

EFFECT OF CATION EXCHANGE HYSTERESIS ON A MIXING PROCEDURE USED IN THE STUDY OF CLAY SUSPENSIONS

Key Words—Cation exchange, Crystalline swelling, Hysteresis, Kinetics, Light transmission, Montmorillonite, Quasi-crystal, Selectivity coefficient.

INTRODUCTION

In studies on the formation and breakdown of quasi-crystals in mixed-ionic systems, researchers have frequently adopted the procedure of mixing together homoionic clay suspensions (e.g., Lahav and Banin 1968b, Shainberg and Otoh 1968, Shainberg and Kaiserman 1969, Bar On *et al* 1970, Frenkel and Shainberg 1981, Schramm and Kwak 1982). In these experiments, the homoionic and often salt-free clay suspensions are mixed in various proportions to obtain targeted exchanger phase compositions. The changes in light transmission or viscosity of the mixtures with exchanger composition are interpreted in terms of quasi-crystal formation and breakdown. This same procedure has also been employed in studies of interactions between clay and cations (Shainberg and Kemper 1969, Keren and Shainberg 1979). In a study on cation exchange in montmorillonite and illite suspensions, Shainberg *et al* (1980) used a variant of the common mixing procedure; they first mixed dry, homoionic clays and then added solutions of the corresponding cations.

The use of the mixing procedure is based on the premises that cation exchange reactions on clays are thermodynamically reversible and that quasi-crystal formation and breakdown are very fast processes. Some exchange reactions, however, exhibit hysteresis; they appear not to be reversible within the time frame of typical cation exchange experiments and result in different exchange isotherms depending on the direction, termed “forward” and “backward”, of the exchange (Fripiat *et al* 1965, Van Bladel and Laudelout 1967, Verburg and Baveye 1994, 1995b). Hysteresis is also manifested by other measurements on clay suspensions. Verburg and Baveye (1995b) showed that for hysteretic cation exchange reactions on smectite clays, light transmission is a history-dependent function of solution or exchanger composition.

The basis for the justification of the mixing procedure was apparently first provided by Shainberg and Kaiserman (1969), who observed that the processes of quasi-crystal formation and breakdown in Na-Ca systems are characterized by very fast kinetics. Formation of Ca-quasi-crystals was found to be instantaneous,

whereas the breakdown took about 10 min. Similar results were obtained by Frenkel and Shainberg (1981) for other cation pairs. Green *et al* (1973) showed, however, that Ca-quasi-crystals continued to grow even after 4 weeks of shaking. Verburg and Baveye (1995a) confirmed these results and presented long-term kinetics data on quasi-crystal formation and breakdown that suggest that these processes may be characterized by a fast initial reaction, followed by a second, much slower reaction. Because the studies of Shainberg and Kaiserman (1969) and Frenkel and Shainberg (1981) only allowed equilibration times of 12 and 30 min, respectively, it is possible that this second slower step was overlooked.

Evidence available in the literature, therefore, suggests that the assumptions underlying the use of the mixing procedure may not be generally valid. In this context, the objective of the present study was to compare the results of the mixing procedure with those corresponding to the forward and backward exchange reactions, in terms of both cation exchange and quasi-crystal formation and breakdown.

EXPERIMENTAL

The clay mineral used in the present study was Camp Berteau montmorillonite from Morocco. Stock suspensions of Na-saturated clay ($<0.5 \mu\text{m}$) were prepared as described by Verburg and Baveye (1995a, 1995b). The clay concentrations of these stock suspensions were 34.0 and 36.2 g clay/kg suspension.

