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Diffusion Coefficients of 1-Alkyl-3-methylimidazolium Ionic Liquids in Water, Methanol, and Acetonitrile at Infinite Dilution[†]

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The diffusion coefficients of several ionic liquids based on the 1-alkyl-3-methylimidazolium cation, $[C_nC_1Im]$, with chloride, tetrafluoroborate, and bis(trifluoromethanesulfonyl)imide, $[Ntf_2]$, anions were measured, using a Taylor dispersion technique, in three solvents (water, methanol, and acetonitrile) as a function of temperature between (283 and 333) K. The diffusion coefficients vary from $0.57 \cdot 10^{-9}\ m^2 \cdot s^{-1}$ for 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_8C_1im][Ntf_2]$, in water to $3.48 \cdot 10^{-9}\ m^2 \cdot s^{-1}$ for 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_2C_1im][Ntf_2]$, in acetonitrile. In general, the diffusivities are lower for water, followed by methanol and acetonitrile, and decrease with an increase in the alkyl side chain of the imidazolium-based ionic liquids. These trends do not follow the Stokes−Einstein relation but can be explained by the solute−solvent interactions. The data were correlated using a modified Wilke−Chang equation in which a correction parameter was introduced. The correction parameter is independent of the temperature and is different for each solvent studied.

1. Introduction

The rate at which a component is transferred from one phase to another depends upon a mass-transfer rate or coefficient and on the degree of departure of the system from equilibrium.[1] The rate coefficients for the various components in a given phase will differ from each other to the greatest extent under conditions where molecular diffusion prevails, but even then the difference is not really large. Under conditions of turbulence, where molecular diffusion is relatively unimportant, the transfer coefficients become much more nearly alike for all components. For making separations, we depend, therefore, almost entirely upon differences in concentration, which exist at equilibrium, and not upon the difference in transfer coefficients. The mass-transfer coefficients are, nevertheless, of great importance since, as they regulate the rate at which equilibrium is approached, they control the time required for separation.

Ionic liquids are a novel class of solvents with promising properties for applications in more sustainable chemical processes. Their novelty and great variety, possible by appropriately combining different anions and cations, open new possibilities for their use but also point out new ways of interpreting and predicting their thermophysical properties, which are still largely unknown. Knowledge of the diffusion of ionic liquids in molecular solvents is specially relevant in two contexts: for chemical process engineering, namely, to develop new reaction and separation media, but also for the determination of the fate of these compounds in the environment, molecular diffusion (especially in water) contributing to the understanding of the transport in natural ecosystems.

Very few studies have been published concerning the diffusion of ionic liquids in common solvents of industrial and environmental importance. In fact, most of the studies published concern the measurement of the self-diffusion coefficient,[2−4] and to the best of our knowledge, only two papers have been published on the interdiffusion coefficient of different ionic liquids in a molecular solvent, in those particular cases, water at room temperature[5] or as a function of temperature between (303 and 323) K.[6]

In this work, we investigate the effect of changing the length of the alkyl side chain in the cation and also the role of different anions on the diffusion coefficients of six different ionic liquids in three molecular solvents: water, methanol, and acetonitrile. The solvents were chosen not only because of their industrial or environmental relevance but also because of the different nature of their molecular interactions. Water and methanol interact mainly through hydrogen bonds and are highly associating liquids, whereas acetonitrile is a dipolar, nonassociating molecule. A previous theoretical study[7] has shown differences in how water, methanol, and acetonitrile interact with imidazolium-based ionic liquids. Although in this simulation work from the literature the molecular species were the solutes in ionic liquid media, the main features of the cross interactions are expected to be maintained in the reverse situation, which is contemplated in the present study.

Herein, the ionic liquids chosen are based on the 1-alkyl-3-methylimidazolium cation with alkyl chains varying from ethyl to *n*-octyl. The effect of changing the length of the alkyl chain is to increase the hydrophobicity of the cation,[8] and differences are expected in their solvation by H-bonded and polar solvents.[7] The anions studied—chloride, tetrafluoroborate, and bis(trifluoromethanesulfonyl)imide $[Ntf_2]$—differ in size and shape, from small and spherical to large and flexible. The $[Ntf_2]$ anion is a widely used noncoordinating anion leading to stable ionic liquids that are poorly miscible with water.[9] The data obtained on the diffusion coefficients were represented using different correlation and prediction schemes.

