

# Force measurement between mica surfaces in electrolyte solutions

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**Abstract:** The forces between two molecularly smooth mica surfaces are measured in monovalent and divalent cations electrolyte solutions by a surface force apparatus (SFA). The properties of  $K^+$ ,  $Na^+$ , and  $Mg^{2+}$  between molecularly smooth mica surfaces are investigated. The Derjagui-Landau-Verwey-Overbeek (DLVO) force and the hydration force are detected in the experiment. The results show that in lower concentrations of a monovalent electrolyte solution (about  $10^{-4}$  mol/L), the force curves are completely in good agreement with those computed by the DLVO theory. However, additional short-range repulsive forces which deviate from the DLVO theory are observed when the concentrations of cations are above the critical bulk concentration, which is different for each electrolyte. The results show the properties of these cations on both the screening effect adsorbed on the mica surface and the hydration in solution. From the results, the interaction energy between two hydrated ions of potassium or sodium can also be estimated.

**Key words:** surface force apparatus (SFA); DLVO force; hydration force; screening effect

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The DLVO theory indicates that there are two independent types of forces that govern the long-range interaction between similar colloidal particles immersed in aqueous solutions, i. e., the attractive van der Waals force and the repulsive double-layer force, which have been extensively studied for many times<sup>[1-3]</sup>. The double-layer force is derived from the overlapping of the electrical double-layer which can be affected by many factors, such as the concentration of cation and the adsorption capacity of cation to the negatively charged mica surface. Unlike the double-layer force, the van der Waals potential is largely insensitive to the variations in electrolyte con-

centration and pH, which is considered as fixed in a first approximation<sup>[1-2,4]</sup>. Furthermore, the van der Waals attraction must always exceed the double-layer repulsion at a sufficiently short distance due to its power law interaction ( $W \propto -1/D^n$ )<sup>[3]</sup>, while the double-layer interaction energy remains finite or increases slowly as  $D \rightarrow 0$ . The balance between the van der Waals attraction and the double-layer repulsion determines the stability of colloidal dispersions<sup>[5]</sup>. However, one cannot say that all the experimental phenomena are readily predicted by the DLVO theory because this theory fails when the surface separation is less than about 5 nm<sup>[1,6-11]</sup>. As the most common solutes in the natural environment, monovalent and divalent ions are thought to play a key role in biological phenomena<sup>[12-14]</sup>, it is necessary to investigate the properties of monovalent and divalent cations which are confined in two mica surfaces just like the confinement in a cell membrane.

The measurement of DLVO forces and other types of micro-forces is always a focus in collide science, and SFA can be used to measure the physical forces, including the van der Waals and the electrostatic forces between surfaces at the nanoscale and molecular level *in situ* and in real time<sup>[15-19]</sup>. After years of improvements by Israelachvili and his co-workers, there are many versions of SFA available in the area, such as SFA Mk I, SFA Mk II, SFA Mk III, SFA 2000<sup>[20]</sup>. The SFA technique can be used in many fields, such as chemical, physical, biological, and geometrical properties. In this work, a brief introduction of the experimental system and process is presented and experimental results are compared with the DLVO theory. Results show that the DLVO forces are consistent with theoretical values in long range and they also have complex factors such as hydrated ion size, force barrier and critical concentration when the hydration force dominates in the short range.

## 1 Methods and Experimental Conditions

In this paper, the normal forces between molecularly smooth mica surfaces in monovalent and divalent ions solutions are measured on SFA 2000. Fig. 1 shows the basic structure of SFA 2000 in our laboratory.

As shown in Fig. 2, a multiple beam interference (MBI)

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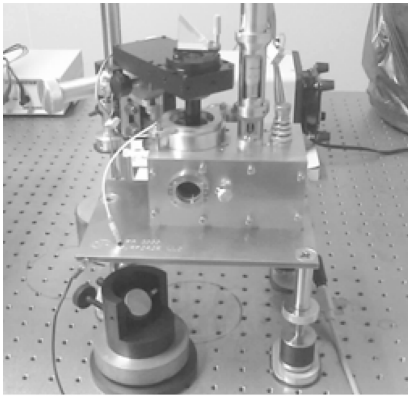


