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THERMODYNAMICS OF ORGANIC CATION EXCHANGE SELECTIVITY IN SMECTITES

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Abstract—The selectivities of clay minerals for larger organic cations over smaller ones have been attributed to favorable clay-organic interactions in clay interlayers and to hydrophobic effects resulting from (partial) dehydration of organic cations in the clay interlayers, but the magnitudes of these energy components have not been estimated. The objective of this study was to differentiate and quantify the contributions of clay-phase and aqueous-phase energy changes to the overall thermodynamics of cation exchange, and thereby to determine which forces control the general selectivity of smectites for organic cations. We compiled literature measurements and estimates for the free energies of overall cation exchange reactions and also for the free energies of organic cation hydration. Our study suggests that organic cation-exchange thermodynamics can be broken into three classes: (1) For two organic cations with identical head-groups, the difference in their cation exchange selectivities is driven almost quantitatively by the difference in their free energies of hydration. Here, the mechanism for organic cation selectivity is almost pure hydrophobic expulsion of the larger cation from water. The clay interlayer simply behaves like a subaqueous phase into which the least hydrophilic organic cations partition and the essentials of such cation exchange selectivity can be explained without any favorable clay-organic interactions. (2) For two organic cations with rather different head-groups, the difference in their cation exchange selectivities is just a small percentage of the difference in their free energies of hydration. This indicates that the clay phase interacts much more strongly with the cation having the smaller head-group, as might be expected on the basis of simple electrostatics. Here, the clay has an intrinsic strong preference for the cation with smaller head-group yet 'selects' for the cation with larger head-group because the aqueous-phase preference for the cation with smaller head-group is even stronger than the clay preference. (3) When the clay is already substantially loaded with organic cations, then van der Waals forces apparently can play a significant role in determining organic cation exchange selectivity differences.

Key Words—Cation Exchange, Enthalpy, Entropy, Free Energy, Hydration Energy, Smectites, Thermodynamics.

INTRODUCTION

Cation exchange is, by definition, a selectivity of the clay mineral adsorbent phase for one cationic adsorbate over another. Smectites, the swelling clay minerals, adsorb organic cations very readily and are broadly selective for organic cations over inorganic. In comparing aqueous organic cations of a given valence, smectites tend to be selective for larger organic cations over smaller and for more branched over less branched (Cowan and White, 1958; Theng *et al.*, 1967; Vansant and Uytterhoeven, 1972; Vansant and Peeters, 1978; Maes *et al.*, 1980; Maes and Cremers, 1986; Mizutani *et al.*, 1995). Organic cation sorption by clays has been reviewed several times (Mortland, 1970; Theng, 1974; Lagaly, 1984; Barrer, 1989; Johnston, 1996). Hypotheses regarding the operant causes of smectite cation exchange selectivity among organic cations include: the stronger van der Waals forces between the smectite surface and the larger, selected cation (Cowan and White, 1958; Theng *et al.*, 1967; Theng, 1974); differences in interlayer hydration status; and electrostatic interactions (Vansant and Uytterhoeven, 1972; Maes *et al.*, 1980), or a combination of all these factors (Maes *et al.*, 1977; Vansant and Peeters, 1978). The van der Waals stabilization within the smectite interlayer was thought to occur through alkyl tail-tail interactions and/or favorable tail-clay interactions (Cowan and White, 1958; Theng *et al.*, 1967; Zhang *et al.*, 1993; Mizutani *et al.*, 1995). Thus, the early concept was that the smectite selects the cation with which it has the most energetically favorable surface interactions.

As organic cation size increases, charge delocalization spreads the cationic charge over a larger molecular volume and makes hydration less favorable (Maes *et al.*, 1980). As sorption of organic cations seems to partially dehydrate smectite interlayers (Maes *et al.*, 1977), the larger, more poorly hydrated cations are selectively adsorbed in the interlayer space (Maes *et al.*, 1980; Maes and Cremers, 1986). Maes *et al.* (1980) realized that hydration energy changes in solution, too, are included in organic cation exchange and in fact 'determine the selectivity order'. Mizutani *et al.* (1995) emphasized this point by demonstrating that the smectite selectivity order for a series of organic cations from water was reversed when the experiments were done in dimethyl sulfoxide

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Table 1. Thermodynamic terms for the cation exchange of ethyl-(EBTMA^{2+}), hexyl-(HBTMA^{2+}), and decyl-α,ω-bistrimethylammonium (DBTMA^{2+}) for inorganic cations on Camp Berteau montmorillonite, derived terms for exchange reactions among the organic cations, and the d_{001} spacings of each wet, organically exchanged clay. Data are adapted from Maes *et al.* (1980).

Cation exchange reaction	ΔG^{a}	ΔH^{a}	ΔH^{b}	$-T\Delta S^{a}$	d_{001} (Å)
	(kJ/mol)				
EBTMA^{2+} for Na^{+} or Ca^{2+}	−17.06[c]	−14.84	−12.96	−2.22	14.4
HBTMA^{2+} for Na^{+} or Ca^{2+}	−19.48	−18.14	−15.72	−1.33	14.2
DBTMA^{2+} for Na^{+} or Ca^{2+}	−22.20	−20.48	−17.72	−1.72	14.3
[HBTMA^{2+} for EBTMA^{2+}][d]	−2.4	−3.3	−2.8	+0.9	14.2
[DBTMA^{2+} for EBTMA^{2+}][d]	−5.1	−5.6	−4.8	+0.5	14.3

[a] Computed from data on organic cation exchange with Ca-smectite.
[b] Computed from data on organic cation exchange with Na-smectite. The observed ΔH when Na^{+} exchanges for Ca^{2+} is ~+2.8 kJ/mol (Maes and Cremers, 1980), in good agreement.
[c] Misprint in the original said −17.26 kJ mol^{-1}.
[d] Energy terms computed from the organic-inorganic cation exchange data by difference.

or acetonitrile. Thus, organic cation exchange selectivity was seen at least partially as a hydrophobic interaction (Mizutani *et al.*, 1995), only partially dependent on attractive clay-cation interactions.

Given these developments, we have two sharply contrasting perspectives on organic cation selectivity: how much of the selectivity is due to favorable cation-surface interactions and how much is due to unfavorable cation-solvent interactions? The objective of this study was to quantify the contributions of clay-phase and aqueous-phase changes to the overall thermodynamics of cation exchange and thereby to determine which forces and phases control the general selectivity of smectites for larger organic cations over smaller.

METHODS

Thermodynamic data for the overall cation exchange process were taken from the literature. Direct measurements of organic cation exchange thermodynamics are elusive (Mizutani *et al.*, 1995), but some appropriately systematic indirect datasets exist. For example, α,ω-bistrimethylammoniumalkane cations readily replace inorganic cations such as Na^{+} and even Ca^{2+} (Table 1, Maes *et al.*, 1980). The free energy change when ethyl-α,ω-bistrimethylammonium (EBTMA^{2+}) exchanges for Ca^{2+} on the Camp Berteau montmorillonite is −17 kJ mol^{-1} and increases to −22 kJ mol^{-1} when decyl-α,ω-bistrimethylammonium (DBTMA^{2+}) replaces Ca^{2+} (Maes *et al.*, 1980). Assuming that free energy relationships are independent of path, one can use such data to derive thermodynamic terms for exchange between organic cations themselves (Table 1). The hypothesis that the exchange reactions are thermodynamically reversible and therefore independent of path is supported by: (1) the fair agreement of the enthalpic terms calculated by difference of the two independent sets of organic-inorganic experiments (Table 1) with the expected value of +2.8 kJ mol^{-1} for Na-Ca exchange (Maes *et al.*, 1980); and (2) the reasonable agreement (Table 1) of the enthalpies for organic-organic exchange calculated from the Na^{+} *vs.* the Ca^{2+} data. This is interesting in light of observations (Zhang *et al.*, 1993) that almost no hexadecyltrimethylammonium (HDTMA^{+}) desorbed after 180 days in 0.1 N NaCl, KCl or CaCl$_2$, indicating that the organic-for-inorganic exchange reactions are not in fact reversible. The present study will only analyze organic-for-organic cation exchange reactions, which are much more reversible (Mizutani *et al.*, 1995).

