

# Direct Force Measurements between Surfaces Coated with Hydrophobic Polymers in Aqueous Solutions

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## **ABSTRACT:**

*Froth flotation is an important process used in the mining industry for separating minerals from each other. The separation process is based on rendering a selected mineral hydrophobic using an appropriate hydrophobizing reagent (collector), so that it can selectively attach onto the surfaces of a rising stream of air bubbles. