On the reason for the increased solubility of CO_2 in [C_nMIM][NTf_2] ionic liquids.

Shelepova Ekaterina A.,[1,2] Medvedev Nikolay N.[1,2*]

[1] *Physics department, Novosibirsk State University, Pirogova 1, 630090, Novosibirsk, Russia*

[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Institutskaya 3, 630090, Novosibirsk, Russia*

* *E-mail: nikmed@kinetics.nsc.ru*

Ionic liquids (ILs) have many unique properties, which explain the increased interest of researchers. In particular, one of these properties is the selectivity of the dissolution of carbon dioxide, which dissolves in ILs much better than N_2, CH_4, and O_2. Literature data show that the high solubility of CO_2 in ILs has entropic rather than enthalpic nature; i.e. it is related to the structure of the solution. The solubility of gases, in particular CO_2, in ILs is often connected with the intermolecular empty volume. In this work, we study the structure and intermolecular voids in the CO_2, O_2, N_2, and CH_4 solutions in [C_nMIM][NTf_2] ILs based on molecular dynamic simulations.

We calculated the radial distribution functions between dissolved gas molecules and various components of the ILs. It has been shown that CO_2 molecules prefer to be located mainly near the anions, and there are fewer of them near the imidazole ring than near the alkyl chains of the cations. Other gases are located near nonpolar alkyl chains, which is especially noticeable in ILs with long alkyl substituents. For all investigated gases, it is shown that the additional empty volume appears near the dissolved gas molecule. Thus, all considered gases locally loosen the ILs. At the same time, CO_2 creates a noticeably smaller amount of the additional empty volume compared to other studied gases, which are less soluble in the investigated ILs. It can be assumed that the dissolution of these gases requires larger energies to form a cavity in which the gas molecule is placed, which leads to their lower solubility. Apparently, this is the reason for the various solubilities of these gases.

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