2. Experimental

2.1. Materials. 1-Butyl-3-methylimidazolium chloride $[C_4C_1Im]$-[Cl] and 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4C_1Im]$-

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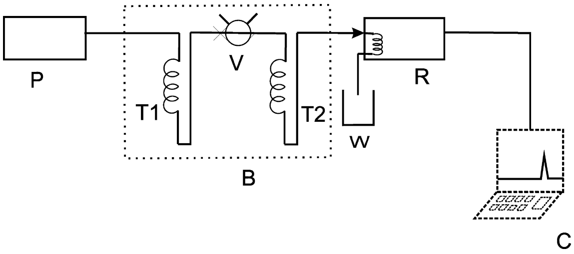

Figure 1. Taylor dispersion−diffusion measurement apparatus: P, HPLC pump; T1, preheating coil; V, six-way valve; T2, diffusion tube; B, thermostatic bath; R, conductivity and refractive index detectors; C, computer; W, waste.

$[BF_4]$) were supplied by Fluka with claimed purities greater than 95 % and 97 %, respectively.

The ionic liquids 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide—$[C_2C_1Im][Ntf_2]$ and $[C_4C_1Im][Ntf_2]$—were prepared, via ion exchange from $[C_2C_1Im][Br]$ and $[C_4C_1Im][Cl]$, by the group of Prof. Wasserscheid (University of Erlanger-Nürnberg, Germany). The ionic liquids have purities greater than 99 %, as determined by NMR analysis, with halide contents in mass fraction lower than $50 \cdot 10^{-6}$. The water content of the two ionic liquid samples, $[C_2C_1Im][Ntf_2]$ and $[C_4C_1Im][Ntf_2]$, was determined by coulometric Karl Fisher titration (Mettler Toledo DL 31) and was found to be $[(3.15 \pm 0.05)$ and $(2.9 \pm 0.1)] \cdot 10^{-3}$ in mass fraction, respectively.

The ionic liquids $[C_6C_1Im][Ntf_2]$ and $[C_8C_1Im][Ntf_2]$ were prepared at the School of Chemistry and Chemical Engineering at Queen's University Belfast. NMR analysis revealed purities greater than 99 %, and the water content, also determined by coulometric Karl Fisher titration, is of $[(1.95 \pm 0.05)$ and $(2.6 \pm 0.1)] \cdot 10^{-3}$ in mass fraction, respectively. The halide content of these liquids was determined by ion chromatography as recommended for water-immiscible ionic liquids by Villagran et al.,[10] and values of $(33 \cdot 10^{-6}$ and $15 \cdot 10^{-6})$ g of chloride per gram of ionic liquid were found for $[C_4C_1Im][Ntf_2]$ and for $[C_8C_1Im][Ntf_2]$, respectively.

Acetonitrile for HPLC from Acros Organics, methanol for HPLC from Sigma Aldrich, and distilled water were used as solvents without further purification, except for acetronitrile which was dried using 3 A molecular sieves.

2.2. Diffusion Coefficient Measurements. Diffusion coefficients were measured using the Taylor dispersion technique, in an apparatus similar to the one reported by Cussler.[11]

A concentration pulse of solute was injected into a laminar flow of solvent (maximum Reynolds number of $1.5 \cdot 10^3$), giving rise to a Gaussian concentration peak after a known length of tube (or elution time). The experimental setup used here is shown in Figure 1. A piston pump (P, ISCO model 360D) was used to provide a constant flow rate of solvent [(0.1 to 0.3) $mL \cdot min^{-1}$ as indicated by the piston pump]. A dilute solution of the solute was injected through a 20 μL sample loop of a six-port injection valve (V, Rheodyne, model 7010) into the stainless steel diffusion tube (from Supelco with an approximate length of 26 m and a stated internal diameter of 0.4 mm, forming a coil with a diameter of 44 cm). This tube was placed in a thermostatic bath B in which the temperature is controlled to within 0.1 °C by means of a temperature controller Julabo, model ED. The total uncertainty of the measured temperatures is estimated on ± 0.5 °C. The concentration profile of solute is obtained using a conductometric detector (Waters, model 432) and a refractive index detector (Waters, model 2414) placed at the extremity of the diffusion tube.

