

Classification

Physics Abstracts

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Effects of a non-adsorbing polymer on colloid stability : force measurements between mica surfaces immersed in dextran solution

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Résumé. — Les forces de surface ont été mesurées entre deux feuilles de mica en configuration de cylindres croisés en présence de chlorure de sodium. Pour différentes concentrations de NaCl (10^{-4} , 10^{-3} , 10^{-2} M), on observe, aux faibles distances, une contribution additionnelle attractive aux forces DLVO quand le dextrane est ajouté à la solution aqueuse. La conséquence la plus frappante de cet effet est que le saut en contact des feuilles de mica survient à des distances plus grandes et pour des forces de compression plus faibles qu'avec l'électrolyte pur ; de plus, même dans des cas où les forces d'hydratation empêchent ce saut en contact (NaCl 10^{-2} M), l'addition de dextrane le permet. Dans tous les cas ce contact se fait à distance nulle, ce qui prouve qu'il n'y a pas de dextrane adsorbé irréversiblement aux surfaces. Ces résultats expérimentaux sont analysés en rapport avec les théories récentes concernant l'effet de la déplétion des polymères sur la stabilité des colloïdes.

Abstract. — The forces between two cylindrically curved mica surfaces have been measured in aqueous dextran solution in the presence of NaCl. At various NaCl concentrations (10^{-4} , 10^{-3} , 10^{-2} M) we observe an additional attractive contribution to DLVO forces when dextran is added to the aqueous solution. The most striking consequence of this effect is that the jumps into primary minimum contact occur at larger distances and at weaker forces than with pure electrolyte solution ; moreover in some cases where hydration forces prevent the jump in primary minimum contact (NaCl 10^{-2} M), the addition of dextran produces this jump. In all cases the primary minimum contact takes place at zero distance which proves that no adsorbed dextran is trapped between the two mica surfaces. These experimental results are analysed and compared with the recent theories of polymer depletion effect on colloid stability.

1. Introduction.

Amongst the many problems related to colloid stability, the aggregative properties of soils have great practical importance. Organic polymers are well known to aggregate and bridge soil mineral particles [1, 2]. Pagliai *et al.* [3] have shown that the stability of soils depends on the concentration and molecular weight of dextrans. Much work has been done both theoretically [4-8] and experimentally [9, 10] on the stabilization of colloidal systems by polymers. Two situa-

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tions are distinguished depending on whether the polymer adsorbs on the particles or not. In both cases, a colloidal system may be stabilized or destabilized. Four behaviours may be encountered : adsorption stabilization or adsorption flocculation, and depletion stabilization or depletion flocculation. While the adsorbing case has been thoroughly investigated, the non-adsorbing case has mainly been studied from a theoretical point of view. Joanny *et al.* [5] have predicted that when the polymer does not adsorb, there is a decrease in polymer concentration near one wall (depletion layer) leading to an attractive contribution between two such walls. Scheutjens and Fler [6] have computed the interaction between two walls across polymer solution in the four cases cited above. Usual techniques for measuring adsorption are inadequate for detecting depletion. Only one technique (Evanescent Wave Induced Fluorescence, EWIF) has been successfully applied to give direct information on the depletion layer [11]. However no measurements of corresponding surface forces have been reported.

In this paper, we report on the effect of the presence of dextran (a neutral polymer) on the forces between two mica surfaces immersed in aqueous NaCl solution. Dextran is an almost perfect statistical compact coil for molecular weights above 2000 [12, 13]. Muscovite mica cleavage plane is generally admitted as a good model for clays in general and illite in particular.

