

RHEOLOGY OF Na-RICH MONTMORILLONITE SUSPENSION AS AFFECTED BY ELECTROLYTE CONCENTRATION AND SHEAR RATE

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Abstract—Rheological measurements were used to evaluate the particle-particle associations of Na-rich montmorillonite in suspensions, under various electrolyte concentrations. A 2% free electrolyte clay suspension showed pseudoplastic flow behavior and had a high apparent viscosity, attributed at low shear rates to the high volume fraction of the suspended clay platelets, the flexibility of the platelets, and the presence of edge-to-edge association. The breaking of edge-to-edge associations and the progressive orientation of the individual platelets in the direction of flow contribute to the reduction in viscosity with increasing shear rate.

The compression of the diffuse double layer at a NaCl concentration of 10 mEq L⁻¹ contributes to the free movement of the individual platelets, even at low shear rates. The flow behavior changed from pseudoplastic to plastic at a NaCl concentration of 100 mEq L⁻¹. At this electrolyte concentration, face-to-face associations of specific junction points at certain areas of the planar surface are probably occurring.

The apparent viscosity of the clay suspension for the two particle-size ranges (<2 and <0.02 μm) at all shear rates converged to a minimum value of 4.5 mPa s at NaCl concentrations of 10–20 mEq L⁻¹. On both sides of the minimum, the lower the shear rate, the greater the slope. The apparent viscosity of a 2% suspension of Na-rich montmorillonite <0.02 μm particles, however, was significantly greater than that observed for a suspension of <2 μm particles. This high apparent viscosity is attributed to the increase in edge surface area and the number of clay particles in a unit volume.

We suggest that edge-to-edge association between Na-rich montmorillonite platelets prevails when the NaCl concentration is below the electrolyte critical concentration, for which the apparent viscosity of the suspension is at its minimum value, whereas face-to-face association prevails at NaCl concentrations above this critical value.

Key Words—Clay-particle Interaction, Clay-suspension Viscosity, Na-rich Montmorillonite.

INTRODUCTION

The aggregate stability and hydraulic conductivity of soils are, to a great extent, results of swelling and flocculation/dispersion of soil clays. Sodium-saturated clays are more susceptible to dispersion than those saturated with divalent ions in solution of low electrolyte concentrations. The presence of electrolytes at concentrations above the flocculation value is necessary to prevent dispersion of the clay. Flocculation of montmorillonite by electrolytes is a result of a change in the particle-particle association, which is determined by the following forces: (1) electrostatic repulsion between double layers of two plate surfaces of similar charge; (2) attraction between adjacent platelets by van der Waals forces (face-to-face interaction, FF; edge-to-edge interaction, EE) and by electrostatic forces (the negatively charged surfaces and the positively charged edges, edge-to-face (E-F), (van Olphen, 1977); and (3) hydration forces that originate from the hydration of the clay surface and the exchangeable cations.

Modification of the interaction between clay particles is possible by changing the solution properties (pH, electrolyte composition and concentration) or by adding organic substances. These interactions can be

evaluated by means of rheological measurements, because the rheological properties of clay suspensions depend on the clay concentration, the size and shape of the clay particles, and the level of interaction between them (van Olphen, 1977). Therefore, Na-rich montmorillonite suspensions at concentrations >2% usually show pseudoplastic behavior that is characterized by the dependence of the viscosity on the shear rate (Keren, 1988). One reason for pseudoplasticity is that the degree of hydration, which depends on the entrapment of water between the flocs, decreases as the shear rate increases. Another reason for the pseudoplastic behavior is the breaking of bonds between clay platelets during flow. The shear stress affects the size of the flocs and the number of bonds between them (Akae and Low, 1988). Flocs that are formed in suspension can be broken by shear forces.

