997).

Furthermore, all correlation coefficients were higher than 0.9847, which ensures a relevant precision and linearity in the data obtained experimentally. Figure 2 shows the plot of measured ln K_{fg} versus 1/T values, and the linear data fits.

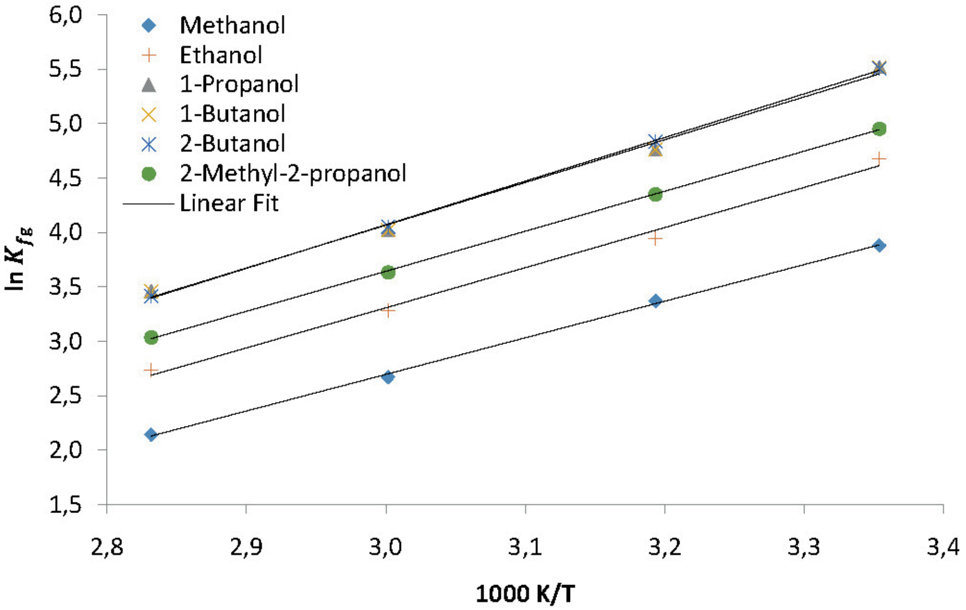

Figure 2. Plot of ln K_{fg} vs 1/T for solutes, and the linear data correlations.

Table 5. presents the values of distribution ratios at infinite dilution K_i^∞ for a series of alkanolsin the ionic liquid [BMIM][CH_3SO_4] at temperatures between 298.15 and 353.15 K, and compares them with literature data available in the study by Dobryakov and Maurer (2008).

Table 5. Distribution ratios at infinite dilution K_i^∞ in a series of four alkanols in the ionic liquid [bmim][CH_3SO_4] at different temperatures (298.15 to 353.15 K).

Solute i	K_i^∞		RSD (%)
	SPME (Present study)	Dilutor Technique (Dobryakov *et al.*,2008).	
	T = 298.15 K		
Methanol	1841 ± 9	1840	0.05
Ethanol	2251 ± 29	2350	4.21
1-Propanol	3958 ± 83	4470	11.45
1-Butanol	7661 ± 157	7844	2.33
2-Butanol	3537 ± 103	3587	1.39
2-Methyl-2-propanol	1564 ± 6	1561	0.19
	T = 313.15 K		
Methanol	1022 ± 49	1004	1.79
Ethanol	1088 ± 37	1142	4.73
1-Propanol	1917 ± 24	2044	6.21
1-Butanol	3476 ± 88	3490	0.40

Table 5. Cont.

Solute i	K_i^∞		RSD (%)
	SPME (Present study)	Dilutor Technique (Dobryakov *et al.*,2008).	
2-Butanol	1555 ± 24	1590	2.20
2-Methyl-2-propanol	723 ± 11	719	
T = 333.15 K			
Methanol	508 ± 2	492	1.79
Ethanol	469 ± 22	458	4.73
1-Propanol	866 ± 9	731	6.21
1-Butanol	1424 ± 49	1204	0.40
2-Butanol	611 ± 16	577	2.20
2-Methyl-2-propanol	314 ± 8	292	0.56
T = 353.15 K			
Methanol	280 ± 6	298	6.04
Ethanol	232 ± 2	222	4.50
1-Propanol	454 ± 10	337	34.72
1-Butanol	681 ± 33	525	29.71
2-Butanol	276 ± 3	252	9.52
2-Methyl-2-propanol	145 ± 3	128	13.28