2. Experimental.

2.1 MATERIALS. — The water used was tridistilled, the second distillation being made from acid potassium permanganate and had very low bubble persistence. The pH value of the water was typically 5.6. The NaCl was obtained from Merck Suprapur 99.5 %, and roasted 6 hours at 600 °C. The concentrated NaCl solutions were filtrated through fluoropore 0.2 μm . Dextran, with molecular weight $M_w = 2 \times 10^6$, was obtained from Sigma (D5376) and used without further purification. The radius of gyration R_G of dextran can be calculated using the relation $R_G = 0.6 M^{0.43}$ determined by Snabre *et al.* [13] (these authors explain the exponent 0.43 by branching), for $M \simeq 2 \times 10^6$, $R_G \simeq 31$ nm.

2.2 METHODS AND PROCEDURE. — The force F between two molecularly smooth curved (of radius $R = 2$ cm) mica surfaces as a function of distance D was measured using the method developed by Israelachvili and extensively described in reference [14]. The apparatus was thermostated at 20 ± 0.1 °C. The separation D between the surfaces was measured with an accuracy of (0.1-0.2) nm. The value F/R is plotted in the graphs as a function of D , and is equal to $2 \pi E$, where E is the corresponding energy between flat surfaces [15]. The mica surfaces are first immersed in water and left for an hour. Then we check that on bringing the surfaces towards each other, they jump into contact from a repeatable distance of ~ 2.5 nm which is a good test for the absence of organic or particulate contamination [16]. Water is then replaced by NaCl solution and after 2 hours, force/distance profiles are determined. Then dextran is added. The results reported are obtained from at least two independent experiments.

3. Results.

The reference distance $D = 0$ is the one obtained when the mica surfaces are contacting in pure NaCl solution. When dextran was added at all used concentrations (0.1 to 0.6 g/l) and for incubation times up to 8 days, the mica surfaces always contacted at the same reference distance $D = 0$ (measured within ± 0.15 nm accuracy). This result shows that no layer of dextran remains on the surfaces (no irreversible adsorption) when they are brought into contact. At all distances where refractive index was measured (10 to 100 nm), it was found equal to that of the pure NaCl solution.

It has already been mentioned that in the presence of macromolecules, force/distance profiles may show a hysteresis. We have shown the importance of this phenomenon in a previous study of forces between mica surfaces bearing adsorbed mucin (BSM) [17]. Luckham and Klein [10]

have extensively studied force/distance profiles in the presence of adsorbed polylysine in compression-decompression cycles. Each curve presented here has been obtained from a first compression when the surfaces were brought from large distance (800 nm) to contact with a monotonic displacement (no receding, no use of piezoelectric tube, use of the differential spring system only [14]). All results obtained with pure NaCl solution are in agreement with those published by Pashley [18].

Figure 1a shows the force/distance profile in NaCl 10^{-4} M and in NaCl 10^{-4} M + dextran 0.3 g/l. In NaCl 10^{-4} M, the surfaces jump into primary minimum contact at $D = 2.0 \pm 0.4$ nm. With dextran 0.3 g/l, this jump occurs at $D = 5.5 \pm 0.4$ nm and at a weaker force. Figure 1b gives the difference between these two curves. An attractive contribution after dextran is added becomes noticeable from 30 nm distance. A weak repulsive contribution for $D > 50$ nm is also measured (Fig. 1a). At a lower concentration (dextran 0.1 g/l), only an attractive contribution is measured (results not shown).

The jump into primary minimum contact occurs at $D = 1.8 \text{ nm} \pm 0.4 \text{ nm}$ in NaCl 10^{-3} M and at $4.0 \pm 0.4 \text{ nm}$ in NaCl 10^{-3} M + dextran 0.1 g/l (Fig. 2a). Figure 2b shows the attractive contribution after the addition of dextran.