The influence of electrolyte concentration on the suspension rheology of some clays has been studied under various conditions (Heath and Tadros, 1982; Rand and Melton, 1977; Rand *et al.*, 1980; Chen *et al.*, 1990; Brandenburg and Lagaly, 1988; Akae and Low, 1988; Nitawaki *et al.*, 1981). The electrolyte concentration has been observed to have a unique influence on the rheological properties of Na-rich montmorillonite suspensions. A minimum in yield stress

and plastic viscosity has been observed in the presence of electrolytes in suspension at low concentration (van Olphen, 1977; Rand *et al.*, 1980; Nitawaki *et al.*, 1981; Chen *et al.*, 1990). Various explanations for this minimum have been suggested. Van Olphen (1977) suggested a destruction of E-F structure following the addition of electrolyte at low concentration. Rand *et al.* (1980) found no evidence for E-F coagulation in the pH range 4–11, in the presence of electrolyte at low concentration. The secondary electroviscous effect was the mechanism proposed by Rand *et al.* (1980) and adopted by Permian and Lagaly (1994) for the minimum in yield stress and plastic viscosity; they suggested that the diffuse double layers around the particles affect their motion. At low electrolyte concentration in clay suspension, the extended diffuse double layer allows more freedom of movement under stress, whereas at higher electrolyte concentration the attractive forces between clay platelets dominate, and the yield stress and plastic viscosity increase again. Contrary to van Olphen's (1977) hypothesis, Chen *et al.* (1990) suggested that Mg^{2+} in octahedral coordination is involved in modifying the rheological properties; Mg^{2+} is released from the clay structure by hydrolysis of the clay at low electrolyte concentrations.

The dependence of flow properties of clay suspensions on electrolyte concentration and shear rate can be explained by changes in particle-particle interactions. Therefore, the present study was undertaken to investigate these relationships further.

MATERIALS AND METHODS

Clay preparation

The $<2 \mu\text{m}$ fraction of montmorillonite from Upton, Wyoming was extracted by allowing larger particles to settle in water and then decanting. The Na-rich clay was prepared by equilibrating the colloidal fraction with 1 mol L^{-1} NaCl solution. This equilibration was repeated three times. The clay was then washed with distilled water and separated in a high-speed centrifuge until the solution was free of Cl^- . Chloride was presumed to be absent when the supernatant liquid gave a negative test with AgNO_3 . The salt-free clay was freeze dried and stored in a desiccator over P_2O_5 .

Clay was suspended in distilled water at a concentration of 30 g kg^{-1} and was stirred for $\sim 12 \text{ h}$. The pH was adjusted to neutral by adding 0.01 N NaOH . The final concentration of the clay suspensions was brought to 20 g kg^{-1} , and the Na^+ concentrations were $0\text{--}0.2 \text{ mol L}^{-1}$. After an additional $\sim 12 \text{ h}$ of stirring, 3 mL samples of clay suspension were transferred to 7 mL plastic vials and were stirred for a further 12 h . The pH of the suspension remained constant.

The suspension at a concentration of 3% by weight of the clay to the liquid was divided into two parts.

The first part, containing $<2 \mu\text{m}$ clay particles, was left untreated. The second part was treated by an ultrasonic disintegrator vibrator (USV) (model Sonifier B-12A, Branson Sonic Power Co.) for 1 h at 50 W . This suspension was then centrifuged for 30 min at $2030 \times g$ (Beckman model J2–21M Induction Drive Centrifuge with JA17 rotor) to obtain a suspension with clay particles of $<0.02 \mu\text{m}$ in size (Keren and Klein, 1995). The total clay concentration in the suspensions was determined. The two parts were used for the rheological measurements as described below.

Rheological measurements

The rheological measurements were performed with a commercial couette-type viscometer with a rotating outer cylinder and a stationary inner cylinder (Haake, Model RV2, Sensor System CV20, Germany). The gap between the outer cylinder and the inner cylinder was 0.32 mm . The viscosity of all suspensions was determined at $25.0^\circ\text{C} \pm 0.2$. The viscometer was calibrated with a standard fluid prior to the measurements. The measuring time was 2 min and the shear rates ranged from 0 to 1000 s^{-1} .

RESULTS AND DISCUSSION

The dependence of shear stress on shear rate for the Na-rich montmorillonite suspension of $<2 \mu\text{m}$ clay particles, and the dependence of apparent viscosity on NaCl concentration and shear rate at pH 7 are presented in Figures 1 and 2, respectively. In accordance with Rand *et al.* (1980), Brandenburg and Lagaly (1988) and Keren (1988), pseudoplastic rheological behavior was observed for the Na-rich montmorillonite suspension in distilled water. The critical shear rate at which the flow curve became linear was 250 s^{-1} and the differential viscosity of the linear part of the curve was 6.2 mPa s . The apparent viscosity of the clay suspension in distilled water was 16.4 mPa s at a shear rate of 100 s^{-1} , and it decreased as the shear rate increased (Figure 1).