The negative free energies in Table 1 agree with the general concept that smectites select larger organic cations over smaller ones (*i.e.* DBTMA^{2+} would readily exchange for EBTMA^{2+} on smectite clays). The overall drivers of the reaction seem to be enthalpic (Maes *et al.*, 1980), with entropy making a relatively small overall contribution (Table 1). However, previous studies (Vansant and Uytterhoeven, 1972) of alkylammonium cation exchange on this same Camp Berteau montmorillonite had found that the exchange of methyl-(MA^{+}) through butyl-ammonium (BA^{+}) cations for Na^{+} was governed entirely by entropy. Enthalpic and entropic contributions will be discussed further below.

In order to estimate the energy changes taking place in the solution phase, and as no direct measurements of energies of hydration for EBTMA^{2+} or DBTMA^{2+} were found in the literature, careful estimates from a literature review (Plyasunov and Shock, 2000) were used (Table 2). The group-additivity estimates of Table 2 imply that the free energy of solvation for DBTMA^{2+} should be ~+6 kJ mol^{-1} relative to that for EBTMA^{2+} (*i.e.* eight methylene groups times 0.72 kJ mol^{-1} each). The enthalpy of solution for DBTMA^{2+} should be ~−30 kJ mol^{-1} (*i.e.* eight -CH$_2$- times −3.76 kJ mol^{-1} each) relative to that for EBTMA^{2+}, and the entropic contribution ($-T\Delta S$) to the hydration energy for

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Table 2. Literature estimates for changes in the thermodynamics of aqueous solvation associated with adding one methylene carbon to an arbitrary organic compound. All energy terms were derived using an ideal gas reference state. The first row estimates (Plyasunov and Shock, 2000) were used in the present study and the two older estimates are presented for comparison.

ΔG (kJ/mol)	ΔH (kJ/mol)	$-T\Delta S$ (inferred, kJ/mol)	Literature reference
0.72 ± 0.06	-3.76 ± 0.22	4.48 ± 0.23	(Plyasunov and Shock, 2000)
0.74	−3.24	3.98	(Cabani *et al.*, 1981)
0.61 to 1.03	−2.82 to −3.83	~4.3	(Abraham, 1984)

DBTMA^{2+} should therefore be ~36 kJ mol^{-1} more positive than that for EBTMA^{2+}. Thus, the increasingly unfavorable free energy of aqueous solvation as the alkyl chain gets longer is mainly an entropic effect, with an unfavorable entropy change overcoming a rather favorable change in enthalpy of hydration (Plyasunov and Shock, 2000).

A few estimates for the free energies, enthalpies, or entropies of hydration for relevant organic cations exist in the literature, and are detailed in Table 3 for the purposes of assessing the applicability of Table 2 to organic cations. In the hydration of alkylammonium cations (Table 3), the trend to less negative ΔG values as the alkyl chain lengthens is consistent with Table 2, though the magnitudes of the changes tend to be larger in Table 3 than predicted by Table 2. It has been pointed out that simple group additivity concepts (Table 2) tend to have difficulty for alkyl chain lengths of three or less (Plyasunov and Shock, 2000), and this seems quite reasonable here considering that the molecules are cationic. Thus, if we define $\Delta\Delta G_{21}$ to be the differences in free energy of hydration between alkylammonium cations with chain length $n = 2$ (*i.e.* $CH_3CH_2NH_3^+$ which we will denote EA$^+$) and $n = 1$ (*i.e.* $CH_3NH_3^+$ or MA$^+$), then $\Delta\Delta G_{21} = +15$ kJ mol^{-1}, $\Delta\Delta G_{32} = +6$ kJ mol^{-1}, and $\Delta\Delta G_{43} = +2$ kJ mol^{-1} (Table 3). These values thus seem to be approaching (asymptotically?) the 0.7 kJ mol^{-1} value listed in Table 2, even though this value was derived for the addition of -CH$_2$- groups to neutral organic molecules.

Note that the enthalpy of hydration for $(CH_3CH_2)_4N^+$ is actually less negative (Table 3) than that of $(CH_3)_4N^+$. Again, this may be due to steric interference of the ethyl groups significantly impeding (compared to the methyl groups) efficient hydration of the cationic center. Upon moving out to the longer alkyl chain lengths, the enthalpy of $(CH_3CH_2CH_2CH_2)_4N^+$ is ~21 kJ mol^{-1} more negative than that for $(CH_3CH_2)_4N^+$ (Nagano *et al.*, 1991). While the ethylene chains may still be too short to provide a valid comparison, this difference compares with a prediction (Table 2) of −30 kJ mol^{-1} for the ΔH of $(CH_3CH_2CH_2CH_2)_4N^+$ *vs.* $(CH_3CH_2)_4N^+$.

In estimating the entropic effect of adding four -CH$_2$- groups to an organic cation, the estimates from Table 3 are 23 to 31 kJ mol^{-1} while Table 2 predicts the difference should be 18 kJ mol^{-1}. The imperfect agree-

Table 3. Literature estimates for thermodynamic terms (all relative to an ideal gas reference state at 298 K and in kJ mol^{-1}) pertaining to the hydration of organic cations.

Cation	ΔG	ΔH	$-T\Delta S$
$CH_3NH_3^+$	−320[a] and −310[b]	−331[b]	+21[b] and +28[c]
$(CH_3)_2NH_2^+$	−287[a] and −285[b]	−305[b]	+20[b]
$(CH_3)_3NH^+$	−256[a] and −262[b]	−280[b]	+18[b]
$(CH_3)_4N^+$	−219[d]	−251[e]	+43[f]
$CH_3CH_2NH_3^+$	−305[a]		
$CH_3CH_2CH_2NH_3^+$	−299[a]		
$CH_3CH_2CH_2CH_2NH_3^+$	−297[a]		
$(CH_3CH_2)_2NH_2^+$	−264[a]		
$(CH_3CH_2)_3NH^+$	−229[a]		
$(CH_3CH_2)_4N^+$	−183[d]	−239[e]	+66[f]
$(CH_3CH_2CH_2)_4N^+$			+97[f]
$(CH_3CH_2CH_2CH_2)_4N^+$		−260[g]	

[a] (Pliego and Riveros, 2002)
[b] (Florian and Warshel, 1997)
[c] (Marcus, 1997)
[d] (Ford and Wang, 1992)
[e] (Nagano *et al.*, 1988)
[f] (Marcus, 1985), p. 125.
[g] (Nagano *et al.*, 1991)

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ment may again be due to localized cationic hydration effects that cannot be accounted for in the predictions of Table 2, and also points out the need for more measurements of the thermodynamics of organic cation hydration. Nonetheless, agreement is good enough to reinforce at least the rough applicability of the values in Table 2 to alkylammonium cations.