The procedure used to determine the forward and backward exchange isotherms is described in detail by Verburg and Baveye (1995a, 1995b). In short, homoionic K and Mg clay suspensions were prepared by saturation of diluted stock suspensions (0.33% by weight) with 0.5 N KCl or $\text{Mg}(\text{ClO}_4)_2$ solutions. After the electrolyte concentration was lowered to 0.025 N the suspensions were shaken with mixed K-Mg perchlorate solutions of the same total normality. The suspensions were centrifuged and the solutions replaced after 4 and 24 h. The total contact time was 48 h. Adsorbed cations were determined by a 24-h extraction with 1N NH_4Ac , correcting for the entrained solution by weight differ-

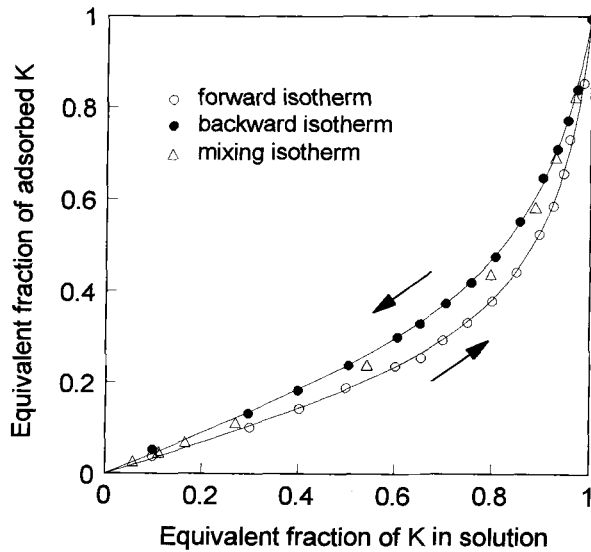


Figure 1. Exchange isotherms for forward and backward reaction and mixing procedure. The solid lines were obtained by fitting the data to a 2-site exchange model (Dufey and Delvaux 1989).

ence. Cation concentrations in supernatants and extracts were determined by inductively coupled plasma (ICP) spectroscopy.

Duplicate samples were prepared, which were used for light transmission measurements. These samples received exactly the same treatment as the ones for the exchange experiment. After 48 h shaking, 0.5-ml aliquots were taken out of the suspensions. The samples were diluted seven-fold with the appropriate solutions. The transmittance of these 1:7 diluted suspensions was measured on a Perkin-Elmer Lambda 4C spectrophotometer at a wavelength of 650nm.

For the mixing experiments, homoionic K and Mg clay suspensions were mixed in various portions. Suspensions of K and Mg saturated clay were prepared in the same way as for the regular exchange experiments. At the point where the samples of the regular exchange experiments were placed in contact with the mixed K-Mg solutions, the samples of the mixing experiment were again suspended in either KClO_4 or $\text{Mg}(\text{ClO}_4)_2$ solutions and shaken for two more hours. Portions of the suspension in each bottle were then transferred quantitatively to plastic weighing boats and added to a sample bottle of clay saturated with the other cation that had lost the same amount of suspension. In this way, a range of solution fractions was obtained and the clay concentration was kept constant throughout. The samples were allowed to shake for another 48 h, during which they were centrifuged after 4 and 24 h, but without removal of the supernatant. After each centrifugation the samples were shaken for 15 minutes on a reciprocal shaker at high speed (as in the regular exchange experiment). The samples were prepared in duplicate. In each pair, one sample was used to obtain

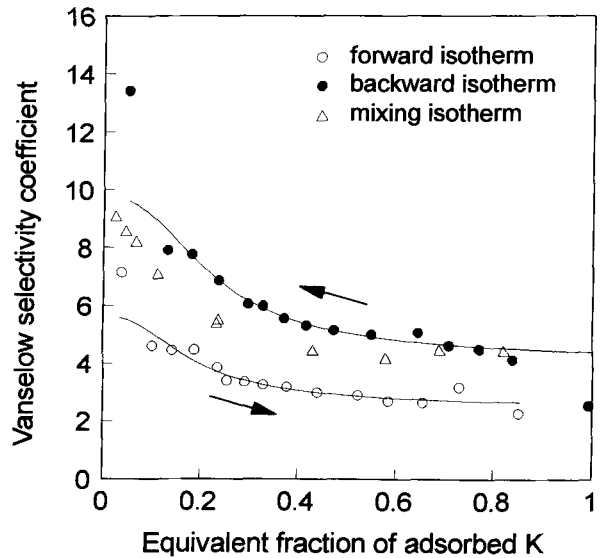


Figure 2. Selectivity coefficient, K_v , plotted as function of the equivalent fraction of adsorbed K for forward, backward, and mixing isotherms. The solid lines correspond with the fits of the forward and backward isotherms in Figure 1. Note that K_v is defined in terms of K replacing Mg for all three isotherms to allow for comparisons.

exchange data and the other was used for light transmission measurement. The exchange samples were centrifuged after 48 h and the clear supernatant collected. Extraction was carried out with 1 N NH_4Ac , taking into account the enclosed liquid. The light transmission samples were diluted seven-fold as in the regular light transmission experiment, using the supernatants of the exchange experiment.

