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Multiscale modeling of ionic liquids: combined DFT, QM/MM MD and vibrational spectroscopic study

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Ionic liquids:

- + have high loading capacity 🙂;
- + thermally stable 🙂 ;
- + nonflammable 🙂 ;
- + nonvolatile 😳 ;
- highly viscous 😕
- expensive 😕

. . .



BF₄





Typical TEM and HRTEM images of the Pd nanoparticles in [Emim][BF₄] and a size histogram of the Pd-NPs.

Katsyuba et al., Chem. Phys. Chem. 2012, 13, 1781



Organometallics, 2012, 31, 1595.

- QM/MM (The simulations included a 30 Å cubic box of 125 [Mmim][BF₄] ion pairs);
- QM: TPSS-D3/def2-TZVP or PM6;
- MM: CL&P force field [from Lopes and Pádua, Theor. Chem. Acc. 2012, 131, 1].



Snapshots of the $Pd_{6}/[Mmim][BF_{4}]$ and $Pd_{19}/[Mmim][BF_{4}]$.

Zvereva et al., J. Phys. Chem. C 2016, 120, 4596



Charge probability for atoms in the Pd_6 and Pd_{19} clusters.

Zvereva et al., J. Phys. Chem. C 2016, 120, 4596



 $\mu = 13.4 \pm 1.6 D$

27.8 ± 9.7 D

 μ (Pd) = 0.5 ± 0.2 D

Zvereva et al., J. Phys. Chem. C 2016, 120, 4596







BE = 20.8 (7.9)

Binding energies in kcal mol⁻¹:

 $BE = E(substrate) + E(Pd_n)-E(substrate/Pd_n adduct)$ (in parenthesis - the London dispersion energy contribution computed within the D3 approach with the Becke–Johnson (BJ) damping function)

PBE0-D3(BJ)/def2-TZVP//TPSS-D3(BJ)/def2-TZVP COSMO

Zvereva et al., Phys. Chem. Chem. Phys. 2014, 16, 20672



Potential of mean force to displace a palladium atom from the Pd₆ cluster in vacuum and the ionic liquid. Distances are given relative to the minimum energy interaction distance

Zvereva et al., submitted to J. Phys. Chem. Lett.



Potential of mean force to displace two Pd₆ clusters in vacuum and in the ionic liquid. Distances are given relative to the minimum energy interaction distance



Zvereva et al., Russ. Chem. Bull., 2009, 9, 1812.

Fragment of the crystal structure of $[C2OHmim][PF_6]$ (**a**) and the same fragment after B3LYP/6-31G** optimization (**b**).



Katsyuba et al. J. Phys. Chem. B, 2013, 117, 9094.

[C₂OHmim][OAc]





Katsyuba et al. J. Phys. Chem. Lett., 2015, 6, 4431.

Iogansen A.V. Spectrochim. Acta, Part A 1999, 55, 1585

$$-\Delta H_{HB} [kcal \cdot mol^{-1}] = 0.29 (I^{1/2} - I_0^{-1/2})$$
$$-\Delta H_{HB} [kcal \cdot mol^{-1}] = 0.33 (vOH^{\text{free}} - vOH^{\text{bonded}})$$

Mata et al. Chem. Phys. Lett. 2011, 507, 185 $E_{HB} [kcal \cdot mol^{-1}] = 269 G_b [atomic units]$ 1/2

	O-H[PF ₆] ⁻	O-H[OAc] ⁻
R(XY)	3.118 Å	2.651 Å
ALL STOR		
νΔΟΗ	92 cm ⁻¹	692 cm^{-1}
	$E_{\rm HB} \sim 3.4 \ \rm kcal \cdot mol^{-}$	$E_{\rm HB} \sim 10.4 \rm kcal \cdot mol^{-1}$
ρ_{b}	0.015 a.u.	0.052 a.u.
	$E_{\rm HB} \sim 3.4 \rm kcal \cdot mol^{-1}$	$E_{\rm HB} \sim 10.2 \text{ kcal} \cdot \text{mol}^{-1}$

Conclusions

- The IL induces a strong polarization in palladium clusters
- The clusters have large induced dipole moments and, as a result, interact strongly with the IL.
- This results in an accumulation of the IL layer of high density around the clusters. The interface layer of *ca*. 3.5 Å thickness has a negative charge on the inner surface composed mainly of anions and an outer positive charge provided by the cations.
- A single palladium atom does not show any noticeable preference for the positive or negative ions and interacts only very weakly with the IL
- The absolute energy of aggregation of the clusters is larger than the difference in the interaction energies of smaller clusters which implies that stabilisation of Pd-NPs in the IL is due to kinetic stabilisation rather than thermodynamic stabilisation

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Thank you for your attention!