The yield stress and the critical shear rate are sensitive measures of the degree of association and can be used as indicators of change in the mode of particle-particle association. These values depend on the number of particle-particle linkages and the energy required to break such linkages. The breakdown of the particle-particle linkages may be related to both the shear forces and the Brownian motion of the clay particle, whereas the build-up is a result of the Brownian motion only (Goodwin, 1975). Thus, it is expected that at greater shear stress the average number of linkages will be lower than that at smaller shear stress, because the forces involving breakdown increase with increasing shear stress, whereas the interaction forces and the Brownian motion remain constant. Thus, the very low yield stress and critical shear rate for the suspension in distilled water (Figure 1) suggest that the attractive

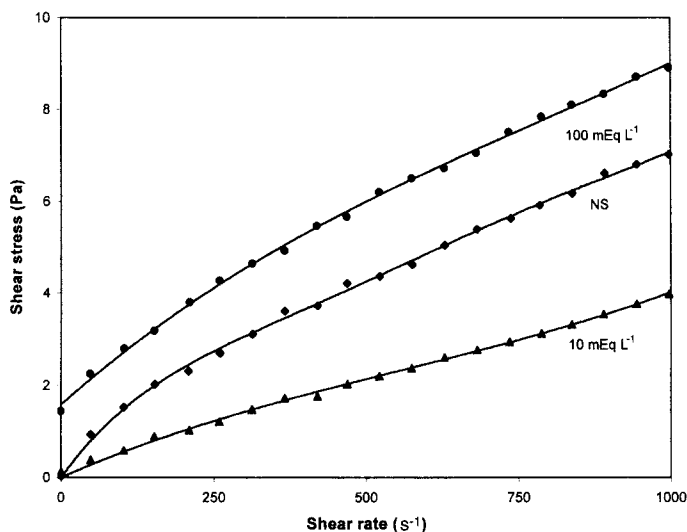


Figure 1. Effect of electrolyte concentration on flow behavior of a 2% Na-rich montmorillonite suspension with $<2 \mu\text{m}$ particles. (NS = no electrolytes added).

forces between Na ion-saturated clay platelets in a suspension without free electrolytes are weak.

The high viscosity of this suspension, however, was probably related to the specific contribution of the high volume fraction of the suspended clay platelets and the presence of a weak edge-to-edge association (Tessier and Pedro, 1981), which probably forms at low shear rates. Assuming that the clay platelets are arranged in a parallel array under flow, the average distance between two adjacent parallel Na-rich montmorillonite platelets in a suspension with a clay concentration of

20 g L^{-1} , is 132 nm . With this assumption, the average thickness of the water layer associated with the planar surface of one side of a platelet is 66 nm , regardless of the platelet size. However, the thickness of the diffuse double layer (DDL) associated with a Na-rich montmorillonite platelet in free electrolyte suspension exceeds 100 nm (the DDL thickness for this clay is 100 nm at a NaCl concentration of $10^{-5} \text{ mol L}^{-1}$, van Olphen, 1977), therefore, the DDL occupies all of the suspension volume. The DDL theory does not consider the short-range repulsive hydration forces associat-