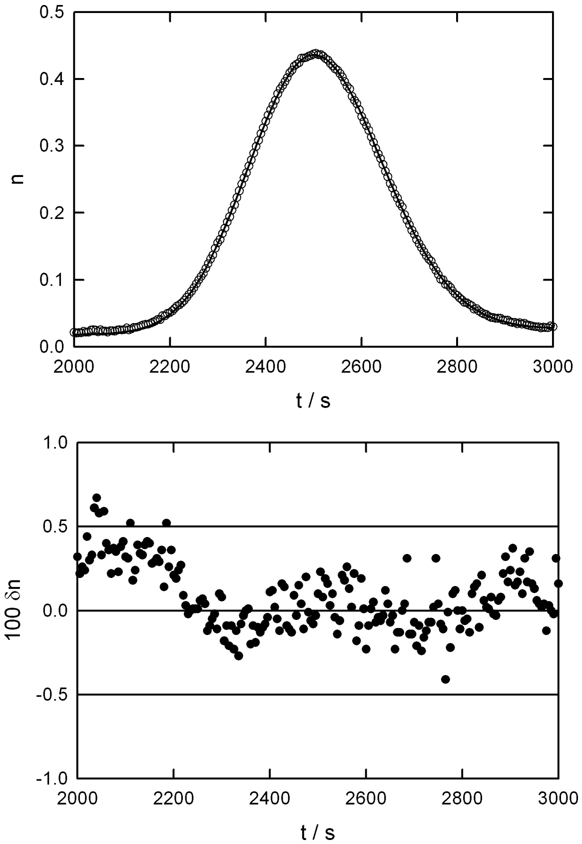

Figure 2. Curve obtained experimentally for the measurement of the diffusion coefficient of $[C_2C_1Im][Ntf_2]$ in water at 303 K. The lower plot shows the relative deviations between the experimental curve and the fitting.

The concentration of the pulse averaged across the tube's cross-section, $\bar{c}$, is given by[11]

$$\bar{c} = \frac{M}{\pi R^2 (4\pi K t)^{0.5}} \exp\left[-\frac{(L - ut)^2}{4Kt}\right] \qquad (1)$$

where M is the total mass of solute in the pulse; R is the tube's radius; L is the distance along the tube; u is the fluid's velocity, and t is the time. K is a dispersion coefficient, directly related to the diffusion coefficient, D_{12}

$$K = D_{12} + \frac{R^2 u^2}{48 D_{12}} \qquad (2)$$

The apparatus was calibrated (determination of R, the tube radius and of L, the distance along the tube) by measuring the diffusion coefficients of sodium chloride in water at 298 K. The values obtained for R and L from this calibration were used for all the experiments. The diffusion coefficient of $[C_4C_1Im][BF_4]$ in water at 303 K measured here—the value obtained is of $(1.28 \pm 0.02) \cdot 10^{-9}$ $m^2 \cdot s^{-1}$—is in good agreement with that found by Su et al.:[5] $(1.30 \pm 0.01) \cdot 10^{-9}$ $m^2 \cdot s^{-1}$. An example of an experimental plot, obtained using the refractive index detector, is depicted in Figure 2 for the diffusion of $[C_2C_1Im][Ntf_2]$ in water at 298 K. As can be observed in the lower plot, the relative deviations between the experimental points and the adjusted function (eq 1) are always lower than ± 0.3 %.

Table 1. Diffusion Coefficients of Ionic Liquids at Infinite Dilution in Different Solvents[a]