Fig. 1 Photograph of SFA 2000

fringe<sup>[20]</sup> is used to determine the distance between the surfaces and also the shape of the surfaces<sup>[3-4, 21]</sup>. For a typical SFA experiment, a pair of fresh mica surfaces are used as the surface substrates (about 1 to 3  $\mu\text{m}$ ), of which on the backside a thin layer silver film (about 55 nm) is coated for providing a good interfering pattern between the reflecting surfaces. The surfaces are glued onto a cylindrical-shaped glass disk and mounted in a cross-cylindrical configuration, which simulates a sphere-on-flat geometry. When white light is normally directed to the surfaces, it reflects back and forth between the silver layers. The transmitted light near the closest contact point between the surfaces creates Newton's rings, which can be seen through a microscope objective. If the light passes through a spectrometer, these wavelengths are split up and appear as an array of fringes in the spectrogram. These fringes are called fringes of equal chromatic order (FECO)<sup>[22]</sup>.

As the substrate of these experiments, the mica surface is widely used for the simple interpretation of surface force measurements due to its unique properties

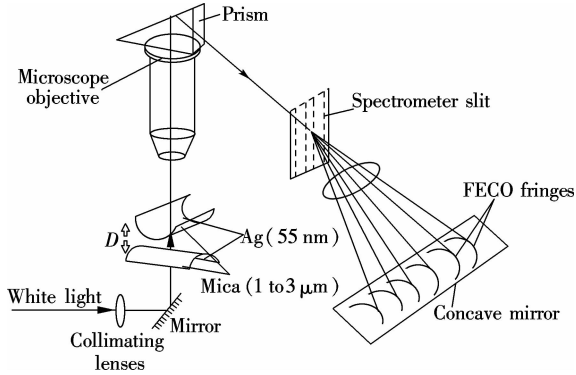


Fig. 2 Schematic of SFA setup

and the mica-water interface is considered to be an ideal system for the study of surface forces which have also been presented in many colloidal systems. Cleaved sheets of muscovite mica display a molecularly smooth planar surface which has a high negative lattice charge due to the periodic replacement of Si atoms by Al<sup>[14]</sup>. The resultant charge of about  $2.1 \times 10^{14}$  negative electronic charges per square centimeter area is exactly balanced in the crystal by surface  $\text{K}^+$  ions on the mica surface<sup>[8]</sup>. In these experiments, the forces between two molecularly smooth mica surfaces are measured over a range of concentrations in aqueous  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Mg}^{2+}$  chloride solutions.

The room temperature is 23 to 27°C measured with a Hg thermometer. Mica is ruby muscovite, grade 1, supplied by S&J Trading Inc. (NY), and the high-purity reagent (99.999% KCl, 99.999% NaCl, 99.99%  $\text{MgCl}_2$ ) is provided by Sigma-Aldrich. The water has a resistivity of typically  $18.25 \text{ M}\Omega \cdot \text{cm}$  and very low bubble persistence after several processes. The pH value of the water lies in the range of 5.4 to 5.8 (due to dissolved  $\text{CO}_2$ ) after deaeration before filling the apparatus. Fig. 3 shows the process of the SFA experiment in our laboratory.

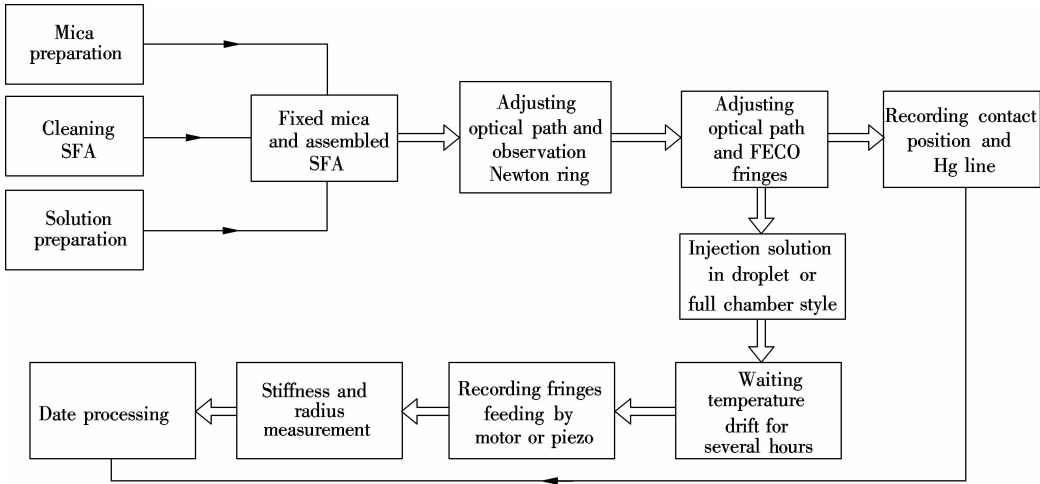


Fig. 3 Outline of the typical SFA experimental process

2 Results and Discussion

The force  $F$  between two molecularly smooth curved

surfaces (of radius  $R$ ) is measured using the method developed by Israelachvili and Adams<sup>[1]</sup>. The value  $F/R$  is plotted in the graphs as a function of the surface separa-