Again, the group-additivity estimates of Table 2 imply that the free energy of solvation for $DBTMA^{2+}$ should be ~+6 kJ mol^{-1} relative to that for $EBTMA^{2+}$. This 6 kJ mol^{-1} may in fact be a lower limit on this value, since $EBTMA^{2+}$ is a short-chain cation. Table 3 clearly shows that adding one -CH_2- to a short alkyl chain tends to result in a change in ΔG somewhat greater than the 0.72 kJ mol^{-1} value, as differences in estimates for the ΔG of hydration for EA^+ (−305 kJ mol^{-1}), propylammonium (PA^+, −299 kJ mol^{-1}), and BA^+ (−297 kJ mol^{-1}) are all >0.72 kJ mol^{-1}. If we assume that changes in ΔG of hydration for butyl−α,ω-bistrimethylammonium ($BBTMA^{2+}$) through $DBTMA^{2+}$ follow the predictions of Table 2, then we might infer that the free energy of solvation for $DBTMA^{2+}$ could be as large as +12 kJ mol^{-1} relative to that for $EBTMA^{2+}$ (*i.e.* +8 kJ mol^{-1} for $EBTMA^{2+}$ to $BBTMA^{2+}$ and another 6*0.72 kJ mol^{-1} for $BBTMA^{2+}$ through $DBTMA^{2+}$). Whether we choose +6 or +12 kJ mol^{-1} for the difference in free energies of solvation for $DBTMA^{2+}$ relative to $EBTMA^{2+}$ will not affect the conclusions of this paper, as will be discussed below.

Thus, on the basis of Table 2 and its (at least asymptotic) agreement with Table 3, we estimate the solvation thermodynamic quantities for $DBTMA^{2+}$ relative to $EBTMA^{2+}$ to be +6 kJ mol^{-1} for ΔG, −30 kJ mol^{-1} for ΔH, and +36 kJ mol^{-1} for $-T\Delta S$.

RESULTS AND DISCUSSION

Through combining the overall cation exchange data from Table 1 with the solvation energy estimates just derived from Table 2, thermodynamic cycles can be constructed to quantify the contributions of the cation exchange reaction in the clay phase *vs.* the bulk aqueous solution phase (Figure 1). As a result of Figure 1, we assert that cation exchange selectivity of montmorillonite for these two organic cations is determined almost entirely by the relative hydration energies of the ions, not by the affinities of the ions for the smectite surface, *i.e.* $DBTMA^{2+}$ is most strongly selected by the clay in spite of its slightly unfavorable adsorption energy, because the free energy gained by having $EBTMA^{2+}$ in aqueous solution more than compensates for the unfavorable free energy of placing $DBTMA^{2+}$ on the clay. This can be rationalized by observing that the interlayer region of smectites must contain cations but allows only partial hydration of those cations, so the more strongly hydrated cations ($EBTMA^{2+}$) will tend to stay in the solution phase where they can remain fully hydrated. On the other hand, less strongly hydrated cations ($DBTMA^{2+}$) will suffer less of an energy penalty for incomplete hydration within the clay interlayer region, so the overall system free energy will be lowest when $DBTMA^{2+}$ partitions into the clay interlayer phase and $EBTMA^{2+}$ partitions into the aqueous phase. That is, the interlayer region is a separate phase (Laird and Shang, 1997) from the bulk solution phase, so cations will partition between the bulk (aqueous) and interlayer (subaqueous) phases according to their hydration energies. The interlayer region is here termed ‘subaqueous’ to denote that the orientational freedom of interlayer water molecules is strongly restricted by the high ionic strength of interlayer solution and by the close proximity of two siloxane surfaces. The preferred orientations of interlayer water (Sposito and Prost, 1982) result in the entropy of adsorbed water being lower than that of bulk water (Keren and Shainberg, 1980; Fu *et al.*, 1990). In addition, the diffusion and dielectric relaxation rates of water molecules in smectite interlayers tend to be slower than in bulk solution (Sposito and Prost, 1982). Furthermore, smectite interlayer regions are often only 3 to 9 Å thick, which may not be room for complete hydration shells to form around cations. Through a combination of these factors, cations in the interlayer region cannot be hydrated as efficiently as they can in bulk solution.

As described in the Methods section, the magnitude of the solution-phase free-energy change ΔG_{hyd} in Figure 1A may be too small because of deviations from the simple additivity concept of Table 2 for very small molecules. That is, the correct value of the −6 kJ mol^{-1} ΔG_{hyd} in Figure 1A might actually be as large as −12 kJ mol^{-1}. If the correct ΔG_{hyd} value is −12 rather than −6 kJ mol^{-1}, then the thermodynamic cycle of Figure 1A implies that the clay phase might find the larger organic cation even more repulsive and show a +7 kJ mol^{-1} unfavorable free energy change ΔG_{clay} when $DBTMA^{2+}$ replaces $EBTMA^{2+}$ in the smectite interlayer. This inference directly contradicts the normal hypothesis that larger organic cations interact more favorably with smectite surfaces than do smaller organic cations. Thus, whether the solution-phase free-energy change in Figure 1A is −6 or −12 kJ mol^{-1}, it must be concluded that solution-phase changes, ΔG_{hyd}, control the overall cation exchange free energy, ΔG_{exch}, and completely dominate the clay-phase preferences, ΔG_{clay}.

Enthalpy

Figure 1 also presents the same sort of thermodynamic cycle for enthalpies of organic cation exchange selectivity, and shows that the relatively small ΔH_{exch} for the overall exchange reaction (Maes *et al.*, 1980) masks large enthalpy changes both in solution and on the clay. The enthalpy change in solution, ΔH_{hyd}, is quite unfavorable (Table 2) because the weak electrostatic and van der Waals interactions of water with eight -CH_2-

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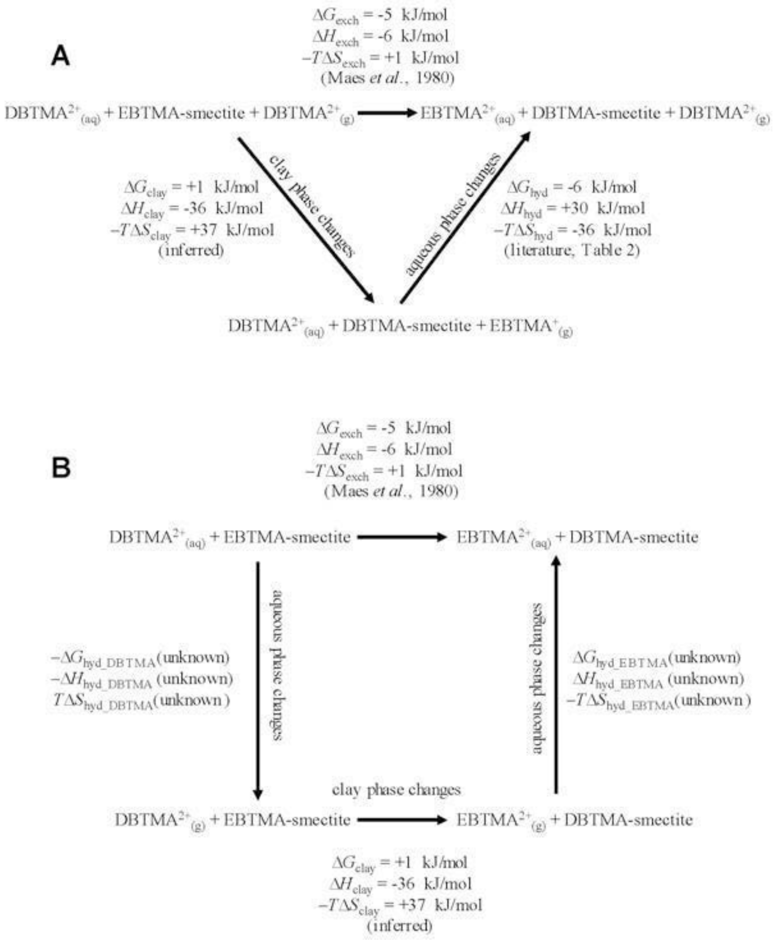