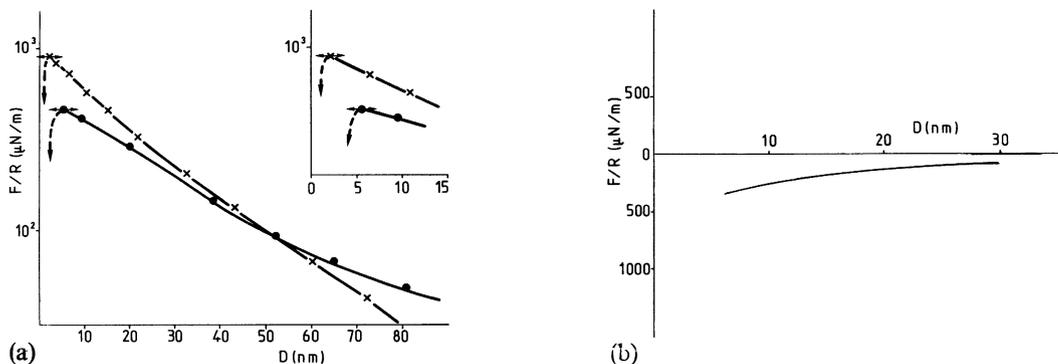


Fig. 1. — (a) Forces measured between mica surfaces in NaCl 10^{-4} M (x) and NaCl 10^{-4} M + dextran 0.3 g/l (●). (b) Difference between the two curves.

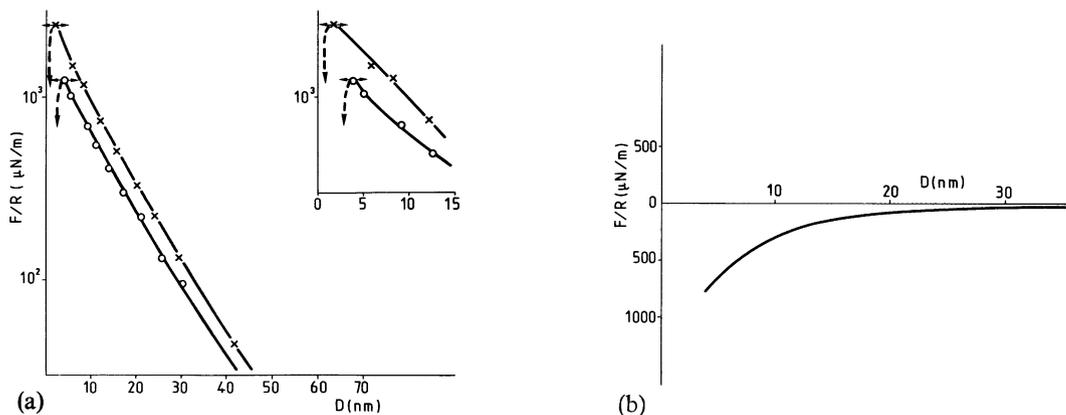


Fig. 2. — (a) Forces measured between mica surfaces in NaCl 10^{-3} M (x) and NaCl 10^{-3} M + dextran 0.1 g/l (○). (b) Difference between the two curves.

In $\text{NaCl } 10^{-2} \text{ M}$, hydration forces remove the primary minimum contact, as was observed by Pashley [18], and we have observed no jump into contact. With dextran 0.1 g/l, a jump into primary minimum contact occurs at $D = 1.6 \pm 0.4 \text{ nm}$ (Fig. 3a). Figure 3b shows the attractive contribution in the presence of dextran. When the dextran concentration is increased to 0.3 g/l, the jump into contact occurs at a weaker force and from almost the same distance. In this case there is a repulsive contribution at distances greater than 10 nm.

4. Discussion.

These first results obtained with a commercial dextran will be discussed in this paper mainly from a qualitative point of view. The adsorption of dextran on clays is still controversial [19, 20]. Adsorption on various types of clays of the same dextran we used was recently found to be two orders of magnitude lower than of other polysaccharides [21]. We have found that no irreversible adsorption of this dextran occurs on mica. Two possibilities then remain : reversible adsorption or depletion. De Gennes [7] has proved that for flexible polymer chains, the interaction between plates is always attractive when the chains can exchange reversibly with a bulk solution. As the repulsive regime is observed within a certain concentration and distance range, it seems that the depletion of dextran molecules at the solution/mica interface takes place. Measurements of the concentration profiles for the same system with the EWIF technique, for instance, would be determinant.