tion distance  $D$ . The value is equal to  $2\pi E$ , in which  $E$  is the corresponding energy between the flat surfaces<sup>[2]</sup>. The theoretical function of 1:1 electrolyte solutions for  $F/R$  is derived from the Poisson-Boltzmann (PB) equation which is shown as

$$\frac{F}{R} = 64\pi\epsilon_0\epsilon\text{tanh}^2\left(\frac{ze\psi_0}{4kT}\right)\kappa e^{-\kappa D} \quad (1)$$

where

$$\kappa = \left( \frac{\sum \rho_{\infty i} e z_i}{\epsilon_0 \epsilon k T} \right)^{1/2} \quad (2)$$

In Eq. (1), all the parameters are known except the surface potential  $\psi_0$  when the experimental conditions are settled. There only exists a numerical solution for the PB equation in the case of 1:2 electrolyte solutions or other types of non-symmetric electrolyte solutions. The characteristic length or thickness of the diffuse electric double-layer, which describes the atmosphere near a charged surface, is known as the Deybe length,  $1/\kappa$ . The Deybe length is defined as

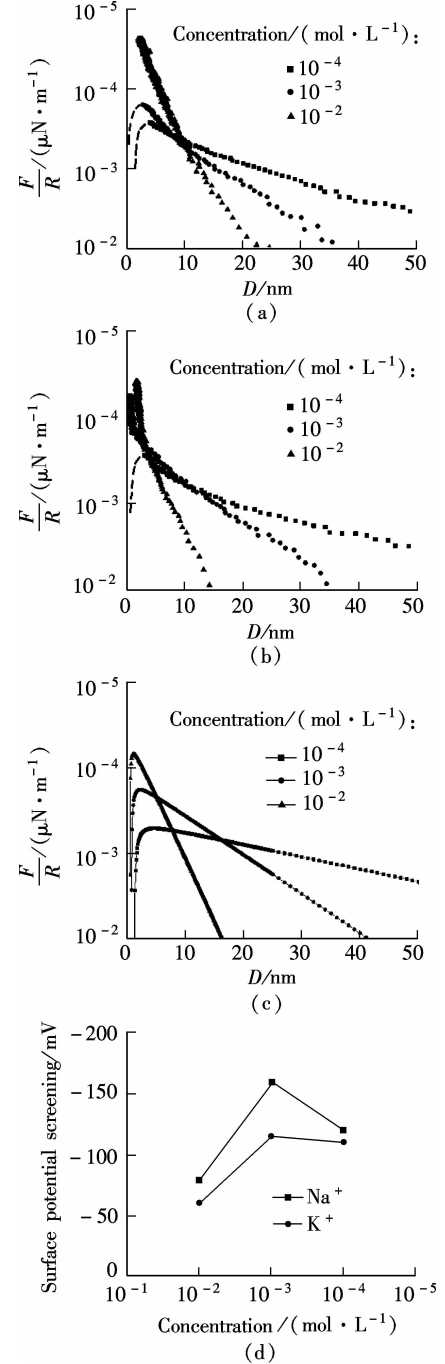
$$\frac{1}{\kappa} = \begin{cases} \frac{0.304}{\sqrt{C}} & \text{for 1:1 electrolytes} \\ \frac{0.176}{\sqrt{C}} & \text{for 1:2 electrolytes} \end{cases} \quad (3)$$

where  $C$  is the concentration, mol/L; the unit of  $1/\kappa$  is nm.

The results of the force measurements as a function of separation are given in NaCl, KCl and MgCl<sub>2</sub> solutions, respectively, as shown in Fig. 4(a), Fig. 4(b) and Fig. 5. For ensuring experimental reproducibility, the mica sheets used in these experiments are all cleaved from the same original sheet.

