Supporting Information

A) Endothermicity of the competitive adsorption of cationic surfactants from aqueous solution

To find an explanation for the endothermic character of cadmium adsorption, some ideas may be searched in the comparison between the present system and that containing cationic surfactants at the solid-liquid interface. The presence of less or more extended endothermic domains on the curves representing the enthalpy of displacement as a function of the amount adsorbed was frequently observed in the case of the adsorption of surfactant cations onto nonporous and mesoporous silica or aluminosilicate materials. The endothermic effect at low surface coverage ratios was mainly ascribed to displacing and destructuring of vicinal water which accompanied the hydrophobic attachment of the surfactant tails to a hydrophobic surface or/and the formation of the primary surface-bound aggregates from the adsorbed surfactant units. The depth and the extent of the hydrophobic domains were related to the hydrophilic-hydrophobic character of the solid supports and thereby the easiness of their surface dewatering. It should be emphasized here that the total surface enthalpy of MCM-41 silica and aluminosilicates, as well as the enthalpy of immersion in water per sq.m, were found to be small in comparison with typical nonporous silica or alumina. Furthermore, the enthalpy of immersion in water was increased from -131 to -180 mJ m⁻² when the pore size changed from 1.8 to 3.7 nm for samples belonging to the same homologous series. For some systems, ion exchange between surface-active cations and some exchangeable co-ions pre-adsorbed at the solid-liquid interface was also postulated to contribute to the decreased exothermicity of the displacement process.

Since Cd²⁺ has no a hydrophobic tail and does not form surface aggregates at the solid-liquid interface, the endothermicity of the adsorption process or the marked difference between the nonporous reference and the mesoporous samples cannot be explained on the basis of only surface dewatering. Ion exchange accompanied by changes in the hydration layers of the adsorbing and desorbing cations may be further considered as responsible for the endothermic character of the overall displacement process.
B) Effect of adsorbent porosity on the charging behavior of mineral oxides

The effect of adsorbent porosity on the charging behavior of mineral oxides (i.e., the location of the point of zero charge PZC, the density and variation of the pH-dependent surface charge) has been the subject of much debate in the literature and some contradictory results have been reported. It seems logical to review the various hypotheses when trying to rationalize the adsorption and calorimetry results obtained in the present study.

Based on such surface ionization models as the MUSIC one proposed by Hiemstra et al.\(^4\), it is clear that determination of the acidity constant for surface hydroxyl (OH) groups (i.e., surface pK\(_a\)), and thus the value of PZC, depend solely on the OH coordination. Since this procedure is sensitive only to the chemical composition and crystalline structure of the solid surface, results should be unaffected by the pore size. Except the data described by Zhuravlev\(^5\) who reported values ranging from 4.0 to 6.1 OH sites per sq. nm for about 100 amorphous silicas, the values obtained by other researchers are much more dispersed\(^6\). The discrepancies observed are probably due to some variations in the fraction of crystalline faces exposed on the surface or /and changes in the crystalline character of the silica walls in mesoporous materials.

Even though many researchers agree that the location of the PZC is hardly affected by the pore size\(^7\)-\(^9\), there is no unanimity of opinion about the influence of the porosity on the surface charge. Baca et al.\(^7\) gave evidence for the little significant change in the surface charge density (i.e., charge number per sq. m) at a fixed pH when passing from non porous to macroporous alumina, in line with the hypothesis of the pore-size independency of the surface charge for a given solid material. This conclusion was at variance with the work by Wang et al.\(^9\) where the surface charge of commercial alumina particles was demonstrated to be enhanced for a mesoporous material. This was verified by Abdullah et al.\(^10, 11\) who ascribed the weak surface acidity of synthetic mesoporous silicas to silanol groups at the inner walls of materials, the number of which correlated well with the degree of mesoporosity. This finding was confirmed by Zhmud\(^12\) who developed a charge regulation model for the surface of porous matrices with cylindrical pores and predicted a decrease in the surface charge with decreasing pore size.
Concerning the surface effect of the confined geometry on the adsorption mode of mineral ions on the oppositely charged surfaces, simulation or molecular modeling studies anticipated the important impact on the adsorption constants $^7$ or sorption coefficients $^9$. In consequence, one may expect that the formation of ion pairs between the adsorbing ions and the surface charged sites through specific interactions (surface complexation) should be more favorable in smaller pores. Zhmud $^{13}$ argued that changes in the solution permittivity close to the solid surface may affect the association constant ($K_{as}$) of each ion pair, thereby resulting in the inner sphere adsorption. According to Wang et al. $^8$, the change in the sorption coefficient should be attributed to the decreased water activity within a nanopore, being responsible for a decrease in the ion hydration and the concomitant increase in the tendency towards inner-sphere complexation.
REFERENCES