		$D_{21}/10^{-9}$ m^2·s^{-1}					
ionic liquid	solvent	283 K	298 K	303 K	313 K	323 K	333 K
$[C_4C_1Im][Cl]$	H_2O	0.83	1.18	1.32	1.66	2.01	2.40
$[C_4C_1Im][BF_4]$	H_2O	0.77	1.14	1.28	1.55	1.97	2.26
$[C_2C_1Im][Ntf_2]$	H_2O	0.61	0.89	0.98	1.27	1.55	1.85
	CH_3CN	1.79	2.29	-	2.78	3.15	3.48
	CH_3OH	1.17	1.60	-	2.03	2.30	2.69
$[C_4C_1Im][Ntf_2]$	H_2O	0.60	0.85	0.96	1.16	1.47	1.74
	CH_3CN	1.70	2.22	-	2.70	3.07	3.45
	CH_3OH	1.11	1.48	-	1.88	2.15	2.43
$[C_6C_1Im][Ntf_2]$	H_2O	0.58	0.83	0.90	1.15	1.39	1.63
	CH_3CN	1.67	2.10	-	2.51	2.74	2.99
	CH_3OH	1.05	1.34	-	1.64	1.99	2.21
$[C_8C_1Im][Ntf_2]$	H_2O	0.57	0.81	0.87	1.05	1.31	1.47
	CH_3CN	1.62	2.00	-	2.31	2.57	2.86
	CH_3OH	0.99	1.32	-	1.59	1.83	2.12

[a] The precision of the results is $0.02 \cdot 10^{-9}$ m^2·s^{-1}, as determined from the scatter of the individual data points.

Table 2. Parameters for the Arrhenius Equation Used to Smooth the Raw Data and the Standard Deviation of the Fit, $s = (\sum(D_i^{\text{exp}} - D_i^{\text{calc}})^2/n - 1)$, Where n Is the Number of Experimental Points

		E_A	D_0	
ionic liquid	solvent	J·mol^{-1}	10^{-7} m^2·s^{-1}	s
$[C_4C_1Im][Cl]$	H_2O	245 ± 1	11.0 ± 0.4	0.01
$[C_4C_1Im][BF_4]$	H_2O	245 ± 3	10.4 ± 0.8	0.02
$[C_2C_1Im][Ntf_2]$	H_2O	255 ± 2	10.8 ± 0.5	0.01
	CH_3CN	150 ± 2	1.47 ± 0.06	0.01
	CH_3OH	184 ± 2	2.6 ± 0.1	0.01
$[C_4C_1Im][Ntf_2]$	H_2O	245 ± 3	7.6 ± 0.5	0.02
	CH_3CN	159 ± 2	1.81 ± 0.08	0.01
	CH_3OH	177 ± 2	2.0 ± 0.1	0.01
$[C_6C_1Im][Ntf_2]$	H_2O	235 ± 2	5.8 ± 0.3	0.02
	CH_3CN	131 ± 2	0.79 ± 0.05	0.02
	CH_3OH	170 ± 2	1.5 ± 0.1	0.02
$[C_8C_1Im][Ntf_2]$	H_2O	214 ± 2	3.1 ± 0.2	0.02
	CH_3CN	126 ± 3	0.66 ± 0.04	0.01
	CH_3OH	170 ± 2	1.5 ± 0.1	0.02

Measurements were made from (283 to 333) K at 10 K intervals and also at 298 K. The concentration of the injected solutions was around 1 % in weight for $[C_4C_1Im][Cl]$ and $[C_4C_1Im][BF_4]$. No difference in the diffusion coefficient was noticed when changing the concentration of ionic liquid, meaning that the data are obtained at infinite dilution.

3. Results and Discussion

The results obtained are listed in Table 1. The values listed are averages of several experiments, and the overall scatter of the data points gives a precision of $(0.02 \cdot 10^{-9})$ m^2·s^{-1}, corresponding to a (1 to 2) % relative error associated with the data. The total uncertainty of the diffusion coefficients is evaluated to be ± 5 % by simple error propagation analysis taking into account the various parameters of the experimental method.

The experimental data were fitted to Arrhenius plots of the form

$$D_{21} = D_0 \exp \frac{-E_A}{RT} \tag{3}$$

where E_A represents the activation energy of the solute for diffusion. The values for E_A and D_0, together with the standard deviations of the fits, are listed in Table 2. It is observed that, for the same solvent, the activation energy does not vary significantly with the anion of the ionic liquid, whereas it significantly changes with the cation, probably meaning that the diffusivity of the ionic liquids is mainly dependent on cationic diffusion. More experimental data, on ionic liquids having different anions, are needed to definitely conclude about the mechanisms of diffusion.