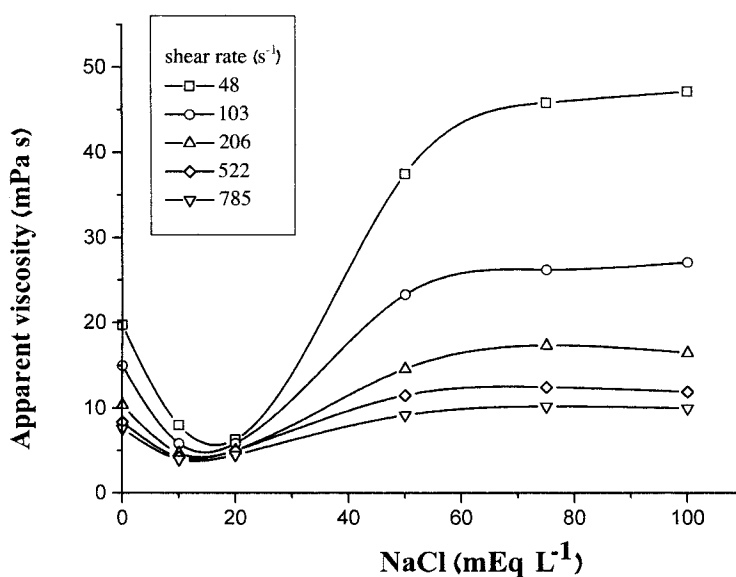


Figure 2. Effect of electrolyte concentration on the apparent viscosity of a 2% Na-rich montmorillonite suspension with $<2 \mu\text{m}$ particles for various shear rates.

ed with the ions in the DDL. The H₂O molecules that move with the clay platelets increase the effective volume (the volume that is greater than the actual volume of the clay platelets themselves) fraction of the moving particles. In addition, the electroviscous phenomenon may change the viscosity, especially at low electrolyte concentrations (see below).

The reduction in the apparent viscosity (Figure 2) as the shear rate increases in the absence of free electrolyte, indicates a shear thinning flow. Because face-to-face associations are not likely to be formed between two adjacent platelets under these experimental conditions, the reduction in viscosity with increasing shear rate can be attributed to two mechanisms: (1) the progressive orientation of the individual platelets in the direction of flow (Rand *et al.*, 1980); and (2) the breaking of the weak edge-to-edge associations between adjacent platelets which form at low shear stress (Keren, 1988).

In accordance with Rand *et al.* (1980), Brandenburg and Lagaly (1988) and Chen *et al.* (1990), the flow behavior of a Na-rich montmorillonite suspension changed significantly in the presence of NaCl (Figure 1). At a concentration of 10 mEq L⁻¹, the viscosity was lower than that obtained for the clay suspension without free electrolyte for any shear rate (Figures 1 and 2). The critical shear rate (Figure 1), at which the flow curve became linear, was 180 s⁻¹, a lower value than that obtained for the clay suspension without free electrolytes (250 s⁻¹). The differential viscosity represented by the linear part of the curve (Figure 1) was 3.8 mPa s, a value which was also lower than that observed for the suspension in the absence of free electrolyte. The absence of yield stress and the low critical shear rate (Figure 1) suggest that the attractive forces between Na ion-saturated clay platelets are very weak at this NaCl concentration. At this concentration (10 mEq L⁻¹), the DDL thickness was reduced to 3.2 nm and the individual platelets could move more freely along the flow direction, even at low shear rates, because of the decreasing effect of the electroviscous phenomenon. This NaCl concentration, however, was still not sufficiently high to allow face-to-face association between clay platelets.

The dependence of shear rate on shear stress of Na-rich montmorillonite suspensions at a NaCl concentration of 100 mEq L⁻¹ is also presented in Figure 1. By comparison of the flow behavior of this suspension with that at lower electrolyte concentrations, four significant changes were observed: (1) the flow behavior changed from pseudoplastic to plastic; (2) a high initial yield stress was obtained (1.35 N m⁻²); (3) the critical shear rate increased to 500 s⁻¹; and (4) the apparent viscosity increased for all shear rates (Figures 1 and 2). This increase in viscosity is not consistent with the data of Rand *et al.* (1980) for the NaCl concentration range of 0–0.8 mol L⁻¹.