At lower temperatures, the interaction between 1-propanol and PDMS was weaker, which was reflected in a 11% deviation from the literature value. However, the behavior at higher temperatures was similar for all analytes. Unlike the methods of stripping gas, in which an inert gas carries the volatile compound, the SPME extraction is based upon the affinity with the fiber. At higher temperatures, the compounds' vapor pressure increases, increasing their concentration in the vapor phase. The adsorption ratio is much higher than the desorption of the compounds in the studied system. This can lead to deviations when compared to other techniques of determination. According to the literature, the activity coefficient (as well as the partition coefficients) may vary with the technique used (Kojimaet al, 1997).

Figure 3 illustrates the results of the linearization of distribution ratios at infinite dilution K_i^∞.

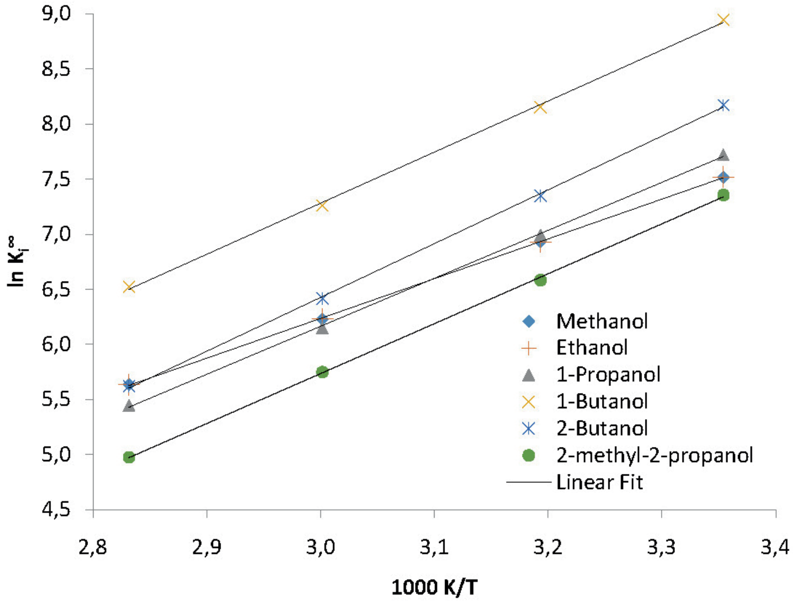

Figure 3. Experimental results of the linearization of K_i^∞ for alcoholsversus temperature.

As expected, the values of the partition coefficient K_i^∞ decreased with increasing temperatures. This fact results from the dominant temperature dependence of the evaporation enthalpy being directly linked to the process of sorption in the PDMS fiber. The deviations were less than 6% for ethanol, and about 9% for 2-methyl-2-propanol. However, the error was less than 6% for 1-butanol and 1-propanol at low temperatures. The deviationswereon the order of 30% at the highest temperatures (333.15 and 353.15 K) studied.

Table 6 presents the values of activity coefficients at infinite dilution, γ_i^∞ for the six studied alkanols in the ionic liquid [BMIM][CH_3SO_4] at temperatures between 298.15 and 353.15 K, and compares obtained values with those reported by Dobryakov et al. (2008).

Table 6. Activity coefficients at infinite dilution γ_i^∞ in a series of six alkanols in the ionic liquid [BMIM][CH_3SO_4] at different temperatures (298.15 to 353.15 K).