Table 3. Diffusivities in Water at 298 K

ions	$D_{21}/10^{-9}$ m^2·s^{-1}
Cl^-	2.03[11]
BF_4^-	1.81
Ntf_2^-	0.87
$C_2C_1im^+$	0.91
$C_4C_1im^+$	0.83
$C_6C_1im^+$	0.79
$C_8C_1im^+$	0.76

The diffusion coefficient of an ionic liquid can be calculated from the diffusivities of the anion and of the cation from

$$D_{21} = \frac{2}{\dfrac{1}{D_{+1}} + \dfrac{1}{D_{-1}}} \tag{4}$$

where D_{+1} is the diffusivity of the cation in the solvent and D_{-1} that of the anion in the solvent. We have used the literature value for the diffusivity of chloride, $[Cl]^{-}$[11], and our experimental data for the diffusion coefficients in water at 298 K to calculate, using eq 4, first the diffusivity of $[C_4C_1Im]^+$ and then the diffusivities of all the anions and cations studied in this work. The values hence obtained are listed in Table 3. The diffusion of the different ions seems to be inversely proportional to the size of the ion, larger cations, or anions corresponding to slower molecular diffusions.

It is observed that the diffusion coefficient, for all the studied ionic liquids, is lower in water, followed by methanol and acetonitrile as illustrated in Figure 3 for the example of $[C_4C_1Im][Ntf_2]$. A first analysis of the diffusion coefficients of the ionic liquids in the solvents, on the basis of their molecular structures, can be done using the Stokes–Einstein equation

$$D_{21} = \frac{k_B T}{6\pi \eta_1 r_2} \tag{5}$$

where k_B is the Boltzmann constant; T is the temperature; η_1 is the viscosity of the solvent; and r_2 is the effective hydrodynamic

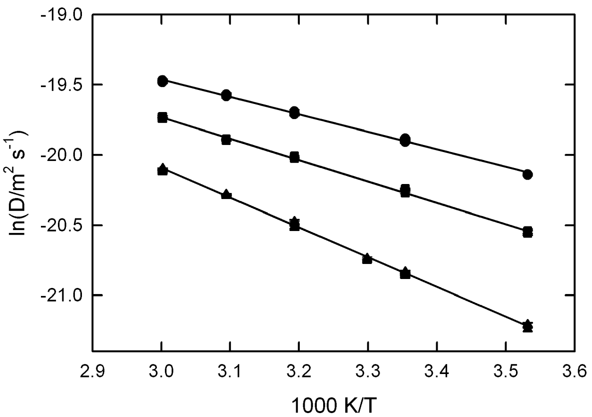

Figure 3. Diffusion coefficients of $[C_4C_1im][Ntf_2]$ at infinite dilution and as a function of temperature in the three solvents: ▲, water; ●, acetonitrile; and ■, methanol.

radius of the solute. This equation is derived from the Stokes equation (classical hydrodynamics) associated with the Einstein model for the diffusion of a spherical particle using simple kinetic theory in the limit of low Reynods number. In the present case, this equation is not valid as the diffusion coefficient for the different ionic liquids in water, acetonitrile, or methanol is not proportional to the inverse of the solvent's viscosity. For example, the diffusion coefficient for $[C_2C_1Im][Ntf_2]$ is, at 298 K, $0.89 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$, $2.29 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$, and $1.60 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$ in water, acetonitrile, and methanol, respectively. The inverse of the viscosity at the same temperature is 1.12 $mPa^{-1} \cdot s^{-1}$, 1.60 $mPa^{-1} \cdot s^{-1}$, and 1.84 $mPa^{-1} \cdot s^{-1}$ for water, acetonitrile, and methanol, respectively. The proportionality, imposed by the Stokes–Einstein equation, is not respected. Deviations from the behavior described by eq 5 have been reported for different supercooled liquids and also for ionic liquids or mixtures containing ionic liquids.[12] This breakdown of the Stokes–Einstein relation is often attributed to the existence of dynamical heterogeneities found in polymers, metallic glasses, supercooled liquids, or ionic liquids.[8]

It has been previously shown by molecular simulation[7] that the interactions between molecular compounds and ionic liquids can differ considerably. If ionic liquids are understood as structured liquids that exhibit medium-range ordering with the existence of persistent microscopic domains,[8] water will interact preferentially with the charged, polar parts of the ionic liquids, while methanol and acetonitrile will be able to interact with both polar and nonpolar regions although in different proportions. These observations explain the relative solubility of the three compounds in the ionic liquids (acetonitrile and methanol are soluble in all compositions, whereas water has mole fraction solubilities around 0.3) and are also compatible with the diffusion coefficients measured for the ionic liquids in the three liquids: the specific H-bond interactions between water and the ionic liquids lead to lower diffusion coefficients in this molecular solvent.