The DLVO forces and the hydration force are shown in Fig. 4(c). The measured double-layer repulsive force is well described by Eq. (1) at a constant surface potential. The dashed line indicates that the van der Waals force attraction causes the surfaces to jump into adhesive contact from the maximum at a short separation of about 3 nm. In Figs. 4(a) and (b), it is apparent that additional short-range (about 3 nm) repulsive forces become dominant and prevent adhesive contact in a primary minimum above a certain concentration specific to each cation. In Na<sup>+</sup> solutions, hydration forces are observed at concentrations above about 10<sup>-2</sup> mol/L, while the K<sup>+</sup> solutions exhibit a hydration force in 10<sup>-3</sup> mol/L. The results suggest that the hydration force arises only when the cations are held to the mica surface in some specific way. According to the mass action model of mica surface charging<sup>[7]</sup>, Na<sup>+</sup> and K<sup>+</sup> present hydration forces at different concentrations, which indicates that the hydrated energy of K<sup>+</sup> is greater than that of Na<sup>+</sup>. The distance at which

the force barrier is broken by the van der Waals force indicates that the hydrated ion radius of Na<sup>+</sup> is greater than that of K<sup>+</sup>. However, most of the leading factors to the hydration forces are still not well understood from many experimental and theoretical studies. In Fig. 4(d), the surface potential of the cation-adsorbed mica surface is obtained according to Figs. 4(a) and (b) and Eq. (1). It is apparent that the surface potential of the mica surface



**Fig. 4** Force measurements between mica surfaces immersed in halogen electrolyte solutions and the theoretical value of monovalent ions. (a) Force measured in KCl solution; (b) Force measured in NaCl solution; (c) Theoretical value of 1:1 electrolyte solutions calculated by DLVO theory; (d) Apparent surface potential of mica in monovalent cation solutions

does not decrease monotonically as the monovalent cation increases.

The results of force measurements for the pure water and the  $Mg^{2+}$  chloride solutions are summarized in Fig. 5. In these cases, the increase in the bulk cation concentration leads to the decrease in the magnitude of the surface potential and the Debye length is almost consistent with the numerical solution of the PB equation for 1:2 electrolytes according to Eq. (2).

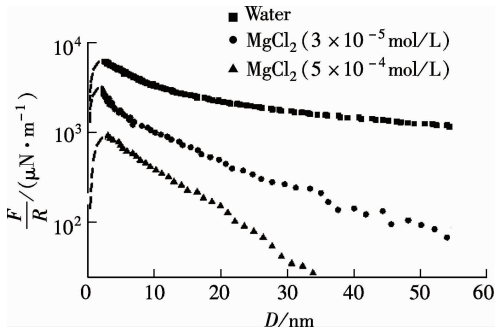


Fig. 5 Force measurement between mica surfaces

### 3 Conclusion

The experimental results are roughly consistent with theoretical predications, indicating that both the SFA experimental system and the experimental process are reliable. Based on the experimental results, we can obtain the profiles of the DLVO force, the hydration force, the adhesive contact and the force barrier in various concentrations. The hydration size can be concluded as  $Mg^{2+} > Na^+ > K^+$ . The surface potential in a lower concentration  $MgCl_2$  solution decreases monotonically compared with that in pure water, which is different from that in  $K^+$  and  $Na^+$  solutions. This suggests that the screening effect of divalent cations to the surface potential of mica is more significant than monovalent cations.

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# 电解质溶液中云母间表面力的测量

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**摘要:**利用表面力仪(SFA)测量一价与二价电解质溶液中分子级光滑的云母表面间作用力. 研究了钾离子、钠离子、镁离子在分子级光滑表面云母间的性质. 实验中测量了 DLVO 作用力及水合力, 结果表明: 在较低浓度的一价离子溶液(约  $10^{-4}$  mol/L)中, 实验中所测得的力与 DLVO 理论力曲线完全一致. 然而在浓度超过反离子临界浓度时, 额外的短程斥力偏离 DLVO 理论值, 临界浓度对于每一种离子是不同的. 实验结果展现了这 3 种离子对云母表面的屏蔽效应差异及在溶液中的水合性质. 此外, 从这些结果可以评估 2 个水合钠离子或者 2 个水合钾离子之间的作用能.

**关键词:**表面力仪; DLVO 力; 水合力; 屏蔽效应

**中图分类号:** O561.4