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www.elsevier.com/locate/memsci

PII: S0376-7388(17)31036-0
DOI: http://dx.doi.org/10.1016/j.memsci.2017.06.053
Reference: MEMSCI15365

To appear in: *Journal of Membrane Science*

Received date: 11 April 2017
Revised date: 20 June 2017
Accepted date: 21 June 2017

Cite this article as: Matteo Minelli, Donald R. Paul and Giulio C. Sarti, On th interpretation of cryogenic sorption isotherms in glassy polymers, *Journal o Membrane Science,* http://dx.doi.org/10.1016/j.memsci.2017.06.053

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On the interpretation of cryogenic sorption isotherms in glassy polymers

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Abstract

Sorption data of nitrogen, argon and krypton in different glassy polymers at different cryogenic temperatures are analyzed, including hydrogen in PIM-1; conventional and high free volume glassy polymers are included. A consistent interpretation of experimental data is obtained by considering penetrant dissolution in a uniform dense glassy polymer, undergoing volume swelling with all penetrants but hydrogen. All the data are properly described by using the NELF model which is appropriate for the solubility in glassy polymers. Remarkably, in each polymer the sorption isotherms of different penetrants are described well by using the same initial polymer density, and the same swelling coefficient value allows satisfactory description of the sorption behavior of one penetrant at different temperatures. For PIM-1, NELF model and molecular dynamics give exactly the same swelling, and desorption after sorption or subsequent sorption-desorption cycles show hysteresis effects clearly associated to irreversible volume changes; in addition, hydrogen sorption in PIM-1 is fully predicted by the NELF model, simply based on nitrogen sorption, as opposed to BET theory. On the bases of the above results the conclusion is drown that BET theory is not applicable to the cryogenic sorption isotherms in glassy polymers.

Keywords: Glassy polymers, polymers of intrinsic microporosity, cryogenic sorption, gas solubility, NELF model

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