Solute i	γ_i^∞		RSD (%)
	SPME (Present study)	Dilutor Technique (Dobryakov*et al.,* 2008)	
	T =298.15 K		
Methanol	0.39 ± 0.02	0.39	0.00
Ethanol	0.68 ± 0.01	0.64	6.25
1-Propanol	1.08 ± 0.01	0.96	12.50
1-Butanol	1.75 ± 0.04	1.68	4.17
2-Butanol	1.49 ± 0.02	1.45	2.76
2-Methyl-2-propanol	1.37 ± 0.01	1.38	0.72
	T = 313.15 K		
Methanol	0.36 ± 0.02	0.36	0.00
Ethanol	0.65 ± 0.02	0.61	6.56
1-Propanol	0.94 ± 0.01	0.88	6.82
1-Butanol	1.46 ± 0.04	1.44	1.39
2-Butanol	1.35 ± 0.02	1.31	3.05
2-Methyl-2-propanol	1.26 ± 0.02	1.27	0.79
	T = 333.15 K		
Methanol	0.33 ± 0.01	0.33	0.00
Ethanol	0.61 ± 0.03	0.62	1.61
1-Propanol	0.76 ± 0.01	0.89	14.61
1-Butanol	1.16 ± 0.04	1.37	15.33
2-Butanol	1.20 ± 0.03	1.27	5.51
2-Methyl-2-propanol	1.10 ± 0.03	1.19	7.56
	T = 353.15 K		
Methanol	0.31 ± 0.01	0.38	18.42
Ethanol	0.58 ± 0.02	0.59	1.69
1-Propanol	0.62 ± 0.01	0.82	24.39
1-Butanol	0.94 ± 0.05	1.21	22.31
2-Butanol	1.10 ± 0.01	1.21	9.09
2-Methyl-2-propanol	1.04 ± 0.02	1.22	14.75

Low values of γ_i^∞ are related to the strongest interactions between solute and solvent (Domanska and Królikowski, 2011). Figure 4 shows that activity coefficients increase with increasing lengths of carbon chains.

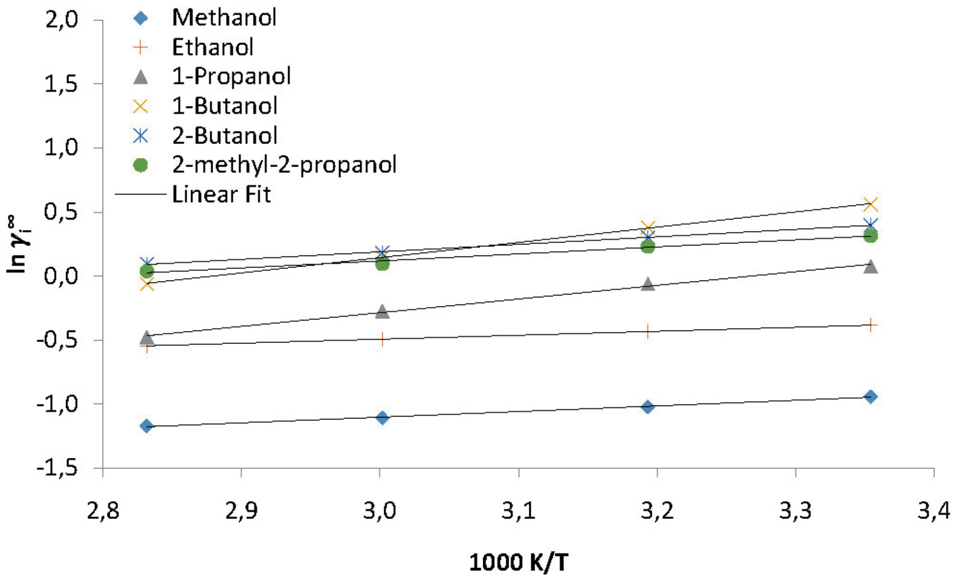

Figure 4. Experimental results for activity coefficients at infinite dilution γ_i^∞ for alkanols in [BMIM][CH_3SO_4]versus temperature.

The results showed that the values of activity coefficients at infinite dilution are reduced with increasing temperatures. This behavior indicates a decrease in solute-solvent repulsive forces (Dobryakovet al.,2008; Domanska and Królikowski, 2011). The presence of delocalized electrons that can interact with the cation and/or anion in the ionic liquid (Dobryakov et al.,2008; Domanska and Królikowski, 2011; Domanska and Marciniak, 2008) explains this behavior, which is common in various solutes in ionic liquids (Dobryakov et al.,2008).

Enthalpy and entropy can be calculated from Equation 4, which shows a relationship between activity coefficients at infinite dilution versus temperature (Ge et al., 2014).

$$\ln\left(\gamma_i^\infty\right) = \frac{H_i^{E,\infty}}{RT} - \frac{S_i^{E,\infty}}{R} \tag{4}$$

Table 7 shows the values of $T_{ref}\cdot\Delta S_i^{E,\infty}$, and . The value of molar excess enthalpy for all compounds was positive. This is consistent with the temperature dependence of the activity coefficient decreasing with increasing temperatures. Table 7 also presents the limiting partial molar excess Gibbs energies $G_i^{E,\infty} = RTln\gamma_i^\infty$ of all studied solutes in [BMIM][CH_3SO_4] at the reference temperature of 298.15 K.

