

## Supporting Information II

### Debye length and anionic transport properties on composite membranes based on Supported Ionic Liquid-Like Phases (SILLPS)

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## 1. Vogel-Fulcher-Tamman analysis

Once the dc-conductivity values are obtained from Nyquist diagrams, its behavior with temperature is found. So, we can see in the Figure SI-2 in the Supporting Information I, that the dc-conductivity is in agreement with a Vogel-Fulcher-Tamman (VFT) equation behavior:

$$\ln\sigma_{dc} = \ln\sigma_{\infty} - \frac{B}{(T - T_{VFT})} \quad (\text{SII-1})$$

Where B is a fitting parameter related to the curvature of the plot that may be seen as the high temperature activation energy of the process underlying the dc-conductivity,  $\sigma_{\infty}$  is the pre-factor related to the conductivity limit at high temperatures and  $T_{VFT}$  is the Vogel temperature considered as the one at which the relaxation time would diverge. The parameter B in the Vogel-Fulcher-Tamman equation, represents the deviation from the linearity of a purely Arrhenius behavior, which the experimental values present when increasing the temperature. This change in trend produces a curvature whose parameter B of the VFT adjustment wants to explain. In our work the parameter B which is related with the curvature of the plot has been well described in terms of three contributions: the free energy, the Vogel temperature and the entropic restrictions. The parameters values obtained from the fitting to Eq.(SII-1) for each temperature are summarized in Table SII-1. A close inspection of this figure shows that conductivity increases with the amount of free ionic liquid (**M5** > **M4** >> **M3**) and when the amount of crosslinking agent decreases (**M3** > **M2**  $\approx$  **M1**), which is, besides, associated to a higher content in polymer supported imidazolium moieties. It should be noted that the Vogel temperature increases for lower crosslinking degrees (**M3** > **M2** > **M1**), but decreases with the amount of free IL in the composite (**M4** > **M5**). Thus, the observed conductivity follows the order  $\sigma(M1) \approx \sigma(M2) < \sigma(M3) < \sigma(M4) < \sigma(M5)$ . For example, at 50 °C the conductivities were  $2.3 \times 10^{-6}$  S/m (**M1**),  $2.2 \times 10^{-6}$  S/m (**M2**),  $5.6 \times 10^{-5}$  S/m (**M3**),  $2.1 \times 10^{-4}$  S/m (**M4**), and  $1.2 \times 10^{-2}$  S/m (**M5**), while at 100 °C were  $2.3 \times 10^{-4}$  S/m (**M1**),  $2.4 \times 10^{-4}$  S/m (**M2**),  $2.5 \times 10^{-3}$  S/m (**M3**),  $2.1 \times 10^{-2}$  S/m (**M4**), and  $7.4 \times 10^{-2}$  S/m (**M5**).

**Table SII-1.** Vogel Fulcher-Tamman (VFT) parameters obtained from the fitting of experimental data shown in figure SI-2 to Eq. (SII-1) for the samples analyzed in this study. The values of  $\chi^2$  parameters represent the sum of the square deviations between the experimental data and theoretical values.

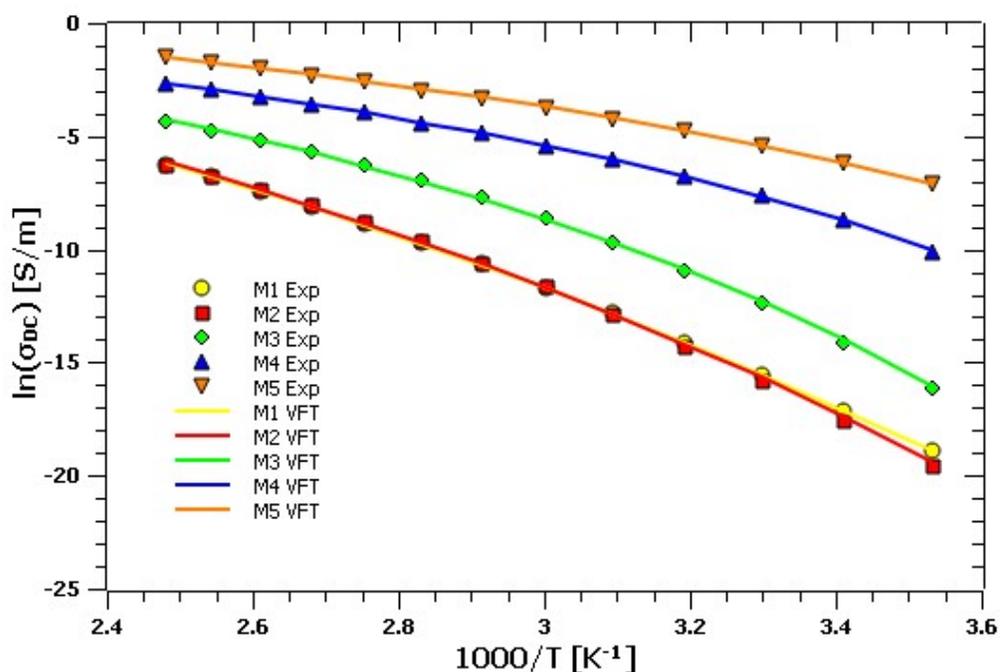
Membrane	$\ln(\sigma_\infty)$	B [ $10^3$ K]	$T_{VFT}$ [K]	$E_{act}$ [kJ mol <sup>-1</sup> ]	$\chi^2$
<b>M1</b>	9.34	4.13	137	34.30	0.05
<b>M2</b>	8.02	3.51	155	29.20	0.04
<b>M3</b>	4.60	1.86	193	15.50	0.05
<b>M4</b>	2.69	1.12	195	9.30	0.01
<b>M5</b>	3.09	1.02	183	8.50	0.01

