

Selective absorption of radioactive strontium and cesium in the formation of montmorillonite gels

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The condensation of gels in the Na-montmorillonite-water system in the presence of the cations Cs^+ , Sr^{2+} , and Ca^{2+} is accompanied by a selective absorption of these cations from the solution.

A Na-montmorillonite suspension in water forms a gel at sufficiently high concentrations. The addition of an electrolyte to the system causes a condensation of the gel; the excess solution forms a separate phase of lower density. In this letter we report a study of the dynamics of this stratification for various ion compositions of the electrolyte, in particular, in the presence of strontium and cesium cations in connection with the removal of these ions for water purification.

In the present experiments we used montmorillonite (bentonite) from a Cherkassy deposit (in the Ukraine). In its natural state, this clay is saturated with calcium cations. The montmorillonite is put in its sodium form by the technique of Ref. 1. An electrolytic solution of a given composition is poured into the prepared suspension, which contains a certain amount of the clay. The total volume of the mixture is brought up to a fixed value (25 ml) by adding distilled water. The suspension is then carefully mixed and left to stand. After a certain time, a transparent solution stratifies out on top of the dense suspension. The volume of this transparent solution increases as time elapses.

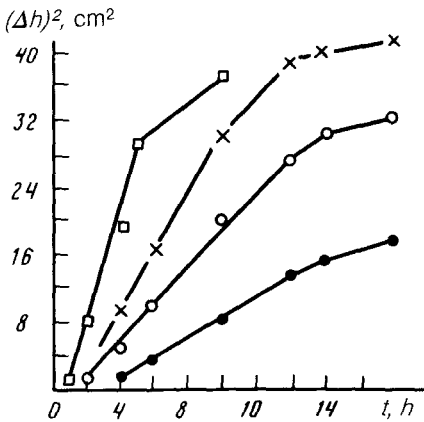


FIG. 1. Square of the lowering of the upper boundary on the montmorillonite gel versus the time in several salt solutions: ●—0.1 M NaCl; ○—0.35 M NaCl; ×—0.7 M NaCl; □—0.1 M CaCl₂.

Figure 1 shows experimental data illustrating the time evolution of the position of the interface between the phases in suspensions containing 1 g of clay per 25 ml of solution, for various ion compositions. Over a broad range of the volume of the dense phase (at $h \gtrsim h_0/3$, where h_0 is the total height of the mixture in the vessel), the experimental points conform to the law

$$\Delta h(t) = h_0 - h = \sqrt{D(t - t_0)}, \quad (1)$$

where the parameters D and t_0 depend on the ion composition and concentration of the suspension. A behavior of the type in (1) can be interpreted in the model of collective diffusion which has been developed for polymer gels,²⁻⁵ by assuming that the parameter t_0 in (1) has the meaning of the time required for the formation of a three-dimensional network of the gel. For simplicity, we take the gel to be a one-dimensional system made up of N particles of mass m , connected by springs. The equations of motion of such a system are

$$\nu \dot{x}_n = -mg(1 - \rho_L/\rho_C) - \frac{\partial}{\partial x_n} U, \quad x_0 \equiv 0. \quad (2)$$

Here ν is the Stokes coefficient of friction, x_n are the vertical coordinates of the particles, g is the acceleration due to gravity, and ρ_L/ρ_C is the ratio of the densities of the water and the clay. The continuum limit of (2) is a heat-conduction equation²⁻⁵ with the boundary condition $(\partial x_n/\partial n)|_N = a - a_0$, where a and a_0 are the initial distance between particles and the distance corresponding to the minimum elastic energy of the springs, respectively. If the springs obey Hooke's law, i.e., $U = \frac{1}{2}k\sum(x_{n+1} - x_n - a_0)^2$ then we find from (2) at $t \gg \nu/k$ a dependence ($g \rightarrow 0$) analogous to (1):

$$\Delta h(t) = u_N(t) = \frac{2}{\sqrt{\pi}} (a - a_0) \sqrt{(k/\nu)t}, \quad u_N = Na - x_N \quad (3)$$

The coefficient D in (1) is therefore determined by the elastic modulus of the gel, its

initial extension $a - a_0$, and the coefficient of friction ν . In the case of polymer gels, the relation between the coefficient of collective diffusion, found from macroscopic measurements, with the microscopic parameters, determined from experiments on inelastic scattering of light, was studied in Refs. 2 and 5. A square-root dependence of the type in (1) and (3) was found in Ref. 4 during the condensation of a gel subjected to reverse osmosis.