It is also observed that the diffusion coefficients decrease, in water, acetonitrile, and methanol, with the increasing alkyl side chain in the cation for the $[C_nC_1Im][Ntf_2]$ ionic liquids studied in this work. This behavior is depicted in Figure 4 for the three solvents studied here, an observation that can be explained by the increasing cation size and also by the interactions between the ionic liquids and the three solvents. In fact, when the alkyl side chain increases in the cation of the $[C_nC_1Im][Ntf_2]$ ionic liquids, the van der Waals interactions between the ionic liquids and the molecular solvents increase and so the diffusivity of the ions globally decreases.

The effect on the diffusion coefficients of the different anions of the ionic liquids was also studied in this work. In Figure 5 are depicted the diffusivities in water of different ionic liquids based on the $[C_2C_1Im]$ and on the $[C_4C_1Im]$ cations using data obtained here and reported by Su et al.[5] and Wong et al.[6] with different anions. For the ionic liquids based on the $[C_4C_1im]$ cation, it is observed that diffusivities in water are lower for $[C_4C_1Im][Ntf_2]$ followed by $[C_4C_1Im][BF_4]$ (with D_{21} very close to that of $[C_4C_1Im][PF_6]$[5]) and $[C_4C_1Im][Cl]$. This trend can be explained by the differences in size of the anion, larger ionic liquids diffusing more slowly than the smaller ones. For the ionic liquids based on the $[C_2C_1im]$ cation, the present data for $[C_2C_1Im][Ntf_2]$ could be compared with the values reported by Wong et al.[6] that include five different anions with quite different molecular structures. The diffusivities of the different ionic liquids do not follow in the present case a dependency with molecular weight of the different anions.

