Swelling of clays and lyotropic liquid crystals

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(Submitted 6 July 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 5, 271–275 (5 September 1981)

The limited and unlimited swelling of clays and lyotropic liquid crystals is analyzed by molecular-field theory for the degree of dissociation of the counterions.

PACS numbers: 65.70. + y

Certain clays and lyotropic liquid crystals exhibit only a limited swelling when water is added [the water-filled gap between the aluminosilicate (AS) or amphiphilic (AP) layers is no larger than 15–20 Å], while other materials of this type exhibit an unlimited swelling. The transition from limited to unlimited swelling can occur either gradually or abruptly. In this letter we will discuss a model which describes several aspects of the swelling of the lamellar phases of clays and lyotropic liquid crystals.

1. The repulsive force acting between two adjacent AS layers of a clay or AP double layers of a lyotropic liquid crystal (below we will refer to these layers as "plates") consists of two forces. First, there is the force associated with the drawing of water into the surface electric field of the dipoles of the plate molecules. According to Refs. 1–3 this force may be written

$$p_1 = v_o^{-1}\,(U_1 + U_2 \cos 2\pi l/d)\exp(-kl). \qquad (1)$$

Here l is the thickness of the layer of water, $1/k$ is the "crystallization" length (a measure of the effect of the plate on the water), d is the diameter of the water molecule, ν_0 is its volume, and the energies $U_{1,2}$ are of the order of 1 kcal/mole and depend on the detailed atomic structure of the plate and on the difference between the temperature and the freezing point of water.

The second force is the osmotic pressure of the dissociated fraction of the plate ions:

$$p_2 = \alpha NT/l, \tag{2}$$

where α is the degree of dissociation, and N is the ion density at the plates.$^{1)}$

The possible distances l for a clay or a lyotropic liquid crystal at equilibrium with a solution having an osmotic pressure p are given by

$$p_1 + p_2 = p + |p_3|, \tag{3}$$

where p_3 is the van der Waals pressure (for thick plates, $p_3 = -A/6\pi l^3$, where A is the Hamaker constant).

2. The dissociation energy of the ions bound to the plates falls off with increasing l, because of an increase in the hydration energy of the water surrounding a given dissociated ion. As l increases, so does $\alpha(l)$.

As the simplest assumption regarding the function $\alpha(l)$ we consider a model in which α is proportional to the average value of the difference $1 - S$ over the water-filled gap, where the order parameter S $(0 < S < 1)$ describes the degree of order of the water bound by the array of hydrogen bonds to the AS plate[5] or the AP plate[6]:

$$\alpha = c_1 (1 - \bar{S}), \quad \bar{S} = l^{-1} \int_{-l/2}^{l/2} S\,dx.$$

Since the melting of water is approximately a second-order phase transition, we further assume that S satisfies an Ornstein-Zernike equation,

$$d^2S/dx^2 = (\tau/a^2)\,S, \quad \tau = (T/T_m) - 1,$$

where T_m is the melting point of ordinary water, and $\alpha \sim d$. If $S = 1$ at the plates, then $S = (\mathrm{ch}\,qx/2)/(\mathrm{ch}\,ql/2)$, $q = \sqrt{\tau}/\alpha$, and

$$\alpha = c_1 [1 - (2/ql)\,\mathrm{th}(ql/2)]. \tag{4}$$

3. We first consider the case $p_3 = 0$ (physically, this condition corresponds to the situation in which $p_3 \ll p$), $U_2 = 0$. The clay or lyotropic liquid crystal first decomposes into two phases during the swelling if $\partial(p_1 + p_2)/\partial l = 0$, $\partial^2(p_1 + p_2)/\partial l^2 = 0$. For simplicity, we consider the case $k/q \gg 1$. Then expanding $p_1 + p_2$ near the point $l = l_0$, at which $df/dl = 0$, $f = \alpha/l$, we find $(x = ql,\ x_0 = ql_0)$

$$p_1 + p_2 = (U_1/v_0)\exp(-kl) + NT\left[f(x_0) + \frac{1}{2} f''(x_0)(x - x_0)^2 + \ldots\right]. \tag{5}$$

The critical point for the decomposition is determined by

$$(-kU_1/v_0)\exp(kx/q) + qNTf''(x_0)(x - x_0) = 0, \quad k/q = -(x - x_0)^{-1} \tag{6}$$

It can be seen from (6) that in the case $k/q \gg 1$ the expansion in (5) is valid, and the values of l in both of the phases which appear are in fact approximately equal to $l_0 = x_0/q$. The critical ion density at the plate is

$$N_c = [-1/f''(x_0)](k/q)^2 (U_1/v_0 T)\exp(-kx_0/q).$$

If we choose α as in (4), then we have $x_0 = 1.6, f = -0.2\,c_1$.

