Local solvent properties of 1-alkyl-3-methylimidazolium ionic liquids

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INTRODUCTION

Room temperature ionic liquids (IL) containing 1-alkyl-3-methylimidazolium cations are well known for the mesoscopic liquid structure[1]. Their structure shows polar domains containing mostly the charged parts of the ions, and non-polar domains containing the alkyl groups. This heterogeneous structure has been linked to the peculiar solvent properties of ionic liquids, such as the ability to dissolve both polar and non-polar substances in a single solvent[2].

In this study we aim to quantify the solvent properties of polar and non-polar domains in the liquid. We do this by calculating the cohesive energy density *ced* and the internal pressure p_i of the domains. The *ced* is the square of Hildebrand's solubility parameter, and the miscibility of two substances is generally inversely proportional to the difference of their *ced*. Another measure for the stiffness of a solvent is the internal pressure p_i. Moreover, the difference between the *ced* and p_i indicates if a liquid is associated; for non-associated liquids, $p_i \approx ced$, while for associated liquids, $ced - p_i \gg 50$MPa[3].

METHODS

The ionic liquids were simulated using Molecular Dynamics simulations of 1-alkyl-3-methylimidazolium cations [$C_x$mim], with x = 2, 4, 6, 8, and nitrate [NO_3] and hexafluorophosphate [PF_6] as anions. We used the CL&P force field, which has been developed specifically for ionic liquids containing imidazolium cations[4].

The cohesive energy density is calculated from the energy of vaporization *ced* = $\Delta_V U/V$. The internal pressure was calculated in two different ways, either from its definition (the partial derivative of the internal energy with respect to the volume on an isotherm), or using the fluctuation formula for the thermal pressure coefficient γ_V:

$$p_i = T\gamma_V - p = \frac{\langle \Delta U \Delta P \rangle}{k_B T} + k_B T\rho - p$$

RESULTS AND DISCUSSION

For the non-polar domains we find *ced* values in the range 280-350MPa, which is a common range for organic liquids, but slightly higher than experimental values for *n*-alkanes. The polar domains have a much higher *ced* values which are reminiscent of molten salts.

The p_i values of the domains are similar to the *ced* values, typical for non-associated liquids. However, for the liquid as a whole, *ced*–p_i is typical for an associated liquid.

The chain length barely affects the values for the separate domains, but its effect on the liquid as a whole is large.

CONCLUSIONS

We find that the polar and non-polar domains of the ionic liquids have significantly different solvent properties. This confirms that the mesoscopic structural heterogeneities are indeed the cause of the fact that these ionic liquids are able to dissolve both polar and non-polar solutes.

ACKNOWLEDGMENTS

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