Let us consider the properties of the montmorillonite gels which arise in solutions of various compositions. As the NaCl concentration (n) in the suspension is varied over the range $(3.4-70) \times 10^{-2} M$, the diffusion coefficient D found from results like those in Fig. 1 is described by the power law $D \sim (n - n_c)^f$, where $f = 0.65$ and $n_c = 3.4 \times 10^{-2} M$ (4 g of clay per liter of water). Since the viscosity of the solution and also (apparently) the typical size of the particles, both of which enter ν , vary only slightly over this range of n , the strong dependence of D on the salt concentration which is observed must be due to the same dependence of the elastic modulus of the gel: $k \sim (n - n_c)^f$. Consequently, the effect of the salt on the properties of the montmorillonite suspension is analogous to the effect of "cross-linking" on the properties of polymer solutions.^{3,6} The exponent f in the case at hand, however, is sharply different from that in the case of polymers. For the latter, according to percolation theory,³ the typical values would be $f = 1.7-1.9$; an experiment (for caseinic gel) yields⁷ $f \approx 2.06$. The observed value of the exponent, $f \approx 0.65$ is close to that predicted by the more general model of the elastic properties of the disordered solid,⁸ in which the elastic elements coupling the particles can be irreversibly destroyed at some critical load. A numerical study⁸ has yielded $f = 0.8 \pm 0.15$.

The addition of Cs^+ , Ca^{2+} , and Sr^{2+} to the system (at a constant ionic strength of the solution) leads at low concentrations to an increase in the diffusion coefficients (Fig. 1 illustrates the data for Ca^{2+}). With increasing concentration of these ions, it results in a change in the nature of the condensation, associated with the loss of integrity of the gel. Montmorillonite clays have the ability to selectively bind the cations⁹⁻¹¹ Cs^+ , Sr^{2+} , and Ca^{2+} . The selectivity is expressed in terms of a function¹⁰ which is given, for $\text{Na}^+ - \text{Cs}^+$ pair, for example, by

$$K(N_{\text{Cs}}^c / N_{\text{ex}}) = \frac{n_{\text{Cs}}^c / n_{\text{Na}}^c}{n_{\text{Cs}}^s / n_{\text{Na}}^s}, \quad (4)$$

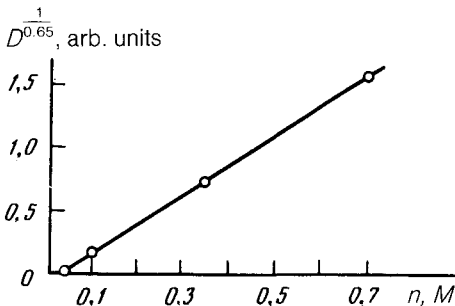


FIG. 2. Collective diffusion coefficient of a montmorillonite gel versus the NaCl concentration.

where $n_{Cs,Na}$ are the concentrations of the ions (the superscripts c and s refer to the clay and to the solution, respectively), and N_{ex} is the number of the exchange sites in the clay. According to Ref. 10, we have $\ln k \approx 13$ at $N_{Cs}^c \sim 10^{-2} N_{ex}$ and $\ln K \approx 3.6$ at $N_{Cs}^c > 10^{-1} N_{ex}$. Taking the balance equations for the substance into account, we find from (4), under the condition $N_{Cs}^t \ll N_{ex}$ ($N_{Cs}^+ = N_{Cs}^c + N_{Cs}^s$),

$$\frac{N_{Cs}^t - N_{Cs}^c}{N_{Cs}^t} \approx K^{-1} (N_{Cs}^t / N_{ex}) \frac{N_{Na}^t - N_{ex} + N_{Cs}^t}{N_{ex} - N_{Cs}^t} \ll 1. \quad (5)$$

