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THERMODYNAMIC CHARACTERIZATION OF CLAY/ELECTROLYTE SYSTEMS

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Abstract—Clay/electrolyte systems are best characterized using a new variable, notional interfacial content (NIC). The NIC approach emphasizes that any division of the total amount of a species present in a clay/electrolyte system into that part which 'belongs' to the clay and that part which 'belongs' to solution is necessarily arbitrary. It carries out this division by choosing one of the species as a reference species and defining it as being completely in a notional bulk solution which had the same composition, but not extent, as the real bulk solution. The NIC of each of the other species present, that is that part of their total amount not in the notional bulk solution, therefore represents the amounts of those species 'belonging' to the clay.

The NIC concept is universal and hence encompasses several other, older terms. For example, by choosing different reference species, the variables hitherto called 'water adsorption' and 'negative adsorption' (which have been used to describe the same phenomenon) may be obtained. Similarly, certain earlier definitions of exchangeable and adsorbed cations (some being pragmatic are not included) as well as that of ion surface excesses may be accounted for. The NIC approach thus provides a rationalization of several earlier terms which are, in fact, plagued by a multiplicity of definition which makes their use very complicated.

Key Words—Adsorption, Cation exchange, Electrolyte, Negative adsorption, Thermodynamics, Water.

INTRODUCTION

Previously, in the characterization of clay/electrolyte systems (classically cation-exchange systems), the particular variables measured have been determined explicitly or implicitly by selection of an exchange model, e.g., Helmholtz or Gouy-Chapman models, etc. Under these circumstances the validity and relevance of variables is dependent upon the correctness of the assumptions inherent in the chosen model. In this paper it is shown how a better, more rigorous approach can be obtained by adopting what is essentially a thermodynamical treatment involving a new variable, notional interfacial content (NIC). The relationship between the NIC and cation-exchange capacity, negative adsorption, water uptake, exchangeable and adsorbed cations, and ion surface-excesses is explained in detail. Adoption of the NIC concept unifies the three major approaches used earlier, that is, thermodynamic, mechanistic modeling (e.g., the Gouy-Chapman model) and practical approaches.

THE CLAY/ELECTROLYTE SYSTEM

In this paper the clay/electrolyte system is defined as consisting of four components, negatively charged clay platelets, uncharged species (e.g., water), cations, and anions, and, unless stated otherwise, is only considered at equilibrium. Positive charges on the clay are not considered, and to avoid unnecessary complication, weakly dissociating acids and bases are neglected. While it is appreciated that part of the charge upon some clays is variable and pH-dependent, in common with most existing modeling studies, only the fixed-charge case is examined.

A generalized model

A generalized clay/electrolyte system allows its ions and uncharged species to reside in a solid phase, a liquid phase (bulk solution), and an interfacial region. In such a system the term *phase* is applied rigorously as being an environment that is not significantly inhomogeneous (Moore, 1962). Following existing practice, the solid phase is considered to contain neither water nor ions which are involved in the equilibrium, and the clay platelet is solely a source of negative charge. Species 'attached' to the clay in the sense of a Helmholtz or Stern layer (Helmholtz, 1879; Stern, 1924) are in the interfacial region.

Cation-exchange capacity (CEC)

The CEC of a clay is defined here as the amount of cations equivalent to the negative charge (α) upon unit mass of the clay. For charge neutrality in a system containing T_+, and T_- equivalents of cations and anions, respectively (where $T_+ = \sum_+ T_k$, and $T_- = \sum_- T_k$, and k is any ion), the sum of the positive charges equals the sum of the negative ones. Therefore,

$$T_+ = T_- + \alpha, \text{ and since } \alpha \equiv \text{CEC}$$
$$\text{CEC} = T_+ - T_-. \quad (1)$$

Defined in this manner, CEC is a fundamental property of the clay and is independent of the condition of the solution, e.g., ionic strength. This usage contrasts

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with other uses of CEC (van Olphen, 1977). In principle, CEC is therefore determinable by measuring the total amounts of cations and anions in the system using, for example, a multiple extraction technique (Zaytseva, 1962).

THE NOTIONAL CLAY/ELECTROLYTE SYSTEM

The requirement for a notional clay/electrolyte system, and hence notional interfacial content, arises from the need to assign part of the species present in the system to the clay, and the rest to the solution. As this separation is the primary step in characterizing the system, it is essential that the means by which it is performed be applicable to any system. Unfortunately, there is no *absolute* way of carrying out this separation when part of the clay's negative charge is counterbalanced by ions in solution, and thus, an arbitrary separation must be imposed. Such a step is common in thermodynamical argument, perhaps the most common example being the arbitrary division of a measured EMF for a cell into two half-cell potentials (Willard *et al.*, 1965; Glasstone, 1962). Thus, in both the electrochemical and clay cases, there is no additional physical property that would determine how the *absolute* separation should be made, and hence it can only be made arbitrarily. If clay/electrolyte systems were known to behave according to the Helmholtz model, an absolute separation could be based on the fact that all the charge-balancing cations reside on the clay surface and hence are physically separable from those in solution. The first task in arbitrarily dividing the total amount of each species between the clay and the solution is to choose one species as a reference species. The reference species can be *any* of the species present in the system but, as will be demonstrated, the choice ultimately depends upon the use to which the data are to be put. In the electrochemical analogy any half-cell can be chosen as the reference cell, although usually the hydrogen/proton couple is selected.

The second task is to assume a distribution for the reference species. In the electrochemical case this second task is equivalent to defining both the value of the standard electrode potential of the reference electrode, usually as zero, and the standard conditions under which it has this value, which, where possible, is usually unit molarity for the oxidized and reduced species. For clays, the reference species' distribution is most conveniently chosen so that the reference species resides entirely in the notional system's bulk solution, i.e., the amount in the notional interfacial region is zero. The notional bulk solution is chosen to have the same composition, *but not the same extent,* as the real bulk solution to maintain the notional system as close as possible to the real system. Thus, defining j as the reference species, the amount of a given species, i, in the notional bulk solution can be expressed as the product of T_j, the total mass of the reference species in the system, and $C_{i(j)}$, the concentration of i with respect to j in the real bulk solution. Therefore,

$$T_i = NIC_{i(j)} + T_j \times C_{i(j)}, \quad (2)$$

where $NIC_{i(j)}$ is the notional interfacial content of i with respect to the reference species, j, and henceforth is written as the i NIC(j). If the reference species itself is considered (i = j),

$$T_j \times C_{j(j)} = T_j \text{ and } NIC_{j(j)} = 0,$$

because by definition j is absent from the notional interfacial region. The most useful dimension for $NIC_{i(j)}$, and therefore for T_i and T_j, is milliequivalents per unit mass of clay, because this value will relate most readily to the units generally used for CEC. It follows that the concentration term, $C_{i(j)}$, will be dimensionless, being a ratio of two equivalents. Although the concentration terms in more common usage are not dimensionless, there is nothing untoward in the treatment used here.

It is worthwhile to underline the generality of the NIC concept. First, the concept applies to *any* distribution of species; it is not dependent on *any* distribution model (Truesdale *et al.*, 1982). Second, the only necessary qualification of the reference species is that it is present in the real bulk solution. The behavior of the reference species is irrelevant and the choice is from *any* species present. Third, once the reference species is chosen, the NIC of all other species present may be estimated. This includes *any* mixtures of variously charged species. From Eq. (2), the NICs for a system are determinable in principle by measuring the total amounts of the species in the system by a multiple stripping procedure (Zaytseva, 1962), or, in the case of water, gravimetrically by heating to dryness, and by measuring the concentrations of the species in the bulk solution. Conventional analysis of the bulk solution will yield concentrations relative to a given volume of solution, and these values will need to be converted to the form required by Eq. (2).

