Peculiarities of HCl sorption from air by weak base anion exchanger with ethylenediamine functional groups: experimental study and DFT simulation

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Motivation:

Fibrous ion exchangers are successfully used to purify air from different toxic compounds, including HCl [1, 2]. At the same time, literature data on the features of interactions and structural characteristics of sorption complexes "functional group - water molecules - HCl" are scarce. Here we present the results of an experimental investigation of HCl sorption from air by polymeric anion exchanger on the base of polyacrylonitrile fiber with ethylenediamine functional groups (PAN-EDA), and computer simulation of the structures of HCl sorption complexes with amino groups of this anion exchanger.

From experimental sorption results it was established Fig.1:

1) **critical relative air humidity for PAN-EDA ion exchanger in the processes of HCl sorption from air is 25-30%;**
2) **the maximum HCl sorption value exceeds the anion exchange capacity (SmaxHCl = 5.2 mmol/g; Ebase = 4.0 mmol/g), i.e. superequivalent sorption is observed.**

? What is the main reason of critical humidity?

? What is the mechanism of superequivalent sorption?

! The main Gole: resolve of this tasks using DFT simulation !

Our approach :

The sorption of HCl by fibrous anion exchanger was studied under dynamic conditions in a wide range of relative air humidity, HCl concentration and thickness of the sorption layer passing the gas-air mixture through a sorption cell in which an ion exchanger of known mass is placed.

For computer DFT simulation DFT/B3LYP/D3/6-31G(3d ,p) level of theory and Firefly (PC GAMESS) software package were used.

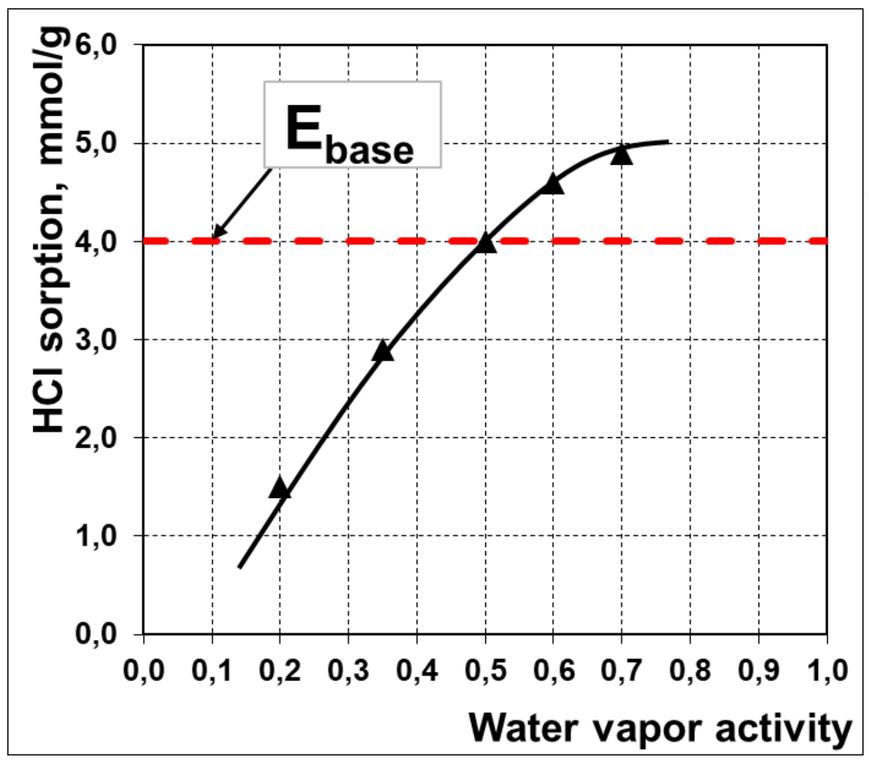

Fig.1 Sorption of HCl by ion exchanger PAN-EDA as a function of relative air humidity. Experimental conditions: temperature 20-22°C; thickness of the filtering layer 9-10 mm; air flow velocity through the filtering layer 0,1m/s; initial HCl concentration 55-57 mg/m³.