Figure 1. Two versions of a thermodynamic cycle for decomposing the energetics of cation exchange. The organic cations are decyl- ($DBTMA^{2+}$) and ethyl-α,ω-bistrimethylammonium ($EBTMA^{2+}$), and the experimental cation exchange data are from Maes *et al*. (1980) as presented in Table 1. Scheme A allows the energy terms for organic cation exchange (upper side of triangle) to be assigned to clay-phase (left side of triangle) and aqueous solution-phase (right side of triangle) contributions. Scheme B is equivalent, but perhaps clearer because presented as a classic Born-Haber cycle, as suggested by journal reviewer Z.Z. Zhang. Note that ΔG_{hyd} of scheme A is simply the sum of $\Delta G_{\mathrm{hyd\_EBTMA}}$ and $-\Delta G_{\mathrm{hyd\_DBTMA}}$ of scheme B, and similarly for ΔH_{hyd} and ΔS_{hyd}.

groups have been removed (Schmid, 2001). Meanwhile, the enthalpy changes in the clay interlayer region, ΔH_{clay}, are inferred (Figure 1A) to be favorable and of even larger magnitude. This may indicate that: (1) the organic cation may be at least partially hydrated in the interlayer region so the enthalpy responds rather like it does in solution; (2) increasing the size of the adsorbed organic cation increases the number of favorable $-CH_2-$ interactions with the clay surface, and that these may be even more favorable than those with water; (3) increasing the size of the organic cations in the interlayer increases the number of tail-tail interactions occurring; and/or (4) the larger organic cations fill much more of the interlayer space so there are more enthalpically favorable clay-organic interactions per unit surface area. If it can be said that enthalpy changes drive the overall exchange reaction (Maes *et al*., 1980), then it does seem that favorable enthalpy changes upon adsorption of the larger cation more than compensate for the unfavorable enthalpy changes in solution.

A slightly different picture is based on Vansant and Uytterhoeven (1972), who saw no temperature dependence between 4 and 55ºC, indicating zero enthalpy for the exchange of MA^+ through BA^+ on Camp Berteau montmorillonite. In this case, the unfavorable enthalpy change in the solution phase (Figure 1A) was apparently balanced exactly by a favorable change in the clay phase.

Entropy

The overall entropy change for the cation exchange reaction is very small (Maes *et al*., 1980), but again this small value masks large changes in entropy that occur both in solution and on the clay (Figure 1A). This time, the entropy changes in solution are very favorable, as the more favorable hydration of $EBTMA^{2+}$ in solution

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relative to DBTMA^{2+} is largely an entropic phenomenon (Table 2), as is typical of hydrophobic hydration (Schmid, 2001). We infer (Figure 1A) that these favorable entropic effects in solution are cancelled by very unfavorable entropic contributions associated with replacing EBTMA^{2+} with DBTMA^{2+} in the clay interlayer. Unfavorable changes in interlayer entropy could arise from: (1) packing of DBTMA^{2+} molecules into a more orderly, homogenous, and restricted arrangement than that of EBTMA^{2+}; (2) loss of configurational entropy due to such packing; (3) loss of conformational entropy upon packing of the DBTMA^{2+} alkyl chains or upon being forced into relatively planar arrangements along the siloxane basal surfaces of the clay minerals; or (4) loss of water from the interlayer to the bulk solution since some water was probably replaced by DBTMA^{2+}.

Again, Vansant and Uytterhoeven (1972) observed the extreme case in which all the free energy of cation exchange was due to entropic effects. In such a case, the favorable entropy changes in solution upon cation exchange (Figure 1A) would need to be only slightly larger in magnitude than the still very unfavorable entropy changes in the clay phase in order to drive the overall exchange reaction. That is, if the entropic contribution in the clay phase $-T\Delta S_{\mathrm{clay}}$ were +31 kJ mol^{-1} in Figure 1A, then the overall free energy of cation exchange ($\Delta G_{\mathrm{exch}} = -5$ kJ mol^{-1}) would be fully accounted for by entropy changes.

As both the overall enthalpy and entropy of cation exchange seem to be small numbers produced by the difference of large numbers in the solution and clay phases (Figure 1), it is not surprising that there is controversy whether entropy (Vansant and Uytterhoeven, 1972) or enthalpy (Maes *et al.*, 1980) govern the overall exchange reactions of organic cations on smectites.

Dependence of organic cation exchange thermodynamics on loading rate

The present results do not depend on a single dataset. We have used 5 kJ mol^{-1} (Figure 1) for the free energy of cation exchange ΔG_{exch} between two divalent organic cations that differ by eight methylene C atoms, and this value was derived from Table 1 (Maes *et al.*, 1980). Cowan and White (1958) is the only other study we know of that measured cation exchange isotherms and thermodynamics for such a range of alkyl chain lengths, spanning the range from ethyl- (EA^{+}) to decylammonium (DA^{+}) monovalent cations. Their data (Cowan and White, 1958) have been analyzed in two different ways as described below, and allow us to compare organic cation exchange thermodynamics at low *vs.* high loading rates.

Low loading rates

Schwarzenbach *et al.* (2003) used the initial slopes of organic cation adsorption isotherms (Cowan and White, 1958) to compute the initial free energies for exchanging each alkylammonium cation for Na^{+} on montmorillonite, *i.e.* they estimated free energies for exchanging the first organic cations onto an otherwise inorganic smectite. When they plotted (Schwarzenbach *et al.*, 2003; Figure 11.4 on p. 435) these free energies of exchange at low organic cation loading rates, the result was approximately linear with alkyl chain length, and the linear regression slope was a ΔG_{exch} of -0.75 kJ mol^{-1} per methylene C in the alkyl tail (Table 4). The raw data (Cowan and White, 1958) span the eight-carbon range from EA^{+} to DA^{+} cations, and so predict (Schwarzenbach *et al.*, 2003) -6 kJ mol^{-1} for the energy of exchange between the two end-members (Figure 2). Note the excellent agreement between Figure 1A and Figure 2 at low loading rates, which are based on completely independent datasets for mono-

Table 4. Estimated incremental free energies of organic cation exchange for Na^{+} or Ca^{2+} on smectites as functions of alkyl chain length. Slopes are computed by simple linear regression, the R^2 are regression statistics, and the intercepts are hypothetical free energies of NH_4^+ exchange into the smectite phase.