The relationship between NIC and CEC

The CEC equals the difference between the sums of the cation and anion NICs with respect to an uncharged species, e.g., water. Thus, from Eq. (1),

$$CEC = \sum_{+} T_k - \sum_{-} T_k,$$

and using Eq. (2) with i relating to charged species (k) only,

$$CEC = \sum_{+} \{NIC_{i(j)} + T_j \times C_{i(j)}\} - \sum_{-} \{NIC_{i(j)} + T_j \times C_{i(j)}\}.$$

Because the sums of the concentrations of anions and cations are equal in the bulk solution,

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$$CEC = \sum_{+} NIC_{i(j)} - \sum_{-} NIC_{i(j)}. \quad (3)$$

The relationship between NIC and negative adsorption

The sum of the anion NICs (water) helps to explain the phenomenon of negative adsorption. So-called negative adsorption (see below for a clarification of adsorption) is manifest as the increase in the total concentration of anions and cations that occurs when a dry, salt-free clay is added to an electrolyte solution. Earlier workers have tended to describe this phenomenon solely in terms of anion behavior (e.g., Wiklander, 1964). The relationship is established by applying Eq. (2) to the mixture. Thus, after rearrangement,

$$NIC_{-(W)} = T_- - T_W \times (C_{-(W)})_f,$$

where $(C_{-(W)})_f$ is the concentration of anions with respect to water in the final bulk solution. Since all the anions and water of the final mixture originate from the electrolyte solution,

$$T_- = T_W \times (C_{-(W)})_o$$

where the subscript o refers to the original electrolyte solution. Therefore,

$$\begin{aligned} NIC_{-(W)} &= T_W \times \{(C_{-(W)})_o - (C_{-(W)})_f\} \\ &= T_W \times \{-\Delta C_{-(W)}\}, \end{aligned} \quad (4)$$

where $\Delta C_{-(W)}$ is the negative adsorption of anions, expressed so as to take positive values. Since the bulk solution must be electrically neutral, this identity is true when $\Delta C_{+(W)}$, the total increase in cation concentration, is substituted for $\Delta C_{-(W)}$.

The link between NIC and negative adsorption can be exploited to explain the relationship between work performed under the heading of negative adsorption of anions (Bolt and Warkentin, 1958; Wiklander, 1964) and that under the heading of water adsorption or water uptake (Dufey and Laudelout, 1976; Edwards and Quirk, 1962; Norrish, 1954). This link has not yet been explained adequately and can give an impression that two distinctly different phenomena exist: water adsorption and anion repulsion. In fact, one approach is the 'inverse' of the other; the two approaches arise directly from the need to choose a reference species arbitrarily. Thus, given that the NICs describe a relative distribution, the above derivation can be rewritten using total anions as the collective reference species, whence,

$$\begin{aligned} NIC_{W(-)} &= T_- \times \{(C_{W(-)})_o - (C_{W(-)})_f\} \\ &= T_- \times \{\Delta C_{W(-)}\}, \end{aligned}$$

where $\Delta C_{W(-)}$ is the 'water uptake,' expressed so as to take positive values. Moreover, given the inverse relationship between the concentration of water with respect to total anions and that of the total anions with respect to water, i.e., $C_{W(-)} = 1/C_{-(W)}$, 'water uptake' can be simply expressed in terms of negative adsorption,

$$\frac{\Delta C_{W(-)}}{(C_{W(-)})_o} = \frac{\Delta C_{-(W)}}{(C_{-(W)})_f} \quad \text{or} \quad \frac{\Delta C_{W(-)}}{(C_{W(-)})_f} = \frac{\Delta C_{-(W)}}{(C_{-(W)})_o}.$$