Models of sorption complexes consisting of two functional groups (PAN-2EDA) and a variable number of water and HCl molecules were chosen for DFT simulation. The geometric characteristics of sorption complexes PAN-2EDA+nH_2O+mHCl (n-number of water molecules (from 2 to 14); m-number of HCl molecules (from 1 to 6)) with functional groups of anion exchanger have been found (Fig.2).

Results of Structural Properties Calculation

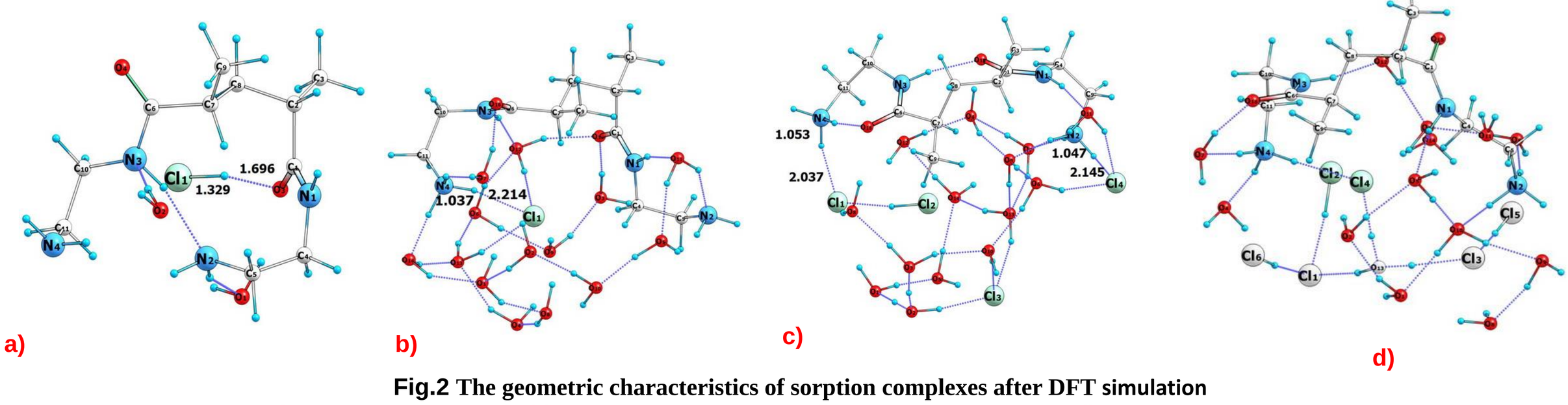

Fig.2 The geometric characteristics of sorption complexes after DFT simulation

a) PAN-2EDA+2H_2O+1HCl b) PAN-2EDA+14H_2O+1HCl c) PAN-2EDA+14H_2O+4HCl d) PAN-2EDA+14H_2O+6HCl

Conclusion

It was established:

1) **dissociation of first HCl molecules in the phase of PAN-EDA ion exchanger with the transfer of protons to the N atoms of the terminal aminogroup occurs at a water content 2-3 H_2O molecules per functional group, which corresponds to the value of critical air humidity in the sorption experiment;**
2) **at a maximum water content (6-7 H_2O molecules per functional group) and the maximum number of HCl (4-6) structuring of the system is observed: non-covalent bonds are formed between HCl molecules with formation of HCl chains which explains the superequivalent sorption observed in sorption experiments.**

[1] Soldatov, V.S. Ion exchangers for air purification / V.S. Soldatov, E.G. Kosandrovich // Ion Exchange Solvent Extraction, A series of advances, A.K. Sengupta (Ed.). – USA: CRC Press Taylor and Francis Group, 2011. – Vol. 20. – P. 45–117.

[2] Kosandrovich, E.G. Fibrous ion exchangers / E.G. Kosandrovich, V.S. Soldatov // Ion exchange technology I: theory and materials, Inamuddin and Mohammad Luqman (Eds.). – UK: Springer, 2012. – P. 299–371.