Table 7. Values of the partial molar excess enthalpies at infinite dilution ($\Delta H_i^{E,\infty}$), excess entropies ($T_{ref}\cdot\Delta S_i^{E,\infty}$), and excess Gibbs energies ($\Delta G_i^{E,\infty}$) of alcohols i in [BMIM][CH_3SO_4] at the reference temperature Tref = 298.15 K.[a]

Solute i	$\Delta H_i^{E,\infty}$ kJ·mol^{-1}	$T_{ref}\cdot\Delta S_i^{E,\infty}$ kJ·mol^{-1}	$\Delta G_i^{E,\infty}$ kJ·mol^{-1}
Methanol	3.67	6.01	-2.33
Ethanol	2.56	3.51	-0.96
1-Propanol	8.89	8.66	0.19
1-Butanol	9.90	8.51	1.39
2-Butanol	4.86	3.88	0.99
2-Methyl-2-propanol	4.56	3.79	0.78

[a] Standard uncertainties (u) are as follows: u($\Delta H_i^{E,\infty}$)= ± 0.5 kJ mol-1, u($\Delta G_i^{E,\infty}$)= ± 0.5 kJ mol-1, and u($T_{ref}\cdot\Delta S_i^{E,\infty}$)= ± 0.05 kJ mol^{-1}.

The evaluation of reproducibility between fibers was performed through the ANOVA test. The analysis of utilized fibers (PDMS 100 µm) was carried out by determining fiber-gas partition coefficients at 298.15 K (Furtado and Coelho, 2012). Three replicates of each utilized fiber were analyzed for each solute. All analyzed fibers were statistically equivalent at 95 % of confidence level by ANOVA tests (Table 8).

Table 8. Inter-fiber comparison by ANOVA test with 95% confidence level using the fiber–gas partition coefficient determined at T= 298.15 K (3 replicates for each fiber; Fcrit= 5.143).[a]

Solute	K_{fg} ±SD[b]			Statistical tests results	
	Fiber 1	Fiber 2	Fiber 3	F-value	Result
Methanol	49.77 ± 0.78	48.70 ± 0.75	49.27 ± 0.67	0.453	OK
Ethanol	110.20±1.60	108.08±1.92	109.26±0.63	1.519	OK
1-Propanol	250.77±0.83	249.23±2.09	250.61±1.01	1.057	OK
1-Butanol	632.51±1.38	633.48±1.49	632.33±1.33	0.585	OK
2-Butanol	239.79±1.00	237.76±1.16	238.09±1.01	3.155	OK
2-Methyl-2-propanol	136.87±1.59	135.60±1.07	138.65±1.33	3.887	OK

[a] Standard uncertainty u(T) = 0.1 K.

[b] SD - Standard Deviation**.**

PDMS loss in each fiber was verified through the t-test. The partition coefficients of solutes were determined before and after experiments, in three replicates for each fiber, and compared using the t-test at 95% confidence level (Furtado and Coelho, 2012). Table 9 shows these results; all fibers passed on the t-test at 95% confidence level.

Table 9. Intra-fiber comparisons by the t-test at the 95% confidence level using partition coefficients determined at T= 298.15 K, before and after experiments (Kfg ± standard deviation; 3 replicates were evaluatedfor each fiber; tcrit= 2.132).

Solute	Fiber 1		Statistical tests results	
	Before	After	T-value	Result
Methanol	49.03±0.78	49.13±0.47	-0.183	OK
Ethanol	110.20±1.61	109.02±1.31	0.983	OK
1-Propanol	250.77±0.83	250.27±0.56	-1.904	OK
1-Butanol	632.51±1.38	631.72±1.36	0.712	OK
2-Butanol	239.79±1.00	239.19±1.01	0.983	OK
2-Methyl-2-propanol	136.87±1.59	137.91±1.49	-0.828	OK
	Fiber 2		Statistical tests results	
	Before	After	T-value	Result
Methanol	48.70±0.75	49.72±0.41	-2.055	OK
Ethanol	108.08±1.92	108.51±0.69	-0.369	OK
1-Propanol	249.23±2.10	250.87±1.34	-1.144	OK
1-Butanol	633.48±1.49	632.60±1.41	0.742	OK
2-Butanol	237.76±4.90	237.97±0.78	-0.265	OK
2-Methyl-2-propanol	135.60±1.07	136.45±1.06	-0.981	OK
	Fiber 3		Statistical tests results	
	Before	After	T-value	Result
Methanol	49.27±0.67	49.07±0.55	0.303	OK
Ethanol	109.26±0.63	109.36±1.23	-0.122	OK
1-Propanol	250.61±1.01	249.95±0.81	0.874	OK
1-Butanol	632.33±1.33	633.23±0.99	-0.941	OK
2-Butanol	238.09±1.01	238.20±0.65	-0.153	OK
2-Methyl-2-propanol	138.65±1.34	139.44±0.84	-0.862	OK