DISCUSSION

Probably the greatest advantage to be gained from the adoption of the NIC concept is the unification of the three major approaches that are used in clay/electrolyte work. These three approaches arise from earlier work having a predilection for thermodynamics (e.g., Thomas, 1965), mechanistic models, e.g., the Gouy-Chapman model (Bolt, 1955), or practical solutions (e.g., Reitemeier, 1946) for characterizing clay/electrolyte systems. No previous work has provided a means of synthesising these as well as does the NIC concept. Nevertheless, the works of Laudelout *et al.* (1968) and Bolt (1967) deserve special mention. The former workers, taking a thermodynamic stance, presented an equation which is essentially identical to that for NIC and applied it to practical work. In doing so, however, they appeared to be unaware of its universal applicability to the mechanistic modeling. Moreover, although these workers mentioned the arbitrariness of their approach, they presented it as being of a practical nature and not a fundamental one. Bolt (1967) introduced the concept of ion surface-excesses in the context of the Gouy-Chapman model, claiming that they are 'experimentally accessible.' However, he did not extend it to other mechanistic models, e.g., the Donnan and Helmholtz models (Donnan, 1935; Helmholtz, 1879), and this concept has remained confined to discussions of the Gouy-Chapman model (van Olphen, 1977). Moreover, in introducing ion surface-excesses, Bolt (1967) separated them from thermodynamic considerations and apparently did not appreciate their thermodynamic character. This contention is reinforced by the fact that Bolt did not indicate that the ion surface-excesses would be arbitrary, even when he recognized that derivative terms, e.g., adsorbed cations, are. Notwithstanding these points, Bolt failed to state that values for ion surface-excesses are, in fact, experimentally inaccessible without assuming, as the Gouy-Chapman model does, that the concentration of water is constant throughout the exchange system.

It is worthwhile to explain that we were unable to appreciate the true value of the work of Laudelout *et al.* (1968) until well after the derivation of NICs because of confusion over the meaning of the term, adsorbed; at least ten different meanings are in current use: (Overbeek, 1952; Davis, 1945; Yong and Warkentin, 1966; Helmy, 1963; Thomas, 1965; Neal, 1977; Murali and Aylemore, 1981). Indeed, in one sense this entire paper provides the case for rationalizing the ideas underlying the use of the term adsorption. It separates the older mechanistic meaning, e.g., that associated with the

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Helmholtz model, from the contemporary need merely for a means of dividing species 'belonging' to the clay from those 'belonging' to the solution.

To emphasize the universal nature of the NIC concept it is necessary to explain how it embraces variables which have arisen earlier from the use of one or other of the mechanistic models, and which it was thought would divide the total ion complement into a part associated with the clay and another with the solution. The terms *adsorbed* or *exchangeable* (e.g., adsorbed sodium, exchangeable sodium) used with the Helmholtz model (e.g., Hesse, 1971) are equivalent to both cation NIC (water) and cation NIC (anion). In the Helmholtz model all cations that counterbalance the clay's negative charge reside at the clay surface and are therefore not in solution; all of the anions and all of the water are in the bulk solution. Thus, under circumstances where the Helmholtz model is valid the introduction of the notional system, with the need for all the reference species to be in the notional bulk solution, duplicates the Helmholtz model when the reference species are anions or water. It follows that anion NIC (water) and water NIC (anion) are both zero; indeed, this condition offers a good practical test of the relevance of the Helmholtz model. The term, adsorbed or exchangeable cation (e.g., exchangeable sodium), when used with the Gouy-Chapman model (Bolt, 1967; van Olphen, 1977), is equivalent to cation NIC (anion). Thus the equation provided by Bolt (1967) includes the term, $C^{+}{}_{o}/(C^{+}{}_{o} + C^{++}{}_{o})$. For the general case this term gives the ratio of the concentration in the bulk solution of one particular cation to the concentrations of them all. Given the condition of electrical neutrality in the bulk solution, this term is identical to the $C_{i(j)}$ term of Eq. (2) when the total anion complement is the reference species. If the Gouy-Chapman model were valid, the water NIC (anion) and anion NIC (water) would not be zero because a value of zero implies an identical interaction for both anions and water with the clay surface. Also, if values of anion NIC (water) are positive, the Gouy-Chapman model can be dismissed. Given that NICs are *entirely* arbitrary, one can understand Bolt's (1967) statement that his definition of adsorbed 'contains a somewhat arbitrary element.' It is important to recognize, as established above, that both of the terms exchangeable and adsorbed have been used in a multitude of different ways. Many of these are defined inadequately, and most are not directly relatable to the NIC concept.