In other words, most of the cesium cations are adsorbed on the surfaces of the clay particles. The situation for Ca^{2+} and Sr^{2+} is analogous. Relation (5) has been tested for solutions of various compositions by chemical and radiochemical analysis. In the latter case, samples containing the isotopes ^{134}Cs , ^{89}Sr , and ^{90}Sr were used. At the lowest concentrations studied, the degree of absorption of the cesium and the strontium is more than 97%, which corresponds to the value $k \approx 50$, in qualitative agreement with Refs. 10 and 11.

The calcium, cesium and strontium forms of the montmorillonite form dense suspensions, in which the distance between the aluminosilicate plates is no greater than^{12,13} 20 Å. The replacement of some of the Na^+ cations by Cs^+ , Sr^{2+} , and Ca^{2+} gives rise to some dense "quasicrystalline" contacts in the suspension.^{1,14} This effect can explain the increase in the coefficient D and thus in the elastic modulus of gels in the presence of these cations. With increasing concentration of the cesium, strontium, and/or calcium, the condensation of the gel is accompanied by the appearance of cracks in various stages of the process. This behavior is in qualitative agreement with the conclusion⁸ that a brittle fracture of a solid occurs far from the percolation threshold, i.e., when there is a large number of bonds between the individual particles. With a further increase in the salt concentration, the clay undergoes a flocculation: The infinite cluster in the suspension is replaced by individual flocs, which precipitate in a manner independent of each other.

In summary, in a certain interval of electrolyte concentrations a suspension of montmorillonite in water forms a gel containing an excess of the solvent. The settling of this gel occurs more rapidly, the greater the number of Cs^+ , Sr^{2+} , or Ca^{2+} cations in the system. These cations selectively settle out in a condensed gel, and the solution that stratifies out is depleted by these cations.

¹G. Lagally, H. Stange, and A. Weiss, *Kolloid Z. Z. Polymere* **250**, 675 (1972).

²T. Tanaka, L. O. Hocker, and G. B. Benedek, *J. Chem. Phys.* **59**, 5151 (1973).

³P. G. De Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca, 1979 (Russ. transl. Mir, Moscow, 1982).

⁴A. M. Hecht and E. Geissler, *J. Chem. Phys.* **73**, 4077 (1980).

⁵T. Tanaka, E. Sato, Y. Hirokawa, S. Hirotsu, and J. Peetermans, *Phys. Rev. Lett.* **55**, 2455 (1985).

⁶D. Stauffer, A. Coniglio, and M. Adam, *Adv. Polym. Sci.* **44**, 103 (1982).

⁷M. Tokita, R. Niki, and K. Hikichi, *J. Chem. Phys.* **83**, 2583 (1985).

⁸M. Sahimi and J. D. Goddard, *Phys. Rev. B* **33**, 7848 (1986).

⁹B. L. Sawney, *Clay and Clay Minerals* **20**, 93 (1972).

- ¹⁰E. Brouwer, B. Baeyens, A. Maes, and A. Gremers, *J. Phys. Chem.* **87**, 1213 (1983).
- ¹¹A. Maes, D. Verheyden, and A. Gremers, *Clays and Clay Minerals* **33**, 251 (1985).
- ¹²J. Brown (ed.), *x-Ray Research Methods and Structure of Clay Minerals* (Russ. transl. Mir, Moscow, 1965).
- ¹³H. Van Olphen, in *Clay Colloid Chemistry*, Wiley, New York, 1977.
- ¹⁴A. A. Vedenov and L. I. Tret'yankova, *Pis'ma Zh. Eksp. Teor. Fiz.* **34**, 258 (1981) [*JETP Lett.* **34**, 258 (1981)].

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