SPME is a technique that can be applied to any system, provided that the compound of interest has affinity with the fiber coating. The methodology is of easy implementation, high accuracy and low cost. However, the analysis can be compromised when there is swelling in the fiber, which can lead to experimental errors due to loss by scraping of material in the protective tube. Another possible problem is condensation on the surface of the polymer. These problems can be solved by correct choice of the correct fiber and precise temperature control in the system, preventing the formation of temperature gradients (Elias et al, 2014; Furtado and Coelho, 2012).

The gas stripping technique is consolidated in the literature. This technique allows the determination of various activity coefficients with a unique experience as well in systems that have low interaction between solute-solvent. However, there are some disadvantages that limit the technique. The activity coefficient values may vary according to the equilibrium cell configuration. The technique cannot be applied to systems in which the compounds of interest have low volatility. Another disadvantage is the necessity to carry out various experiments to ensure that the equilibrium is achieved (Kojima et al, 1997). Despite some disadvantages, the SPME technique is accurate, fast and low cost, which has major advantages compared to consolidated techniques such as gas stripping.

CONCLUSION

The HS-SPME/GC/FID method was employed to measure infinite dilution activity coefficients γ_i^∞ in a series of alkanols in ionic liquid [BMIM][CH_3SO_4] at four different temperatures. In the present study, two interesting features related to the determination of activity coefficients at infinite dilution were observed: increased temperatures lead to increased attraction between solute and solvent resulting in decreased activity coefficients; reduction in chain lengths of alkanols reduces activity coefficients and other factors related to chemical interactions that result from interactions between delocalized electrons and cation and/or anion in the ionic liquid (Dobryakov et al.,2008).

The solid phase microextraction SPME technique applied for the determination of activity coefficients at infinite dilution was efficient, rapid, and inexpensive and validated as providing satisfactory results. The results suggest that SPME can be applied to determine activity coefficients at infinite dilution of solutes in ionic liquid solvents despite the observed deviations ranging from 0.7 to 23.0%; corresponding deviations reported in the literature present similar discrepancy ranges. Therefore, the results produced in this study indicate that ionic liquid is qualified as a selective solvent for separation processes. Basically, the results might provide information whether a certain ionic liquid qualifies as a selective solvent for separation processes, which at present is a matter of particular interest in chemical engineering.

NOMENCLATURE

γ_i^∞	Activity coefficient at infinite dilution of solute i
$\Delta H_i^{E,\infty}$	Partial molar excess enthalpy at infinite dilution (KJ·mol-1)
ρ_s	Solvent density (g·cm^{-3})
a	Coefficient of density equation (g·cm^{-3})
b	Coefficient of density equation (g·cm^{-3}·K^{-1})
B_{11}	Second virial coefficient (m^3·mol^{-1})
FID	Flame Ionization Detector
GC	Gas Chromatography
K_{fg}	Fiber-gas partition coefficient
K_i^∞	Partition coefficient liquid-gas at infinite dilution
M_s	Molar mass of solvent (g·mol^{-1})
n_i^0	Initial mass of solute i in the system (g)
n_i^f	Mass of solute i on the fiber (g)
PDMS	Polydimethylsiloxane
P_i^{sat}	Saturation pressure of the solute at temperature T (Pa)
PID	Proportional-integral-derivative controller
PTFE	Polytetrafluoroethylene
R	Gas constant (J·mol^{-1} K^{-1})
R²	Determination coefficient
SPME	Solid Phase Micro Extraction
T	Temperature (K)
V_f	Volume of the polymeric coating of the SPME fiber (μL)
v_i^0	Molar volume of solute as liquid (m^3 105)
V_g	Volume of gas phase (μL)

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