McConnell *et al.* (1964) stated that the addition to a mixed electrolyte solution of an inert substance with an uncharged surface results in the larger ions being at a greater concentration in the bulk solution than the smaller ones. This 'geometric' effect is due to the smaller ions having access to the space which is enclosed between the inert substance's surface and one radius-distance of the larger ion; space denied to the larger ion. According to this argument, the negative adsorption observed when a dry clay is added to an electrolyte solution represents the sum of both the effect of the clay's electric field upon the ions and the 'geometric' effect. While the theory of McConnell *et al.* (1964) is interesting and seems to explain a number of otherwise unresolved anomalies, e.g., 'exclusion of aqueous KCl by blood charcoal,' it is difficult to see how it can operate without involving a charged bulk solution. This problem is particularly evident when an inert and uncharged surface is added to a solution of a single salt consisting of a large anion and small cation. Notwithstanding this reservation, our calculations using hydrated potassium and magnesium ions (which have a relatively large difference in ionic radii), together with the equations of McConnell *et al.* (1964), suggest that the effect will be insignificant in clay studies. Thus, if 1 g of powder with a surface area of 8×10^5 m^2/kg (approximately that of a smectite) were added to 1 ml of a potassium and magnesium nitrate solution, the Mg concentration would increase by approximately 12% relative to that of the K. Under more typical experimental conditions, e.g., a solid to liquid ratio (w/v) of 0.04, the increase is only 0.2%. Concern for the 'geometric' effect might be the unexpressed reason why in experiments upon negative adsorption some workers (e.g., Bolt and Warkentin, 1958; Edwards and Quirk, 1962; De Haan and Bolt, 1963) preferred to start with the sample of clay already in contact with electrolyte, whereas others used dry clays (e.g., Bower and Goertzen, 1955; Posner and Quirk, 1964; Schofield and Talibuddin, 1948). There appears to be no significant difference in the magnitude of the results from either approach.

This paper, in common with most earlier work on cation exchange, assumes the absence of any positive charge upon the clay that would involve anion exchange. The effect of allowing for positive charges upon the clay is under consideration. Nevertheless a preliminary analysis shows that whereas Eq. (2) will be unaffected by this change, Eqs. (1) and (3) will need to be modified with a net exchange capacity (cation-exchange capacity minus anion-exchange capacity) replacing CEC. However, Eq. (4), with its assumption that there are no anions upon a dry salt-free clay, will no longer apply.

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Резюме—Системы глина/электролит можно охарактеризовать самым лучшим образом (при использовании новой переменной) воображаемым межслойным содержанием (ВМС). ВМС подчеркивает, что какое либо разделение всего материала, присутствующего в системе глина/электролит, на часть, которая "принадлежит" раствору и на часть, которая принадлежит глине, является полностью произвольным. Такой (ВМС) подход совершает это разделение, выбирая одну из составляющих как основу и определяя ее как находящуюся полностью в воображаемом растворе, имеющим такой же самой состав, но не такой же размер как действительный раствор. ВМС других составляющих, что является частью их полного количества, ненаходящейся в воображаемом растворе, представляет тогда величины составляющих, "принадлежащих" глине.