In qualitative agreement with Asakura *et al.* [4] and Joanny *et al.* [5], an attractive regime is observed in every case. This effect is noticeable at distances up to 30-40 nm and may be determinant in many cases. Increasing dextran concentration reduces the distance at which attraction is detectable (Fig. 3b), in agreement with Ausseré *et al.* [11] who measured depletion profiles with Xanthan with the same molecular weight and concentrations. Moreover, a repulsive contribution is obtained at larger distances (Fig. 3b) in agreement with Scheutjens and Fleer [6]. The effect of increasing dextran concentration at fixed ionic strength is to reduce the height of the force barrier (Fig. 3a).

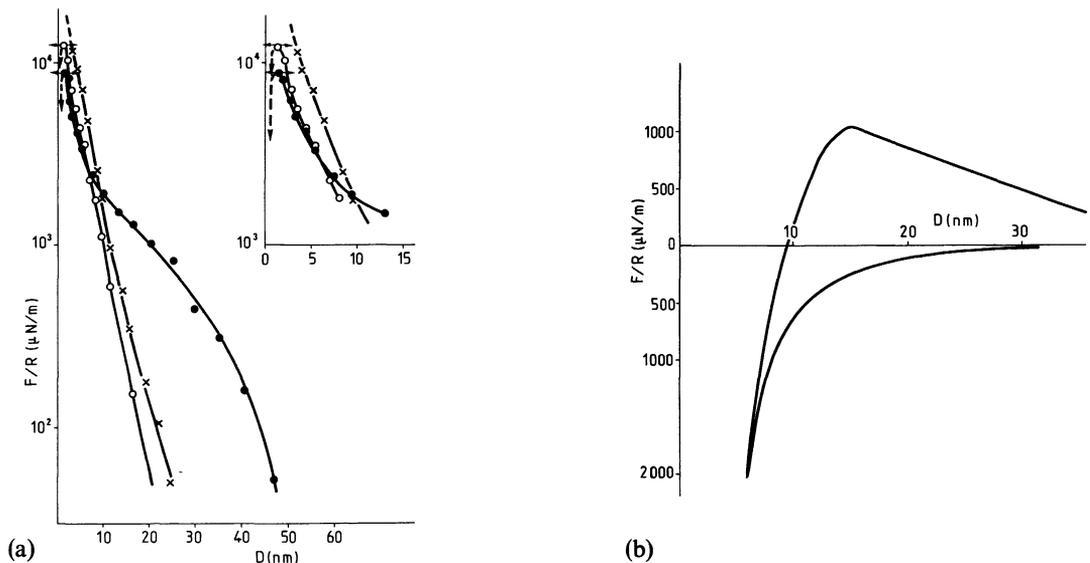


Fig. 3. — (a) Forces measured between surfaces in $\text{NaCl } 10^{-2} \text{ M}$ (\times); $\text{NaCl } 10^{-2} \text{ M} + \text{dextran } 0.1 \text{ g/l}$ (\circ) and $\text{NaCl } 10^{-2} \text{ M} + \text{dextran } 0.3 \text{ g/l}$ (\bullet). (b) Difference between $\text{NaCl } 10^{-2} \text{ M}$ reference curve and curves obtained with dextran.

Increase of NaCl concentration increases the attractive contribution (Fig. 1b and Fig. 3b). As far as a quantitative comparison with the theory of depletion effects is concerned, a simple evaluation of depletion attraction from osmotic pressure, calculations [4] in the dilute case ($c < c^* = M_w/(4/3 \pi R_G^3) \simeq 30$ g/l with $R_G \simeq 31$ nm, c^* is the first overlap concentration) gives a value of $E \simeq F/2 \pi R \simeq 10^{-2}$ $\mu\text{J}/\text{m}^2$. The effect we observed is much higher than one may evaluate theoretically in a dilute system.