The high initial yield stress, critical shear rate, and viscosity data suggest that clay particles interact at this electrolyte concentration. The thickness of the DDL decreases further, to 1.0 nm when the NaCl concentration in the suspension increases to 100 mEq L⁻¹. If the electroviscous effect was the dominant mechanism, the suspension viscosity would be expected to decrease as the solution concentration increased from 10 to 100 mEq L⁻¹. The observed increase in viscosity, however, may suggest that clay association is the main mechanism that affects the viscosity at such a NaCl concentration. Norrish (1954) and Foster *et al.* (1955) observed that the *c*-axis spacing of Na-rich montmorillonite in NaCl solution decreased progressively by increasing electrolyte concentration until a concentration of 0.25 mol L⁻¹ was reached. The spacing then decreased abruptly from ~4.0 to 1.9 nm. According to the theory of flocculation (Reerink and Overbeek, 1954; Ottewill *et al.*, 1960), this abrupt decrease in *c*-axis spacing would not have occurred unless the platelets were in energy "well". Thus, Na-rich montmorillonite does not begin to flocculate in the face-to-face association until the NaCl concentration reaches 0.25 mol L⁻¹. However, Keren *et al.* (1988) observed a flocculation value of 44 mEq L⁻¹ for Na-rich montmorillonite at pH 9.8. The presence of a negative charge on the edge surfaces at this pH, the observed flocculation value of 44 mEq L⁻¹, and the high gel volume, suggested that an open structure with a face-to-face association predominates at specific locations, assuming that the electrostatic charge was distributed unevenly on the planar surfaces. Thus, face-to-face associations between platelets may form at junction points in areas having either lower or higher specific charge (*C*) density (the average value for montmorillonite is 0.117 C m⁻²). This electrolyte concentration is sufficient to compress the diffuse double layer to an extent which allows the platelets to approach one another and form associations between the specific areas of lower or higher surface charge densities. This can occur because the individual platelets are flexible (Tessier and Pedro, 1981). Thus, the reduction in repulsion energy as the electrolyte concentration increases (above 20 mEq L⁻¹), allows the platelets to approach each other sufficiently to form face-to-face associations at certain areas on the planar surfaces. At this moderate NaCl concentration, a platelet network structure may form in the suspension, as described by Keren *et al.* (1988). The increase in viscosity observed at this concentration range (Figure 2) is probably related to the formation of such an open structure.

The dependence of apparent viscosity on NaCl concentration and shear rate for suspensions of Na-rich montmorillonite of clay particles of <2 μm at pH 7 is given in Figure 2. At low concentration, the viscosity decreased as the NaCl concentration increased, reached a minimum at concentrations of 10–20

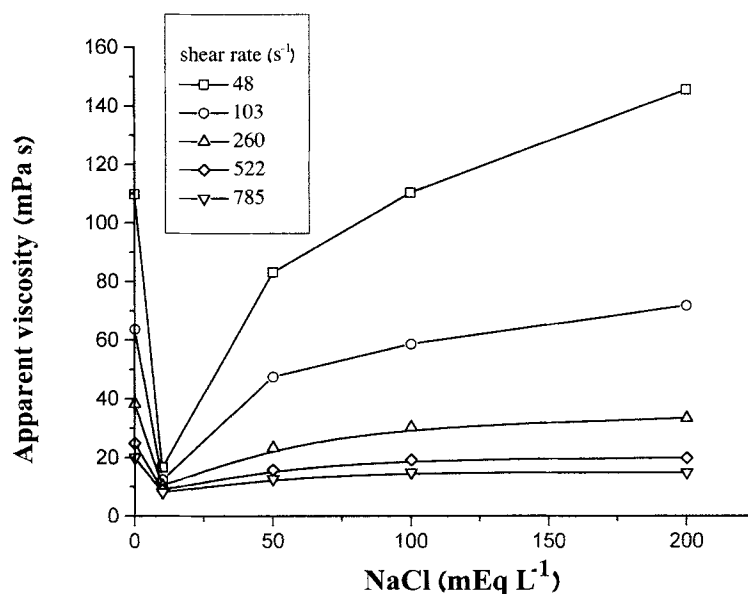


Figure 3. Effect of electrolyte concentration on the apparent viscosity of a 2% Na-rich montmorillonite suspension with $<0.02 \mu\text{m}$ particles for various shear rates.

mEq L^{-1} , and then increased. Note that the apparent viscosity for all shear rates converged to the same minimum of 4.5 mPa s at the same NaCl concentration. Note also that the slope of the curves depends on the shear rate: the lower the shear rate, the greater the slope at NaCl concentrations below and above the minimum viscosity point. The negligible effect of shear rate on suspension viscosity at this minimum suggests that the interaction between clay platelets is weak and electroviscous effects are not significant at this NaCl concentration. This minimum in viscosity for all shear rates may support the mechanisms suggested above.

The constant viscosity of the suspension in the NaCl concentration range of $75\text{--}100 \text{ mEq L}^{-1}$ at any given shear rate (Figure 2) suggests that the maximum stability of the clay-particle structure in suspension was reached at a NaCl concentration of 75 mEq L^{-1} . The

dependence of viscosity on shear rate indicates that the clay-particle structure breaks down as the shear rate increases.