Концепция ВМС является универсальной и поэтому включает несколько других, ранее введенных понятий. Например, выбирая различные основные составляющие, можно определить величины прежде называемые "адсорбция воды" и "отрицательная адсорбция" которые использовались до описания такого же самого явления. Подобным образом можно поступить с некоторыми прежними определениями обменных и адсорбированных катионов (некоторые прагматические не включаются), также как и определениями избыточных ионных поверхностей. Таким образом подход ВМС обеспечивает рационализацию нескольких прежних терминов, которые, в действительности, страдают многозначностью, что сильно осложняет их использование. [E.C.]

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Resümee—Ton/Elektrolyt-Systeme werden am besten charakterisiert, wenn man eine neue Variable, "notional interfacial content" (NIC), verwendet. Der NIC betont, daß jegliche Aufteilung des Gesamtgehaltes einer vorhandenen Substanz in einem Ton/Elektrolyt-System in den Anteil, der zum Ton "gehört," und den anderen Anteil, der zur Lösung "gehört," willkürlich sein muß. Durch den NIC wird diese Aufteilung so durchgeführt, daß die eine der Substanzen als eine Bezugssubstanz verwendet wird. Diese Substanz wird dadurch definiert, daß sie vollständig in einer theoretischen Durchschnittslösung vorhanden ist, die die gleiche Zusammensetzung aber nicht das gleiche Ausmaß hat wie die tatsächliche Durchschnittslösung. Der NIC jeder anderen anwesenden Substanz, d.h. der Teil des Gesamtbetrages, der nicht in der theoretischen Durchschnittslösung ist, stellt dann die Substanzgehalte dar, die zum Ton "gehören."

Das NIC-Konzept ist universell und beinhaltet mehrere andere, früher verwendete Begriffe. Zum Beispiel kann man durch die Wahl verschiedener Bezugssubstanzen die Variablen, die bisher als "Wasseradsorption" und "negative Adsorption" bezeichnet wurden und dasselbe Phänomen beschrieben haben, erhalten. In ähnlicher Weise lassen sich gewisse frühere Definitionen für austauschbare und adsorbierte Kationen bzw. auch für den Ionenüberschuß an Oberflächen berücksichtigen (pragmatische Definitionen werden nicht berücksichtigt). Das NIC-Konzept ermöglicht daher die Rationalisierung mehrerer, früher üblicher Begriffe, die durch eine Vielzahl von Definitionsmöglichkeiten verwirrend sind. [U.W.]

Résumé—Les systèmes argile/électrolyte peuvent être le mieux caractérisés par l'utilisation d'une nouvelle variable, le contenu interface notionale (NIC). NIC souligne que toute division de la quantité totale d'une espèce présente dans un système argile/électrolyte en la partie qui "appartient" à l'argile et la partie qui "appartient" à la solution est nécéssairement arbitraire. L'approche NIC éffectue cette division en choisissant une des espèces comme espèce de réference et en la definissant comme étant complètement dans une solution en masse notionale qui a la même composition, mais pas la même étendue que la solution en masse réelle. Le NIC de toutes les autres espèces présentes, c'est à dire la partie de leur quantité totale ne se trouvant pas dans la solution en masse notionale représente par conséquent les quantités de ces espèces "appartenant" à l'argile.

Le concept NIC est universel et comprend donc plusieurs autres termes plus anciens. Par exemple, en choisissant des espèces de réference différentes, les variables appellées jusqu'à présent "adsorption d'eau" et "adsorption négative" (qui ont été utilisées pour décrire le même phénomène) peuvent être obtenues. De même, on peut répondre de certaines definitions du passé de cations échangeables et adsorbés (certaines étant pragmatiques ne sont pas inclues) ainsi qe d'excès de surfaces d'ions. L'approche NIC fournit de cette manière une rationalisation de plusieurs termes du passé qui sont en fait encombrés d'une multiplicité de définitions qui rend leur emploi très compliqué. [D.J.]

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