RESULTS AND DISCUSSION

The mixing procedure leads to an isotherm that is intermediate between the forward (K replacing Mg) and backward (Mg replacing K) isotherms (Figure 1). It is approaching the backward isotherm at high K fraction and, if any trend is discernible at all at low K fractions, seems there to be slightly closer to the forward isotherm. These tendencies appear a little more clearly when the Vanselow selectivity coefficient, K_v , (e.g., McBride 1994) is plotted as a function of the equivalent fraction of adsorbed K (Figure 2).

The curve for K_v associated with the mixing isotherm remains constant down to an equivalent fraction of adsorbed K of 0.4, below which there is a strong increase in K_v . Following, e.g., Banin (1968), Van Bladel *et al* (1973), Keren (1979), and Shainberg *et al* (1980), one may be tempted to interpret this change in the slope of the K_v curve in terms of quasi-crystal formation or breakdown. Whatever the outcome of this type of analysis, a different conclusion would be reached if instead of the K_v curve associated with the mixing isotherm, one used for example the curve for K_v associated with the forward isotherm. Indeed, the latter

curve does not exhibit an abrupt change in slope around the value of 0.4 of the equivalent fraction of adsorbed K; the change is gradual and occurs over a range of equivalent fractions.

In terms of light transmission, the mixing curve is also intermediate between the forward and backward isotherms (Figure 3). The transmittance values of the forward and backward curves are lower than those reported by Verburg and Baveye (1995a, 1995b), even though the estimated clay concentration in both experiments was the same. It is not uncommon, however, for different clay batches to have different sizes of quasi-crystals due to slight differences in the preparation procedure (Lahav and Banin 1968a). The estimated experimental error in Figure 3 is, therefore, only a measure for the variability in the experimental data obtained with this particular batch of clay stock suspension.

Following a suggestion made by Laird (1987), Verburg and Baveye (1995a, 1995b) explained the hysteresis in quasi-crystal formation and breakdown in terms of activation energy barriers that need to be overcome for platelet collapse or separation. These energy barriers prevent instantaneous collapse or separation of the platelets. Because the original clay micro-structures of K and Mg montmorillonite are different, this contributes to causing the observed hysteresis.

Mg-saturated smectites form relatively large quasi-crystals (Banin and Lahav 1968, Frenkel and Shainberg 1981, Schramm and Kwak 1982). In the replacement of Mg by K during the forward reaction the same activation energy barrier that prohibits breakdown of the Mg-quasi-crystals prevents K from adsorbing in the interlayer spaces inside the quasi-crystals. This leads to demixing of cations: K ions only adsorb on the outer surfaces of quasi-crystals, while the interlayers are saturated with Mg. The demixing persists until the fraction of K in solution is high enough for K ions to overcome the activation energy barrier for the breakdown of Mg-quasi-crystals. Due to the height of this activation energy barrier, the process of quasi-crystal breakdown extends over a period of at least five months (Verburg and Baveye 1995a). K-quasi-crystals can only be formed if the activation energy barrier is overcome, causing the collapse of platelets to the 15 Å spacing, characteristic for K-montmorillonite. Verburg and Baveye (1995a) found that this hardly occurs in 0.025N solutions. During the initial saturation with KCl at 0.5N, however, small K-quasi-crystals were formed (Verburg and Baveye 1995a). This leads to the observed cross-over of the forward and backward curves in Figure 3. Upon exchange with Mg in the backward direction, there is again a demixing effect, but it is far less pronounced than in the forward reaction due to the small size of the K-quasi-crystals. With increasing amounts of Mg in solution the K-quasi-crystals are broken down and Mg-quasi-crystals are formed. The Mg-quasi-crystals can be formed in 0.025N solutions,