In the case of a semi-dilute system, the magnitude of the depletion attraction would be : $E \simeq F/2 \pi R \simeq kT/\xi^2$, where ξ is taken as the radius of gyration of the polymer (cf. Eq. (3.2) of Ref. [5]). We have $F/R \simeq 24$ J/m^2 , which is closer to the observed attractive contribution.

To investigate further this discrepancy, other possibilities may be considered. It must be pointed out that the surface forces measurement technique is very sensitive to the presence of impurities [22-25] and that any analysis of the results must include such a possibility. If there were ionic impurities, they would provoke a decrease of the decay-lengths of the forces, opposite to that shown in figure 1 (the lowest ionic strength). If there were hydrophobic impurities adsorbing on mica, they would produce an attractive contribution [16]. However, such impurities, if present, would have been noticed and would influence upon the contact which always occurred at the reference distance $D = 0 \pm 0.15$ nm.

It is worth mentioning that, when the dextran-NaCl solution was replaced by a pure NaCl solution, the force-distance profiles were identical to the ones measured in NaCl prior to the addition of dextran.

Finally, we have performed measurements with high quality dextran [27] (molecular weight $M_w = 1\,400\,000$, $M_w/M_n = 1.965$). The experimental results shown in figure 4 are qualitatively and quantitatively similar to the ones obtained with commercial dextran.

In any case, the observed phenomenon cannot be attributed to the sole dextran effect. Comparison of the figures 1b, 2b and 3b makes it obvious that the attractive contribution is dramatically enhanced by NaCl. In references [12] and [28] the salting-out effects for dextran and the increase of its radius of gyration with ionic strength are described. The effect of the salt on the attractive contribution remains unexplained at present.

5. Conclusion.

These results show that, in the non-adsorbing case, on top of the usual surface forces, an additional contribution is measured. This contribution depends on the polymer concentration and NaCl concentration. At large distances, repulsive interactions may be observed in some cases. At small

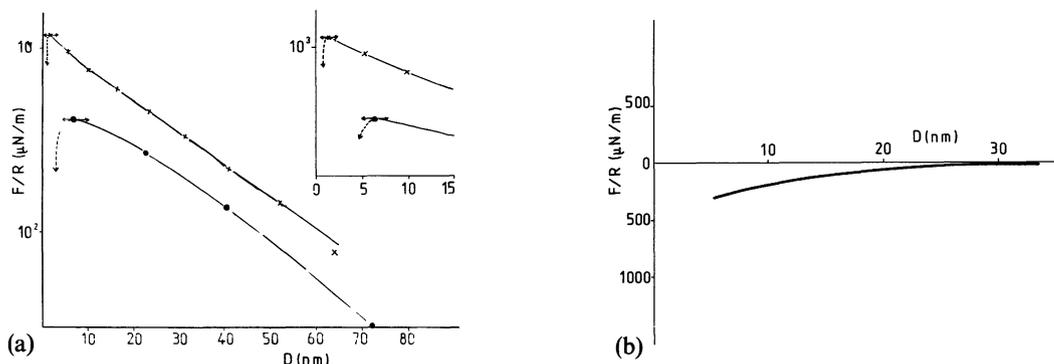


Fig. 4. — (a) Forces measured between surfaces in NaCl 10^{-4} M (x); NaCl 10^{-4} M + dextran 0.15 g/l (o). Here this dextran was non-commercial [27]. (b) Difference between NaCl 10^{-4} M reference curve and curve obtained with dextran.

distances, an attractive contribution is always obtained. This interaction is so important that it can produce a jump into primary minimum contact in cases when hydration forces prevent it in pure NaCl solution. These results seem to be related to depletion (non-adsorption) of dextran. They cannot, however, be entirely explained by the recent theories of depletion effects. This observed effect may be very important for the stability of colloids. Our study also shows that dextran, even at low concentrations in clay soils, may have a determinant influence on their properties.

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