Confirmation of the Nanopore Inner-Sphere Enhancement (NISE) Theory Using Flow Calorimetry and EPR

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Introduction
Recent research into the adsorption of cations on zeolite minerals shows that nanopore channels ≤0.5 nm can enhance the adsorption of ions, especially weakly hydrated ones.1,2 This occurs due to the removal of hydrating water molecules inside the small nanopore channel. A new adsorption theory, called the nanopore inner-sphere enhancement (NISE) theory explains this unusual adsorption mechanism. The NISE theory has been confirmed for Na adsorption on various zeolites using NMR spectroscopy.3

NISE Theory: The ability of an ion to adsorb on an adsorption site located inside a nanopore channel will significantly increase if the ion’s ability to dehydrate is enhanced by the physical environment of the adsorption site.

Monovalent ions will generally adsorb weakly due to the weak electrostatic attraction to the adsorption sites. The NISE theory predicts that monovalent ions will adsorb strongly if the adsorption site is located inside nanopore channels with channel dimensions small enough to weaken the ion’s ability to stay hydrated. The hydration energies of monovalent ions are generally already quite weak to begin with.

Divalent ions generally adsorb strongly on due to their strong electrostatic attraction. The nanopore channels will not easily stabilize the dehydrated divalent cation unless the channel dimensions are very small. This is because the hydration energies of divalent ions are generally quite strong. In very small nanopore channels, the divalent ions will dehydrate and their adsorption strength will increase significantly. Accordingly, the NISE theory explains why the adsorption of monovalent cations outperforms the adsorption of divalent cations on adsorption sites located in medium-sized nanopore channels.

Objectives:
1) Monitor the heat of reaction of Na-Ca ion exchange reactions, and
2) Confirm the predictions made by the NISE theory concerning inner-sphere and outer-sphere adsorption mechanisms by divalent cations as a function of pore channel dimensions.

Materials & Methods
Zeolite Y (FAU)
Pore dimensions: 0.74 nm x 0.74 nm
Surface area: 700 m$^2$ g$^{-1}$
SiO$_2$:Al$_2$O$_3$ Ratio: 80:1

ZSM-5 (MFI)
Pore dimensions: 0.51 nm x 0.55 nm
0.53 nm x 0.56 nm
Surface area: 425 m$^2$ g$^{-1}$
SiO$_2$:Al$_2$O$_3$ Ratio: 80:1

Mordenite (MOR)
Pore dimensions: 0.70 nm x 0.65 nm
0.26 nm x 0.57 nm
Surface area: 500 m$^2$ g$^{-1}$
SiO$_2$:Al$_2$O$_3$ Ratio: 90:1

NOTE: Zeolite nanopores are interconnected and ions can move freely between different pore channels.

Flow Adsorption Calorimetry (FAC) Study
Room temperature. Used 45 to 100 mg of solid saturated with 10 mM Ca(ACO)$_3$ at pH=5.35 carrier solution. Injection of 20 mM NaACO at pH = 5.40.

Electron Paramagnetic Resonance (EPR) Study
Samples: Zeolite slurry with 20 mM Na plus 20 mM of Cu$^{2+}$ at pH 2.5 or Mn$^{2+}$ at pH 5.3. Solids concentration was 0.5 g, equilibrated overnight, centrifuged, liquid decanted and water washed once. The solids were analyzed on a Bruker 380E X-band EPR spectrometer at 9.779 GHz.

Citations:

Flow Calorimetry
Heat of exchange of Ca by Na (red) followed by heat of exchange of Na by Ca (black) on various zeolites.

ZSM-5 Na ads. is strong & endothermic. Ca ads. is weak & exothermic. Notice exotherm at 15 min; this is a unique feature of this size range.

Mordenite
Strong Na & Ca adsorption. Similar strength & pattern for both.

Explanations:
Adsorption and dehydration are endothermic. Na/Ca exchange is entropy (ΔS) driven.
Desorption andhydration are exothermic. Ca/Na exchange is enthalpy (ΔH) driven.

Outer sphere adsorption is weak: Na & Ca on zeolite Y Ca on ZSM-5
Inner sphere adsorption is strong: Na on ZSM-5 Na & Ca on mordenite

Conclusions
• NISE theory is consistent with flow calorimetry for Na$^+$-Ca$^{2+}$ ion exchange and EPR spectra for Mn$^{2+}$ and Cu$^{2+}$.
• Flow calorimetry also captures a small exotherm that was reproduced on all ZSM-5 samples. This may be a signature heat exchange feature in medium sized pore channels for inner-sphere outer-sphere exchange.
• EPR spectra of Cu$^{2+}$ on ZSM-5 suggests that the hydration energy of divalent cations is not a perfect predictor of the ease of dehydration of ions in constrained environments. Cu ions are subject to the Jahn-Teller effect, which causes a distortion in the coordination of its hydration sphere.

EPR spectra of Mn on zeolite Y and ZSM-5 are similar to spectra of aqueous Mn. This indicates adsorption is outer sphere. Spectrum broadening of Mn on mordenite is asymmetrical. This indicates a strong surface inner sphere interaction.