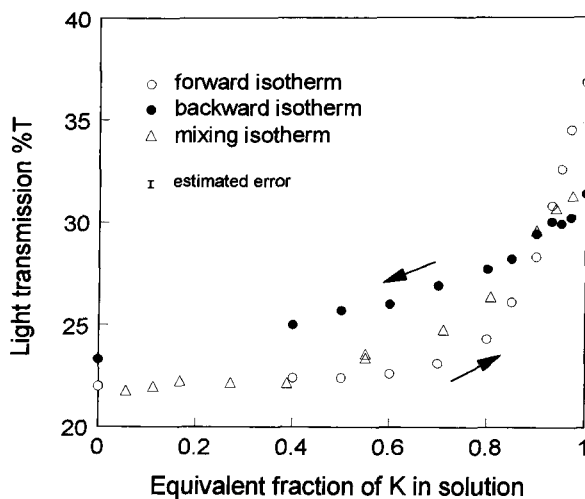


Figure 3. Light transmission for forward and backward reactions and mixing procedure as function of equivalent fraction of K in solution. The replicate samples for the mixing case at a solution fraction of K = 0.55 give an idea of the reproducibility of the light transmission measurements.

because the energy for collapse of platelets to the 19 Å spacing typical of Mg-montmorillonite is much less than the energy needed for collapse to 15 Å-spacing. This probably also contributes to the slow breakdown during the forward reaction: any platelet that is separated from a Mg-quasi-crystal at an early stage (i.e., at low K-fraction) is rapidly integrated into another Mg-quasi-crystal. According to the evidence presented by Verburg and Baveye (1995a), the formation of Mg-quasi-crystals also has a relaxation time beyond 5 months.

Because the slow breakdown of K-quasi-crystals and the slow but continual formation and breakdown of Mg-quasi-crystals are the major factors determining the shape and position of the forward and backward curves in Figure 3, they also need to be taken into account in the interpretation of the mixing isotherm data. In this respect, the basic conclusions of Lahav and Banin (1968), Shainberg and Otoh (1968), and Schramm and Kwak (1982) are still valid. Because of the demixing effect, introduction of a small amount of K in the system does not lead to breakdown of the Mg-quasi-crystals and, upon increasing the equivalent fraction of K in solution from 0.6 to 0.9, a sharp decrease in quasi-crystal size is observed due to the breakdown of Mg-quasi-crystals.

In addition, a feature of the light transmission and viscosity isotherms presented by Schramm and Kwak (1982) that has been ignored so far can possibly be explained in terms of the above inhibition of formation of K-quasi-crystals during the forward reaction and inheritance of K-quasi-crystals during the backward reaction. The data presented by Schramm and Kwak (1982) suggest that during K- and Na- exchange with Ca, the quasi-crystals first decrease drastically in size,

but then recover slightly at high Na or K fractions. This slight increase in quasi-crystal size was apparently ignored as measurement error, based on the relatively high estimated error in the experimental data. Indeed, if the mixing isotherm were to reflect the true equilibrium values, the plot of quasi-crystal size versus K or Na-fraction should be a continuously decreasing function, reflecting the increasing portion of tiny Na or K quasi-crystals. The above interpretation of the forward and backward isotherms suggests, however, that the minimum in the observed isotherm of quasi-crystal size (Figure 6 of Schramm and Kwak 1982) represents not only a mixture of Mg-quasi-crystals and K- or Na-quasi-crystals, but also contains single K- or Na-saturated platelets formed by breakdown of originally Mg-saturated quasi-crystals.

In conclusion, both in terms of cation exchange and light transmission, the mixing procedure leads to curves that are intermediate between the forward and backward isotherms and make a transition from one to the other. This behavior of the K_v and light transmittance curves is likely related to the extent of the hysteresis gap, which in turn depends on the activation energy barriers for quasi-crystal formation and breakdown. The magnitude of these energy barriers is determined by, *inter alia*, the electrolyte composition and concentration, and the surface charge density of the clay. In addition, factors like the clay concentration or the mechanical agitation affect the number of successful collisions between platelets in the quasi-crystal formation process. The extent to which the mixing isotherms reflect true equilibria will, therefore, depend on the conditions imposed on the system by the experiment.

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