**Hydrocarbon Mass Transfer in Ionic Liquids.**

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**Highlights**

* Determination of hydrocarbon diffusion coefficients at infinite dilution in ILs
* Hydrocarbon diffusion is highly influenced by the ionic liquid viscosities
* A modified Wilke-Chang correlation successfully predicts the diffusion coefficients

**1. Introduction**

The experimental values of diffusion coefficients are of special importance in the theory of transport properties and to predict the rate-limiting factor for chemical processes and engineering design [1]. Herein, the Taylor dispersion method has been used for the first time to measure the diffusion coefficients at infinite dilution of *n*-heptane and toluene in two ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) and 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf2N]). The importance of both ILs lies in their remarkable extraction properties in the aromatic/aliphatic separation process by liquid-liquid extraction [2]. A correlation based on the Wilke-Chang equation has been proposed to estimate the diffusion coefficients that satisfactorily predicts the temperature dependence.

**2. Methods**

The experimental equipment consists of a KDS Legato 200 metering pump which provides a constant and a laminar flow, a PEEK diffusion tubing (10 m length and 0.375·10-3 m inner radius) located in a thermostatic incubator, and a Refractive Index Detector Agilent 1260 Infinity II which records the concentration gradient signal at the end of the diffusion tubing. The experiments were performed at temperatures between (298.2 and 333.2) K and a constant laminar flow of 50 L·min-1 for 20 L of samples with a hydrocarbon concentration of (0.02-0.10) mol·dm-3 in excess.

**3. Results and discussion**

Toluene presents higher values of diffusion coefficients than *n*-heptane in the [emim][DCA] IL because of the lower toluene molecular volume, meanwhile both toluene and *n*-heptane show similar values in the [4empy][Tf2N] IL due to high effect of the solvent viscosity on the hydrocarbon diffusion (Figure 1). Meanwhile at a temperature of 298.2 K the [emim][DCA] IL has a viscosity of 15.1 mPa·s, the [4empy][Tf2N] viscosity presents a much higher value of 34.5 mPa·s [3]. Therefore, the higher [4empy][Tf2N] viscosity leads to a lower influence of the solute molecular volume on the diffusion coefficients.

It has been observed that the Wilke-Chang correlation [4] does not correctly predict these diffusion coefficients; it tends to underestimate them at low temperatures and overestimate them at high temperatures, with an average deviation of 17.5%. The association parameter seems to be a nonconstant value influenced by the temperature in ILs, therefore a modified Wilke-Chang equation is proposed and expressed as:



being *φmod*(*T*) the association parameter dependent on temperature as *φmod*(*T*)=a1·*T*+a2. The modified Wilke-Chang equation correctly represents the temperature effect on the diffusion coefficients and estimates them with an average deviation of 2.6% (Figure 1).

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**Figure 1.** Diffusion coefficient at infinite dilution of *n*-heptane and toluene in [emim][DCA] and [4empy][Tf2N] ILs and dotted lines for Wilke-Chang modified correlation.

**4. Conclusions**

The hydrocarbon diffusion is faster in [emim][DCA] because of the much lower values of its viscosity, and the difference between *n*-heptane and toluene diffusion coefficients are due to their respective molecular volume. On the contrary, the high viscosity of [4empy][Tf2N] IL leads to lower and similar diffusion coefficients of both hydrocarbons, prevailing the effect of the viscosity over the effect of the hydrocarbon molecular volume. The Wilke-Chang correlation, the most common one used to estimate the diffusion coefficients, unsuccessfully predicts the temperature dependence with an average deviation of 17.5%. A modified Wilke-Chang correlation has been proposed to properly estimate the dependence of the temperature on the association parameter. This correlation has shown a good fit in the studied temperature range with an average deviation of 2.6%.

**References**

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