The calculated activation energy from VFT equation ( $E_{act} = R B$ ) considering all the range of temperatures follows the trend

$$E_{act}(M1) = 34.3 \frac{kJ}{mol} < E_{act}(M2) = 31.2 \frac{kJ}{mol} < E_{act}(M3) = 15.5 \frac{kJ}{mol} < E_{act}(M4) = 9.3 \frac{kJ}{mol} < E_{act}(M5) = 8.5 \frac{kJ}{mol}$$

. Again, the lower activation energy for **M3** relative to the films **M2** and **M1** can be correlated with the increase in imidazolium units in the polymeric network and the associated decrease in crosslinking that favors an increased mobility of the polymeric chains and the ionic fragments. For **M4** and **M5**, having the same crosslinking degree, the activation energy decreases when increasing the amount of BMIM [NTf<sub>2</sub>] incorporated. It must be noted that these  $E_{act}$  values are of the order, although slightly lower, of that on related composite materials like a film similar to **M5** (12.2 kJ/mol) or a PBI membrane containing a 5% of BMIM [NTf<sub>2</sub>] (10.9 kJ/mol). These results suggest that the anionic conduction in these films can occurs following two mechanisms, the hopping between the

imidazolium units and a vehicle-type mechanism. The low activation energies displayed by the polymeric imidazolium networks containing additional BMIM [NTf<sub>2</sub>] are very attractive for their application in polymer electrolyte membranes in energy applications, as the transport mechanism is less energy demanding.



**Figure SII-1.** Temperature dependence of conductivity for the different samples studied. The lines represent the fit of experimental data following the VFT equation Eq. (SII-1).

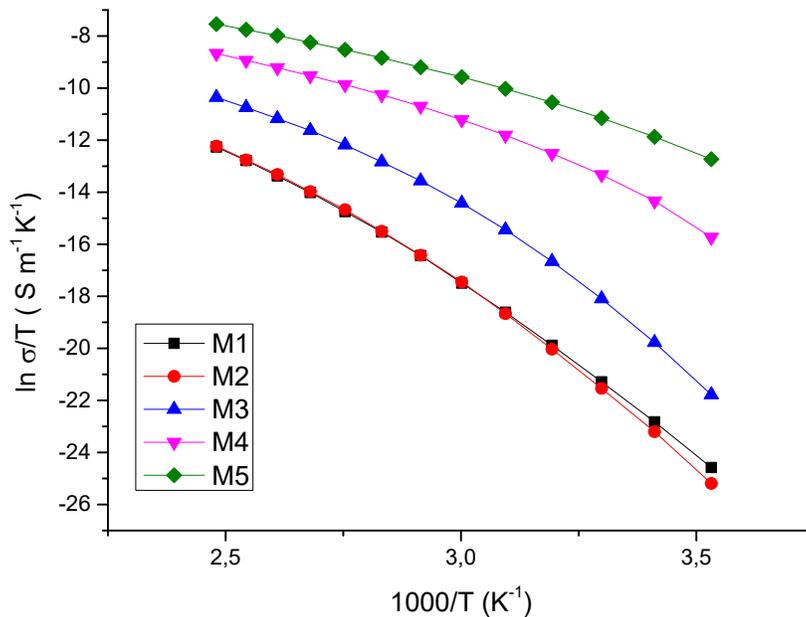
The Vogel temperature increases for lower crosslinking degrees, and decreases with the amount of free IL in the composite. From the values of activation energies obtained from VFT, it is suggesting that the anionic conduction in the films can occur following two processes, the hopping between the imidazolium units, and a vehicle-type mechanism.

## 2. Conductivity and Eyring equation

On the other hand, the temperature dependence of conductivity can be analyzed in terms of the Eyring's absolute rates theory as

$$\sigma(T) \approx C \cdot T \cdot \exp\left(-\frac{\Delta g^\ddagger(T)}{RT}\right) = C \cdot T \cdot \exp\left(\frac{\Delta s^\ddagger(T)}{R} - \frac{\Delta h^\ddagger(T)}{RT}\right). \quad (\text{SII-2})$$

Eq. (SII-2) constitutes an Arrhenius-like law in which  $\Delta g^\ddagger(T) = \Delta h^\ddagger(T) - T \Delta s^\ddagger(T)$  has been considered.  $C$  is a pre-factor that only depends of the frequency,  $\Delta g^\ddagger(T)$  is the activation Gibbs free energy of the microscopic charge conduction process in the sample,  $\Delta s^\ddagger(T)$  is related with the thermodynamic activation of entropy associated with the macroscopic structural changes of the material that give rise to entropic restrictions during the motion of the charges carrier,  $\Delta h^\ddagger(T)$  is the enthalpy change associated to the conduction process,  $T$  is the absolute temperature and  $R$  the gas constant. Since the charge transport is thermally activated, the energy  $\Delta g^\ddagger(T)$  involves the formation of the activated complex linked to ion hopping. The values of  $\Delta h^\ddagger(T)$  and  $\Delta s^\ddagger(T)$  can be obtained from the slope and the  $T$ -intercept of the plot  $\ln(\sigma/T)$  vs.  $1000/T$ , respectively, see Figure SII-2.



**Figure SII-2.** Temperature dependence of  $\ln(\sigma/T)$  for the different composite membranes. Lines are eye-guides.