Slope (kJ/mol C)	R^2	Intercept (kJ/mol)	Number C in longest chain	Exchanged cation	Reference
−1.373	0.94	+6	10	Na^{+}	Cowan and White (1958), high loading[a]
−0.754	0.81	−11	10	Na^{+}	Cowan and White (1958), low loading[a]
−0.347	0.92	−1	4	Na^{+}	Theng *et al.* (1967)
−0.311	0.96	−3	4	Na^{+}	Vansant and Uytterhoeven (1972)
−1.198	0.99	+4	4	Na^{+}	Vansant and Peeters (1978)
−1.533	0.95	+23	4	Ca^{2+}	Theng *et al.* (1967)
−0.687	0.96	−15	10	Ca^{2+}	Maes *et al.* (1980)

[a] The Cowan and White (1958) data have been analyzed two ways. The original analysis in their paper used only data for which the organic cation occupied more than half the CEC of the clay, and is designated ‘high loading’. The initial slopes of their isotherm data were also analyzed by Schwarzenbach *et al.* (2003) to estimate free energies of ion exchange at very low occupancy of organic cations on the CEC, and are designated ‘low loading’.

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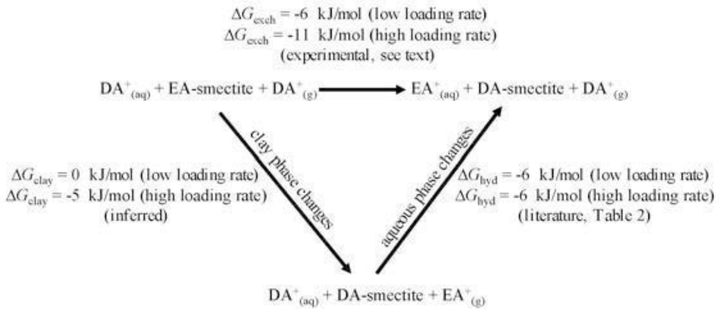

Figure 2. A thermodynamic cycle that allows organic cation exchange free energies (ΔG_{exch}, top side of triangle) to be assigned to clay-phase (ΔG_{clay}, left side of triangle) and solution-phase (ΔG_{hyd}, right side of triangle) contributions. The organic cations are decylammonium (DA$^+$) and ethylammonium (EA$^+$), and the experimental cation exchange data are from Cowan and White (1958). The ΔG_{exch} at low loading rates were calculated from the data by Schwarzenbach *et al.* (2003) and ΔG_{exch} at high loading rates were calculated by Cowan and White (1958).

valent ammoniumalkanes (Cowan and White, 1958; Schwarzenbach *et al.*, 2003) and divalent α,ω-bistrimethylammoniumalkanes (Maes *et al.*, 1980). Despite the differences in valence and head-group in these two cases, both free energies of cation exchange (Figures 1 and 2) agree almost exactly with the prediction (Table 2) of the hydration energy differences between the two cations. Thus, we conclude that (at least at low organic cation loading rates) the free energy of organic cation exchange is almost entirely accounted for by differential cation hydration in the bulk solution phase, not by clay mineral selection. That is, clay mineral selectivity for a larger relative to a smaller organic cation can be fully explained without hypothesizing any favorable interaction between the clay and the larger organic cation. A better way to describe this cation exchange selectivity in smectite systems is that the smaller organic cation is selected by the bulk aqueous phase. The clay interlayer region must contain cations, so the overall system free energy will be lowest when the larger organic cations partition into the 'subaqueous' clay interlayer phase while the smaller organic cations partition into the bulk aqueous phase. As Maes and Cremers (1986) phrased it, the clay acts like an 'anionic solvent with solvation powers smaller than water'.

Note that Schwarzenbach *et al.* (2003, p. 436) concluded that "we may be justified in estimating the hydrophobic contribution to be about 20% of the excess free energy of aqueous solution in the corresponding hydrocarbon", whereas we have just used the same data to infer that this hydrophobic contribution is roughly 100%. This discrepancy arises because Schwarzenbach *et al.* (2003) use the 'pure liquid compound' reference state (p. 78) for estimating the free energy of hydration per methylene C. Use of that reference state seems to confuse the issue, because then the free energy of 'hydration' includes not only hydration but also the energy of dissociating the organic molecule from its pure liquid phase and placing it in water. That is, the 'pure liquid compound' reference state is not a good reference state for hydration energy because every compound's hydration energy is referenced to a different cohesive energy. The cohesive energy increases with molecular size, so hydration energies relative to 'pure liquid compound' reference states are larger (more positive and less favorable) than pure hydration energies (referenced to the gas phase). As a result, Schwarzenbach *et al.* (2003) arrived at a value for the free energy of hydration near +4 kJ mol^{-1} (p. 435) per methylene C for a variety of alkanes and alcohols, whereas Plyasunov and Shock (2000) referenced all organic compounds to the ideal gas state to arrive at +0.72 kJ mol^{-1} per methylene C (Table 2). The latter value is a much purer hydration free energy and entirely explains the free energy of cation exchange (Figures 1 and 2). Thus, we must disagree with the excellent textbook and assert that the hydrophobic effect contributes close to 100% of the free energy of organic cation exchange on montmorillonite, at least when the organic cation loading of the clay surfaces is low.

Other data for free energies of cation exchange for series of cations with systematically lengthening alkyl chains also tend to scatter around -0.72 kJ mol^{-1} methylene C (Table 4). We have already discussed the data for chains up to 10 C atoms long (Cowan and White, 1958; Maes *et al.*, 1980). The slopes derived from the other four datasets (in three papers, Table 4) that studied alkyl chains up to four C show some bifurcation but yield an average -0.85 kJ/mol C, in reasonable agreement with the -0.72 kJ mol^{-1} from solution-phase hydration free energies alone (Table 2).

High loading rates

The situation may be somewhat different when the organic cations begin to dominate the properties of the clay system. Cowan and White (1958) confined their thermodynamic analysis to the portions of their isotherms for which more than half the CEC was populated by the organic cations rather than Na$^+$. The free energies derived at these high organic cation loading rates (Cowan and

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White, 1958) show larger selectivity differences among the organic cations. The overall slope (Table 4) is -1.37 kJ mol^{-1} C, and if one considers only their results for alkylammonium cations with chains five C or longer, the slope is -1.79 kJ mol^{-1} C. The latter value is more than twice the expected difference in free energies of hydration (-0.72 kJ mol^{-1} C, Table 2), implying that the free energy changes for exchanging the larger cations onto the clay are also favorable by ~-1 kJ mol^{-1} C. The value of -1.37 kJ mol^{-1} C, or -11 kJ mol^{-1} for ΔG_{exch} of DA$^+$ for EA$^+$, was used for the high-loading rate case in Figure 2. The analysis of Figure 2 shows that, at high surface loading rates, enhanced van der Waals interactions among the larger organic cations in the clay interlayer cause ΔG_{clay} to make a significant contribution (50 to 60%) to the overall free energy of cation exchange ΔG_{exch}. A 60% contribution from favorable van der Waals energy in the clay phase may be approaching the upper limit of what is possible, because Cowan and White (1958) used a relatively high-charged (CEC = 118 cmol/kg) montmorillonite in conjunction with the alkylammonium cations that feature minimal head-group size. That is, the maximum ΔG_{exch} slope seen by Cowan and White (1958) was -1.79 kJ/mol C, this value is larger than any other in Table 4, and using this value in Figure 2 would result in $\Delta G_{\text{clay}}/\Delta G_{\text{exch}} = 8/14 = 57\%$.

