

CO₂ absorption in protic ionic liquids

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The gas absorption and separation processes in ionic liquids (ILs) assume significant importance among the different applications of ILs. For the improvement of these processes the in depth understanding of solvation, thus, solute-solvent interactions is required. Recently the physisorbed CO₂ and its influence on the carbene formation (chemisorption) in 1-ethyl-3-methylimidazolium acetate [1, 2] were studied in our group. So far the characteristics of the CO₂ absorption in protic ionic liquids (PILs) – which can be easily synthesized via neutralization of Brønsted acid and base – remain uncovered from the microscopic point of view. Interestingly, there are many open questions concerning CO₂ absorption in PILs. For example, how do the PILs in principle dissolve and interact with CO₂? Does the PIL structure change when CO₂ enters? Do CO₂ molecules tend to be apart or aggregate, and if CO₂ clusters are formed, what is the structure of these clusters? To answer these points, we studied the CO₂ absorption by ab initio molecular dynamics simulations at the example of ethylammonium nitrate. Microheterogeneity of the alkyl chains and the extended hydrogen bond network were observed. Thus, the entire structure of the investigated PIL mixed with CO₂ resembles closely the one of the pure liquid. Our data indicates that while CO₂ most likely creates an energy loss due to entering the liquid via the too small voids, this is fully compensated by specific attractive interaction of CO₂ with the cation and anions of ethylammonium nitrate. This result might serve as an explanation for the question why the ionic liquid is not swelling through CO₂ uptake. The CO₂ cluster formation, which shows a structure similar to supercritical CO₂, is determined by the unpolar groups in CO₂ solvation shell.

[1] O. Hollóczki, Z. Kelemen, L. Könczöl, D. Szieberth, L. Nyulászi, A. Stark, B. Kirchner, *ChemPhysChem* **2013**, *14*, 315–320.

[2] O. Hollóczki, D. S. Firaha, J. Friedrich, M. Brehm, R. Cybik, M. Wild, A. Stark, B. Kirchner, *J. Phys. Chem. B* **2013**, *117*, 5898–5907.