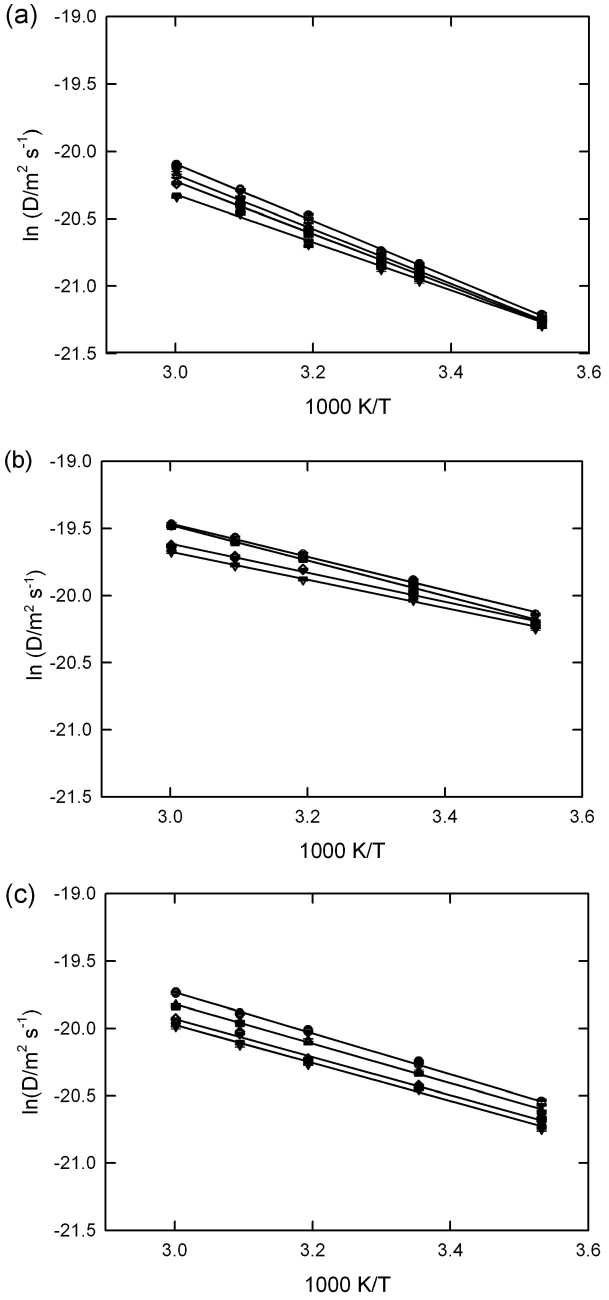

Figure 4. Diffusion coefficients in water (a), acetonitrile (b), and methanol (c) of ionic liquids based on the Ntf_2^- anion and with the cations: ○, $C_2C_1m^+$; △, $C_4C_1im^+$; ◇, $C_6C_1im^+$; ▽, $C_8C_1im^+$.

A common correlation for the diffusivity of organic compounds is the modified Wilke–Chang equation[11,13]

$$D_{21}C' \cdot \frac{(M_1)^{0.5}}{\eta_1 V_2^{0.6}} T \qquad (6)$$

where M_1 and η_1 are the molar mass and the viscosity of the solvent expressed in $g \cdot mol^{-1}$ and in $mPa \cdot s$, respectively; and V_2 is the molar volume of the solute at its normal boiling point, taken here as the molar volume of the ionic liquid studied at the experimental temperature.[2,14–16] Because the original Wilke–Chang equation underestimates the diffusion coefficients measured in this work, we have corrected the original empirical coefficient C, now designated as C', and a good agreement was

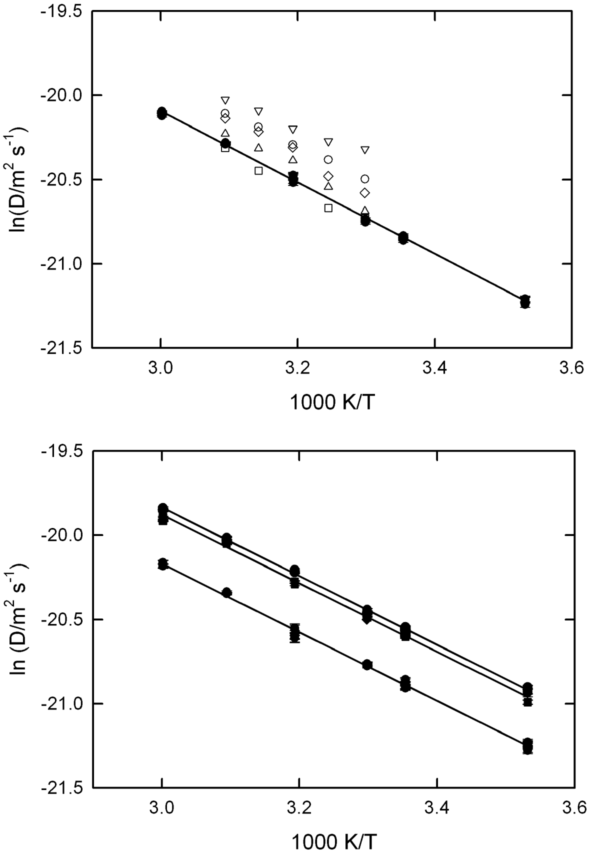

Figure 5. Diffusion coefficients in water of different ionic liquids based on the 1-ethyl-3-methylimidazolium cation, $C_2C_1im^+$ (upper plot), and on the 1-butyl-3-methylimidazolium cation, $C_4C_1im^+$ (lower plot). In the upper plot, the $C_2C_1im^+$ cation with the anions: ●, Ntf_2^-, this work; ▽, tetrafluoroborate, BF_4^-; ○, dicyanamide,[6] $C_2N_3^-$; △, ethylsulfate,[6] $C_2H_5SO_4^-$; ◇, trifluoromehtanesulfonate,[6] $CF_3SO_3^-$; □, 2-(2-methoxyethoxy)ethylsulfate,[6] $MDEGSO_4^-$. In the lower plot, the $C_4C_1im^+$ cation with the anions: △, Ntf_2^-, this work; □, BF_4^-, this work; ○, Cl^-, this work; ◆, hexafluorophosphate,[5] PF_6^-; +, tetrafluoroborate,[5] BF_4^-.