The dual interpretations of Cowan and White's (1958) data at both high and low (Schwarzenbach *et al.*, 2003) organic cation loading rates remind us again that smectite cation selectivities are dependent on the nature of the interlayer phase (Laird and Shang, 1997). For the series of alkylammonium cations studied (Cowan and White, 1958), initial adsorption to the previously inorganic montmorillonite seemed to be driven entirely by hydrophobic effects (Figure 2), with the clay itself relatively indifferent to one organic cation *vs.* another. This is reasonable, given that all R-NH$_3^+$ head-groups could probably bind to the siloxane surfaces in similar fashion and that tail-tail interactions would be unlikely at low loading rates. At low organic cation loading rates, the predominantly Na-smectite would be selective for NH$_4^+$ over Na$^+$, and this is reflected in the extrapolated free energy for initial NH$_4^+$ exchange (intercept values in Table 4), which is favorable at -11 kJ mol^{-1}.

As loading rates increased, alkyl tail-tail interactions become more likely and augment the hydrophobic driving force with favorable van der Waals forces in the clay phase. Finally, at high loading rates the smectites interlayer is essentially an organic phase, favoring the partitioning of large organics over small ones. Such an interlayer organic phase would not be conducive to the sorption of inorganic cations, so the extrapolated free energy of NH$_4^+$ exchange (intercept values in Table 4) into the smectites loaded heavily with organic cations is unfavorable at +6 kJ mol^{-1}.

Interestingly, the only three slopes in Table 3 that are significantly steeper than -0.75 kJ mol^{-1} C are also the only three datasets with positive intercepts. Thus for each of those three datasets, two lines of evidence might be interpreted as indications that the analyses overweighted data at high organic loading rates: (1) incremental free energies of organic cation exchange were greater than incremental free energies of hydration; and (2) extrapolated free energies of NH$_4^+$ exchange for Na$^+$ or Ca^{2+} were positive. For Cowan and White (1958), we know they overweighted their data at high loading rates because they deliberately discarded data at low loading rates. Vansant and Peeters (1978) showed that alkyl-ammonium cation exchange selectivity coefficients, K$_s$, changed drastically upon significant saturation of the CEC by organic cations, such that apparent, non-standard free energies of cation exchange, $-RT\ln K_s$, typically changed sign at high loading rates. They seem to have systematically underestimated the smectite selectivities for alkylammonium cations due to overestimating the clay CEC (Vansant and Peeters, 1978). A related effect was therefore to systematically underestimate the alkylammonium loading rate, which meant they were overweighting high loading rates in an attempt to integrate over all loading rates. The third dataset with large slope and positive intercept (Table 4) was the Ca-montmorillonite study of Theng *et al.* (1967). Viewing their isotherms (Figure 2 of Theng *et al.*, 1967), it seems that a modern treatment of heterovalent cation exchange at their stated ionic strength (<0.1 mol/L) should yield negative free energies of exchange for all organic cations at almost all loading rates. In contrast, their free energies were all positive, even for tetrabutylammonium-Ca exchange. A revised analysis of their data was not attempted.

Thermodynamics of exchange for organic cations with different head-groups

Another test of our ideas is to compare relative free energies of cation exchange directly with relative free energies of hydration for a broader array of organic molecules (Figure 3). Broad datasets (Theng *et al.*, 1967; Vansant and Peeter, 1978) and estimates for free energies of hydration (Table 3) allow us to include secondary, tertiary and quaternary ammonium cations in the analysis, and the relationships within a given dataset are reasonably linear (Figure 3). Note that Figure 3 implies that just a few percent (2.8 to 10.5%) of the difference in hydration energy is translated into ion exchange energy, *i.e.* the clay phase has a generally strong energetic preference for the unselected cation, with the smectite apparently favoring the smaller organic cation by some 90 to 97% of the difference in hydration energy. Such a preference could not come about because the smectite interlayers are hydrated almost as fully as bulk solution, because d_{001} spacings collapse to 13–17 Å (Theng *et al.*, 1967) by 50% loading of the CEC, even in water (McBride and Mortland, 1975). Rather, the implication of Figure 3 is that the smectite surfaces intrinsically favor smaller organic cation head-

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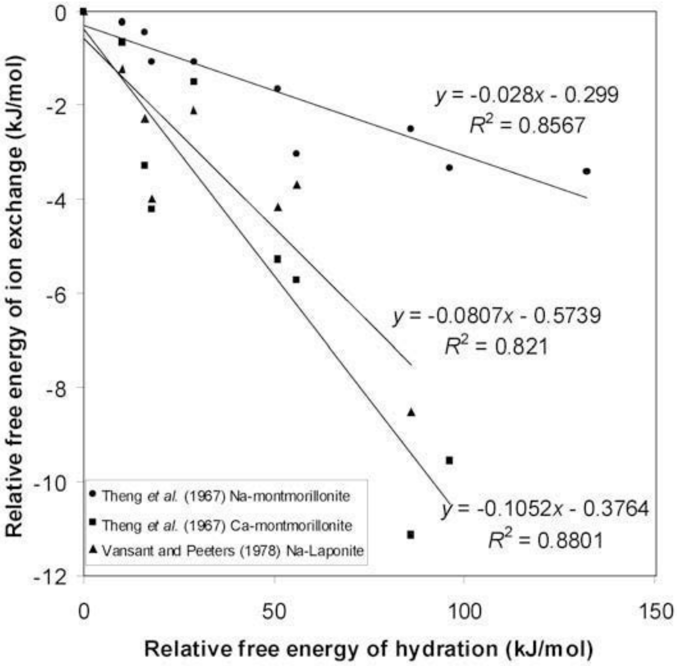

Figure 3. Relationship between estimated relative free energies of hydration and cation exchange among a variety of primary, secondary, tertiary, and quaternary ammonium cations. The zero is set at the hydration energy of methylammonium (-315 kJ mol^{-1}), and all relative hydration energies were then computed from Table 3. Similarly, the zero for relative free energy of cation exchange is set at the value in each paper for methylammonium exchange for Na$^+$ or Ca^{2+}.

groups because electrostatic interactions are better optimized. A very similar hypothesis was proposed in our recent study of inorganic cation exchange thermodynamics (Teppen and Miller, 2006), in which smectite phases were shown to favor Na$^+$ or K$^+$ over Cs$^+$ on their surfaces by wide margins of at least 87% of the relative hydration energies despite the smectite selectively adsorbing Cs$^+$. The inescapable conclusion in both the inorganic (Teppen and Miller, 2006) and the organic (Figure 3) cases is that the origin of cation exchange 'selectivity' by smectites is the selectivity of the bulk aqueous phase for the more strongly hydrated cation.

Note that the findings in Figures 1–3 emphatically disagree with the various hypotheses that the basis for organic cation exchange selectivity in clays is greater attraction (either van der Waals or electrostatic) of the selected cation to smectite surfaces, except in cases where the smectite is already an organic-rich surface. Indeed, our remarks above, in conjunction with Figure 2 (at low loading rates), that differences in hydration energy account for roughly 100% of the free energy of cation exchange may be the best-case scenario and apply only when the head-groups are identical. Figure 3 shows that it may be typical for the selectivity of the solution phase (for the smaller, more strongly hydrated cation) to account for much more than 100% of the overall cation exchange energy, because the energy gained in this manner must also pay the unfavorable energy price for putting the larger organic cation on the clay phase.

Parsimony

The concept resulting from this paper is very simple, namely that the free energy of aqueous cation exchange for two isovalent organic cations is, in the first approximation, equal to the simple difference in their free energies of hydration. The cation with the less favorable hydration energy should be more likely to partition into the subaqueous interlayer phase. Support for the simple nature of this implied mechanism is found in experiments with different solvents: Mizutani *et al.* (1995) showed that smectites select the largest organic cation from aqueous suspension, but reversed their selectivity and adsorbed the smallest organic cation from organic solvents. Thus, the selectivity sequence must be controlled by the solvent and not by interactions with clay surfaces.