If $N < N_c$, therefore, the clay or the lyotropic liquid crystal separates into layers with decreasing p during the swelling, and two phases appear (these phases may be called "quasicrystalline" and "lamellar"; their periods are l_1 and l_2, respectively). In the case $N > N_c$, the separation into layers does not occur, and the swelling is gradual. As for the ordinary van der Waals isotherm, the area rule should hold (Fig. 1) during the separation into layers. These conclusions are in qualitative agreement with experiment.[3,8]

4. Let us consider the case $U_2 = 0, p = 0$. If there is no dissociation of ions, the swelling which occurs upon the addition of water will be limited.[9] If the amount of water exceeds the limit (corresponding to a water-layer thickness l_3; Fig. 1), a purely aqueous phase begins to peel away.

If dissociation is possible, then at thermodynamic equilibrium the swelling upon the addition of water will occur in the lamellar phase until the osmotic pressure of the ions at the center of the water-filled layer becomes comparable to the osmotic pressure of the true solution of the molecules of the lyotropic liquid crystal in water[10] or comparable to the attractive forces between the (differently charged) surfaces and ends of the plates of the clay.[4]

An abrupt transition from the quasicrystalline phase to the lamellar phase during swelling in an electrolytic solution can be caused by a weakening of the ionic force (according to Norrish; see Ref. 11). The Debye screening length increases, the osmotic pressure of the ions at the center of the water layer increases,[4] and, as the concentration of the electrolyte falls to the critical value, the curve of the van der Waals attractive force, $|p_3|$, touches the curve of $p_1 + p_2$ (as the ionic force is reduced further, there is an intersection) in the region of the lamellar phase (the point l_4 in Fig. 1).

A transition from the quasicrystalline to the lamellar phase may also be caused by heating[12]: With increasing $\alpha(\tau)$, the curves of $|p_3|$ and $p_1 + p_2$ may intersect.

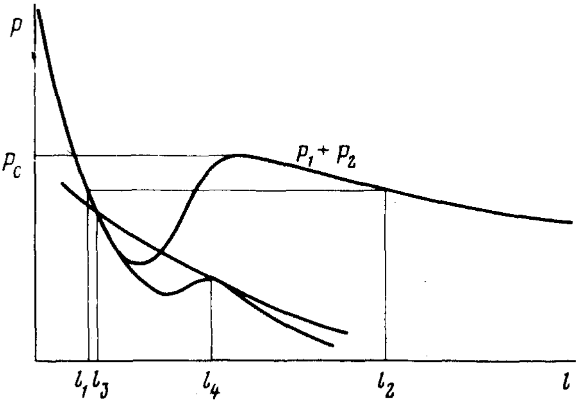

FIG. 1.

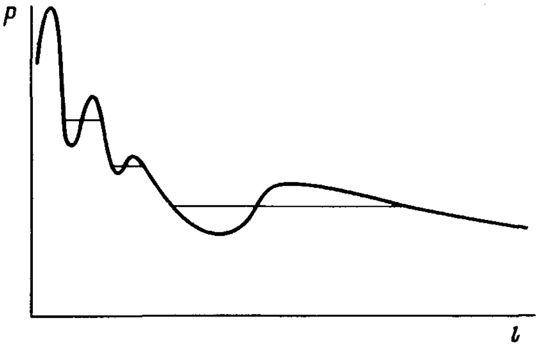

FIG. 2.

5. Oscillations of the pressure p_1 ($U_2 \neq 0$) lead to "shelves" with $l = \text{const}$ on the curves of the period of the quasicrystalline structure vs the osmotic pressure, $l = l(p)$, during the swelling of clays.[11] The various quasicrystalline phases corresponding to the different oscillations of p_1 may also coexist in a swollen clay[11,13] (Fig. 2).

6. In the case of clays, the dissociation of the ions bound to the aluminosilicate plates during the swelling reduces the compression of these plates (in their plane) by undissociated ions[14] and thus leads to an increase[2)] in the lattice constants a and b (in the plane of the plates) with increasing thickness of the water layer,

$$\Delta b = -c_2(1-\alpha) = -c_2 + c_1 c_2 [1 - (2/ql) \operatorname{th} ql/2],$$

in qualitative agreement with experiment.[16]

7. If the lamellar phase of a swollen clay subjected to an external pressure of p is at equilibrium with water which is not under pressure, then the limiting swelling will fall off with increasing pressure, in accordance with (3), and the lamellar phase will disappear at a pressure exceeding the critical pressure (p_c in Fig. 1). This conclusion agrees with experimental results on the swelling of clay under pressure[17] (the experimental critical pressure is $p_c \sim 10$ atm).

1) At large values of l we must take into account the redistribution of ions in the water layer which results from their mutual repulsion.[3] If an external electrolyte is present, Debye screening should be taken into account.[4]

2) In the case of a slight swelling, a and b initially decrease with increasing thickness of the water layer, because of a decrease in the tendency of the cations of hexagonal cavities to push the aluminosilicate plates apart.[15]

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Translated by Dave Parsons
Edited by S. J. Amoretty