obtained with a (2 to 3) % standard deviation for the diffusivities of the different ionic liquids in the three solvents. C' was found to be independent of temperature and equal to $1.22 \cdot 10^{-7}$ for acetonitrile, $1.76 \cdot 10^{-7}$ for water, and $1.37 \cdot 10^{-7}$ for methanol. The Wilke–Chang correlation with the newly calculated parameter C' was used to correlate other diffusivities reported in the literature.[5,6] The standard deviations obtained are slightly higher than in the present case with a maximum of 9 % for the diffusion of $[C_2C_1Im][BF_4]$ in water at 303 K.[6]

We have also tried to correlate the diffusion coefficients of the different ionic liquids with their molecular weight. As is shown in Figure 6 for the diffusivities in water, the diffusion coefficients do not correlate satisfactorily with the size or weight of the solutes. Even if the correlation seems to work for ionic liquids of the same family where, for example, only the alkyl side chain of the cation varies, it completely fails when comparing the diffusivities of ionic liquids having different anions.

4. Conclusions

In this study, diffusion coefficients of several ionic liquids were measured as a function of temperature using the Taylor dispersion method. It is observed that for all ionic liquids and all solvents the diffusion coefficients follow the expected trend with temperature, the increase of the diffusivities being slightly more important in water than in acetonitrile or methanol.

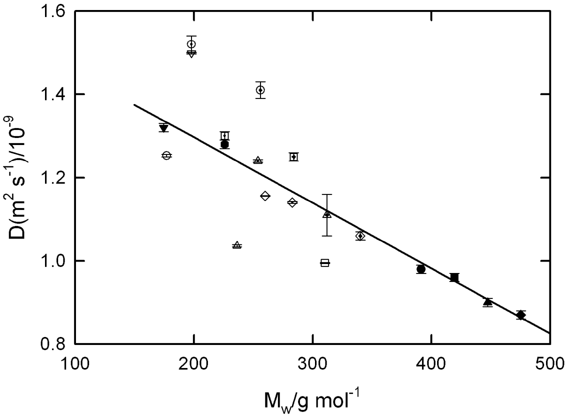

Figure 6. Diffusion coefficients in water at 30 °C as a function of the molar mass of different ionic liquids: ●, $[C_2C_1Im][Ntf_2]$, this work; ■, $[C_4C_1Im][Ntf_2]$, this work; ▲, $[C_6C_1Im][Ntf_2]$, this work; ◆, $[C_8C_1Im][Ntf_2]$, this work; ▼, $[C_4C_1Im][Cl]$, this work; ⬢, $[C_4C_1Im][BF_4]$, this work; ○, $[C_2C_1Im][BF_4]$;[5] □, $[C_4C_1Im][BF_4]$;[5] △, $[C_6C_1Im][BF_4]$;[5] ◇, $[C_8C_1Im][BF_4]$;[5] ⊙, $[C_2C_1Im][PF_6]$;[5] ⊡, $[C_4C_1Im][PF_6]$;[5] △, $[C_6C_1Im][PF_6]$;[5] ◇ with a dot in the middle, $[C_8C_1Im][PF_6]$;[5] ▽, $[C_2C_1Im][BF_4]$;[6] ○, $[C_2C_1Im][C_2N_3]$;[6] △, $[C_2C_1Im][C_2H_5SO_4]$;[6] ◇, $[C_2C_1Im][CF_3SO_3]$;[6] □, $[C_2C_1Im][MDEGSO_4]$.

The diffusivities of all the ionic liquids are lower in water followed by methanol and acetonitrile. This trend does not follow the Stokes–Einstein relation but can be explained by the solute–solvent interactions that are more significant in associating solvents like water or methanol than in polar species like acetonitrile.[7,17] It is also observed that the diffusivities decrease, for all three solvents, with the number of carbon atoms of the alkyl side chain for ionic liquids of the family of $[C_nC_1Im][Ntf_2]$. This is explained by the more important size and additional van der Waals interactions between the solvents and the ionic liquids with larger alkyl side chains.

The data obtained were correlated by a modified Wilke–Chang equation in which a correction parameter is included, independent of temperature but different for each one of the solvents studied. A simple heuristic relation between the molecular weight of the solute and the measured diffusivities fails to predict the trend found experimentally.

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