Both Maes *et al.* (1980) and Mizutani *et al.* (1995) realized that hydration energy differences play a significant role in determining organic cation selectivity. Indeed, Maes and Cremers (1986) state that selectivity of smectites for larger and more branched organic cations "is ascribed to the lowering of the alkylammonium ion hydration upon adsorption in the interlamellar space". However, these authors concentrated on hydration in the clay phase and also argued that van der Waals interactions between the organic cations and the smectite (Maes *et al.*, 1977; Mizutani *et al.*, 1995) or charge delocalization as it affects electrostatic interaction with the clay surface (Maes *et al.*, 1980; Maes and Cremers,

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1986) play key roles in determining selectivity. The present treatment is simpler in that the available cation selectivity data can be interpreted on the basis of simple partitioning concepts alone. There is no need in Figures 1 or 2 to invoke any sort of van der Waals, polarization, or other favorable interactions between organics and the clay surface. At high organic cation loading rates (Figure 2), there are apparently organic-organic van der Waals interactions that can account for slightly more than half the adsorption energy, with the other half coming from partitioning of the larger cation out of water. At low organic loading rates, the present treatment reveals that the free energy of the clay phase is rather indifferent to which organic cation is intercalated (Figures 1 and 2) as long as the cationic head-groups are identical. Both the aqueous solution phase and the hydrated smectite phases are condensed phases that enthalpically favor the larger organic cation but entropically favor the smaller organic cation. On balance, the aqueous phase has more orientational flexiblity and thus a greater ability to optimize its interactions with either solute, and selects the smaller organic cation for entropic reasons. The inorganic clay phase has very little preference for either cation (enthalpically favoring the larger, but entropically favoring the smaller in equal measure) so accepts the larger organic cation that has been rejected by the aqueous phase.

Applications

The simplicity of this concept, if it holds up, would allow one to estimate predictively the thermodynamics of organic cation exchange on smectite clays whenever the free energies of hydration are known for two moderately similar organic cations. For example, this treatment would predict that, for the four-C amines in Table 3, the ranking of smectite selectivity for those cations would be:

$$(CH_3)_4N^+ > (CH_3CH_2)_2NH_2^+ > CH_3CH_2CH_2CH_2NH_3^+$$

because this is the ordering of their free energies of hydration (Table 3)

$$-219 > -264 > -297 \text{ kJ mol}^{-1}$$

which agrees with the experimental selectivity sequence (Theng *et al.*, 1967; Vansant and Peeters, 1978) as well as the general empirical selectivity trend (Maes and Cremers, 1986)

quaternary > tertiary > secondary > primary ammonium cations.

Note that the free energies of hydration for $(CH_3)_4N^+$ and $CH_3CH_2CH_2CH_2NH_3^+$ predict that the free energy of cation exchange would be −78 kJ/mol, while the experimental estimate is just −2.3 kJ mol^{-1} (Theng *et al.*, 1967). These data imply (Figure 3) that the clay phase strongly favors $CH_3CH_2CH_2CH_2NH_3^+$ over $(CH_3)_4N^+$ by some 75 kJ mol^{-1}. In other words, the clay phase itself strongly favors the unselected cation. This makes sense from the standpoint of electrostatics because the $(CH_3)_4N^+$-smectite interlayers are some 0.3 to 1.0 Å thicker than those of $CH_3CH_2CH_2CH_2NH_3^+$-smectites (Theng *et al.*, 1967), so clay-cation electrostatic interactions must be weaker in the former case. Also, the clay interlayer is a condensed phase that is at least partially hydrated, so it is reasonable that the clay interacts most favorably with the same species as does the bulk solution. However, the interlayer region is physically restricted and ion hydration is probably lowered upon adsorption (Maes *et al.*, 1977), so the difference in hydration between two cations should be less pronounced than it would be in bulk solution. Finally, earlier hypotheses (Theng *et al.*, 1967) may still be valid, namely that $CH_3CH_2CH_2CH_2NH_3^+$ molecules are able to make more optimal van der Waals contacts with clay surfaces than the bulkier $(CH_3)_4N^+$.

Furthermore, measured thermodynamic data like those in Table 3 could be extended to larger compounds by group-additivity trends like those given in Table 2 (Plyasunov and Shock, 2000), to compensate partially for the paucity of hydration data on organic cations. In making such predictions, the critical number for our concept is not the absolute hydration energy of either cation, but the difference in their hydration energies. Thus, the free energies of exchange for pairs of more exotic cations might be estimated by group-additivity energies (Plyasunov and Shock, 2000) for the difference in structure between the two cations. For example, Mizutani *et al.* (1995) measured the apparent equilibrium constant for exchange of the organic di-cation $(CH_2CH_2N^+(CH_3)_3)_2$ for $(CH_2N^+(CH_3)_3)_2$, on saponite to be 1.60, which implies that the free energy of exchange is −1.2 kJ mol^{-1}. As the two cations differ by only two methylene groups, Table 2 would predict the free energy of exchange to be −1.4 kJ mol^{-1}, in fair agreement with experiment.

One might even extend the concept that isovalent cation exchange is a partitioning between bulk solution and a subaqueous clay phase to organic-inorganic cation exchange selectivity. Smectites are very selective for organic cations over Na^+ and even Ca^{2+} (Maes *et al.*, 1980), but K^+ and Cs^+ are less strongly hydrated cations (free energies of hydration are ~−304 and −258 kJ/mol, respectively (Marcus, 1985)). These free energy values, compared with those in Table 3, infer the hypotheses that smectites should show slight cation exchange selectivities for K^+ over $CH_3NH_3^+$, and marked selectivities for Cs^+ over $CH_3NH_3^+$, $CH_3CH_2NH_3^+$, or $(CH_3)_2NH_2^+$. Furthermore, there should be no appreciable aqueous-phase selectivity for K^+ *vs.* $CH_3CH_2NH_3^+$, Cs^+ *vs.* $(CH_3)_3NH^+$, or Cs^+ *vs.* $(CH_3CH_2)_2NH_2^+$, as the free energies of hydration are almost equal within each pair. These three pairs would thus provide interesting tests of whether smectite surfaces inherently prefer the organic or the inorganic cation out of each pair.

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CONCLUSIONS

It is apparent from an analysis of the exchange thermodynamics (Figure 1) that the selectivity of swelling clay minerals for larger organic cations over smaller ones is driven by the stronger aqueous-phase hydration of the unselected cation. That is, the bulk aqueous phase exhibits a strong selectivity for the smaller organic cation, driven by a stronger free energy of hydration and especially its entropic component. Thus, the essentials of such cation exchange selectivity can be explained without any recourse to clay-organic interactions. While the interaction of the organic molecule with the clay mineral is only a secondary factor to the dominant solution-phase hydration interaction, it does seem (Figure 1) that adsorption of the larger organic cation by the clay is enthalpically favorable and entropically unfavorable compared to the smaller cation.

On the basis of this study, we advance the following hypotheses: (1) for two organic cations with identical head-groups, the difference in their cation exchange selectivities at low loading rates is driven almost quantitatively by the difference in their free energies of hydration. In this situation, differences in attractive forces between the two organic cations and the clay surfaces seem almost nil, with the smectite phase apparently indifferent to which organic cation it contains. Thus, the mechanism for organic cation sorption is almost pure hydrophobic expulsion of the larger cation from water.