The apparent viscosity of a 2% Na-rich montmorillonite suspension of $<0.02 \mu\text{m}$ particles at various NaCl concentrations and shear rates is given in Figure 3. In general, the changes in the apparent viscosity with NaCl concentration and shear rate were similar to those observed for the suspension of the clay particles of $<2 \mu\text{m}$ (Figure 2). In accordance with Brandenburg and Lagaly (1988), who studied much higher concentrations of suspension (5% Na-rich montmorillonite), the apparent viscosity of the clay suspension of particles of $<0.02 \mu\text{m}$ was significantly greater than that observed for the suspension with particle size $<2 \mu\text{m}$ at any shear rate (Table 1).

Studies of sols of Wyoming bentonite suggest that the particles are aligned edge-to-edge in positions of potential minima. No evidence for corrugated ribbons formed by edge-to-face interaction, or for micelle formation by surface association of the plates, has been observed over the pH range 6.9–13 (M'Ewen and Mould, 1957; M'Ewen and Pratt, 1957). A similar conclusion was reached by Tessier and Pedro (1981) from scanning and transmission electron microscopy. Assuming that the dimensions of an average plate of montmorillonite are $1 \times 1 \mu\text{m}$ for the larger and $0.02 \times 0.02 \mu\text{m}$ for the smaller platelets, the specific surface area of the edges are 1.5 and $76 \text{ m}^2 \text{ g}^{-1}$ for the larger and smaller platelets, respectively. The specific planar surface, however, is $\sim 760 \text{ m}^2 \text{ g}^{-1}$ for both particle sizes. On this basis, the fraction of the edge sur-

Table 1. The apparent viscosity of a 2% Na-rich montmorillonite suspension of two particle-size ranges (<2 and $<0.02 \mu\text{m}$) at two shear rates (48 and 785 s^{-1}) and various NaCl concentrations.

NaCl Concentration mEq L^{-1}	Apparent viscosity, mPa s					
	48			785		
	$<0.02 \mu\text{m}$	$<2 \mu\text{m}$	$\eta_{0.02}/\eta_2$	$<0.02 \mu\text{m}$	$<2 \mu\text{m}$	$\eta_{0.02}/\eta_2$
0	110.0	20.0	5.5	20.0	7.5	2.7
10	17.0	8.0	2.1	8.0	4.0	2.0
20	—	6.0	—	—	4.5	—
50	83.0	38.0	2.2	13.0	9.0	1.4
100	110.0	46.0	2.4	15.0	10.0	1.5
200	146.0	—	—	15.0	—	—

face area is 0.2% and 9% of the total surface area for the larger and smaller clay platelets, respectively. Because the suspension concentration was 2% by weight of the clay to the liquid for the two systems, the higher apparent viscosity for the smaller particles is attributed to their greater edge surface area (which increases the likelihood of edge-to-edge association), and greater number of clay particles per unit volume of suspension. The higher viscosities obtained for the smaller clay platelets at any shear rate may also support the hypothesis that edge-to-edge association is dominant at low electrolyte concentrations.

Whereas the viscosity of the suspension with the smaller particle size was significantly higher than that with the larger clay particles, the minimum value of the apparent viscosity was observed at the same NaCl concentration (Figure 2). The suspension viscosity at this minimum is independent of shear rate, as found for the larger clay particles. This suggests that there is no clay particle association (or that the association is very weak) at this electrolyte concentration, even when the surface area of the edges is relatively high (9% of the total surface area). As observed for the larger particle sizes, the viscosity at this electrolyte concentration would appear to be related directly to the number of clay particles in a unit volume of suspension. As the electrolyte concentration increases above the value for which the viscosity is a minimum, the increase in viscosity is related to face-to-face interaction, as demonstrated by Keren *et al.* (1988).

The apparent viscosity ratios between clay particle sizes of <0.02 and $<2 \mu\text{m}$ at various NaCl concentrations are given in Table 1. The greatest ratio was obtained for the electrolyte-free suspensions at both shear rates (5.5 and 2.7 at shear rates of 48 and 785 s^{-1} , respectively) and decreased as the electrolyte concentration increased. This trend may also support the hypothesis that the surface area of the edges becomes more significant in the clay particles association when the clay particle size decreases.

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