(2) For two organic cations with rather different head-groups (*e.g.* a primary *vs.* a quaternary amine), the difference in their cation exchange selectivities is just a small percentage of the difference in their free energies of hydration. This indicates that the clay phase interacts much more strongly with the cation having the smaller head-group, as might be expected on the basis of simple electrostatics. In this context, van der Waals forces between the organics and clay surface play a role too small to be discernible against the substantial electrostatic background. This situation is like isovalent inorganic cation exchange (Teppen and Miller, 2006), in which the clay itself has a strong preference for the smaller cation yet 'selects' for the cation with larger head-group because the aqueous-phase preference for the smaller cation is even stronger than the clay preference.

(3) One situation in which van der Waals forces apparently play a significant role in determining the selectivity of organic cations is when the clay is already substantially loaded with organic cations. In this case, organic cation selectivity differences are enhanced because the differences in free energy of hydration (contributing just under half of the free energy in one case study) are augmented by van der Waals forces in the clay interlayer (contributing the other half), with both driving sorption of the larger cation to the clay.

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REFERENCES

Abraham, M.H. (1984) Thermodynamics of solution of homologous series of solutes in water. *Journal of the Chemical Society, Faraday Transactions*, **80**, 153–181.

Barrer, R.M. (1989) Clay-minerals as selective and shape-selective sorbents. *Pure and Applied Chemistry*, **61**, 1903–1912.

Cabani, S., Gianni, P., Mollica, V. and Lepori, L. (1981) Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous-solution. *Journal of Solution Chemistry*, **10**, 563–595.

Cowan, C.T. and White, D. (1958) The mechanisms of exchange reactions occurring between sodium montmorillonite and various n-primary aliphatic amine salts. *Transactions of the Faraday Society*, **54**, 691–697.

Florian, J. and Warshel, A. (1997) Langevin dipoles model for ab initio calculations of chemical processes in solution: Parameterization and application to hydration free energies of neutral and ionic solutes and conformational analysis in aqueous solution. *Journal of Physical Chemistry B*, **101**, 5583–5595.

Ford, G.P. and Wang, B.Z. (1992) The optimized ellipsoidal cavity and its application to the self-consistent reaction field calculation of hydration energies of cations and neutral molecules. *Journal of Computational Chemistry*, **13**, 229–239.

Fu, M.H., Zhang, Z.Z. and Low, P.F. (1990) Changes in the properties of a montmorillonite system during the adsorption and desorption of water: Hysteresis. *Clays and Clay Minerals*, **38**, 485–492.

Johnston, C.T. (1996) Sorption of organic compounds on clay minerals: A surface functional approach. Pp. 1–44 in: *Reactions of Organic Pollutants with Clays* (B.L. Sawhney, editor). CMS Workshop Volume **8**, The Clay Minerals Society, Bloomington, Indiana.

Keren, R. and Shainberg, I. (1980) Water vapor isotherms and heat of immersion of Na- and Ca-montmorillonite systems. III. Thermodynamics. *Clays and Clay Minerals*, **28**, 204–210.

Lagaly, G. (1984) Clay organic interactions. *Philosophical Transactions of the Royal Society of London Series A – Mathematical, Physical and Engineering Sciences*, **311**, 315–332.

Laird, D.A. and Shang, C. (1997) Relationship between cation exchange selectivity and crystalline swelling in expanding 2:1 phyllosilicates. *Clays and Clay Minerals*, **45**, 681–689.

Maes, A. and Cremers, A. (1986) Highly selective ion exchange in clay minerals and zeolites. Pp. 254–295 in: *Geochemical Processes at Mineral Surfaces* (J.A. Davis and K.F. Hayes, editors). ACS Symposium Series **323**, American Chemical Society, Washington, D.C.

Maes, A., Marynen, P. and Cremers, A. (1977) Ion-exchange adsorption of alkylammonium ions – alternative view. *Clays and Clay Minerals*, **25**, 309–310.

Maes, A., van Leemput, L., Cremers, A. and Uytterhoeven, J. (1980) Electron-density distribution as a parameter in understanding organic cation-exchange in montmorillonite. *Journal of Colloid and Interface Science*, **77**, 14–20.

Marcus, Y. (1985) *Ion Solvation*. John Wiley & Sons, New York, 306 pp.

https://doi.org/10.1346/CCMN.2007.0550201 Published online by Cambridge University Press

Marcus, Y. (1997) *Ion Properties*. Marcel Dekker, New York, 259 pp.

McBride, M.B. and Mortland, M.M. (1975) Surface properties of mixed Cu(II)-tetraalkylammonium montmorillonites. *Clay Minerals*, **10**, 357–368.

Mizutani, T., Takano, T. and Ogoshi, H. (1995) Selectivity of adsorption of organic ammonium ions onto smectite clays. *Langmuir*, **11**, 880–884.

Mortland, M.M. (1970) Clay-organic complexes and interactions. *Advances in Agronomy*, **22**, 75–117.

Nagano, Y., Sakiyama, M., Fujiwara, T. and Kondo, Y. (1988) Thermochemical study of tetramethylammonium and tetraethylammonium halides – nonionic cohesive energies in the crystals and hydration enthalpies of the cations. *Journal of Physical Chemistry*, **92**, 5823–5827.

Nagano, Y., Mizuno, H., Sakiyama, M., Fujiwara, T. and Kondo, Y. (1991) Hydration enthalpy of Tetra-Normal-Butylammonium Ion. *Journal of Physical Chemistry*, **95**, 2536–2540.

Pliego, J.R. and Riveros, J.M. (2002) Gibbs energy of solvation of organic ions in aqueous and dimethyl sulfoxide solutions. *Physical Chemistry Chemical Physics*, **4**, 1622–1627.

Plyasunov, A.V. and Shock, E.L. (2000) Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa. *Geochimica et Cosmochimica Acta*, **64**, 439–468.

Schmid, R. (2001) Recent advances in the description of the structure of water, the hydrophobic effect, and the like-dissolves-like rule. *Monatshefte für Chemie*, **132**, 1295–1326.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (2003) *Environmental Organic Chemistry*, 2nd edition. Wiley-Interscience, New York, 1000 pp.

Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites. *Chemical Reviews*, **82**, 553–573.

Teppen, B.J. and Miller, D.M. (2006) Hydration energy determines isovalent cation exchange selectivity by clay minerals. Soil Science Society of America Journal, **70**, 31–40.

Theng, B.K.G. (1974) *The Chemistry of Clay-Organic Reactions*. John Wiley & Sons, New York, 343 pp.

Theng, B.K.G., Greenland, D.J. and Quirk, J.P. (1967) Adsorption of alkylammonium cations by montmorillonite. *Clay Minerals*, **7**, 1–17.

Vansant, E.F. and Peeters, G. (1978) Exchange of alkylammonium ions on Na-Laponite. *Clays and Clay Minerals*, **26**, 279–284.

Vansant, E.F. and Uytterhoeven, J.B. (1972) Thermodynamics of exchange of *n*-alkylammonium ions on Na-montmorillonite. *Clays and Clay Minerals*, **20**, 47–54.

Zhang, Z.Z., Sparks, D.L. and Scrivner, N.C. (1993) Sorption and desorption of quaternary amine cations on clays. *Environmental Science and Technology*, **27**, 1625–1631.

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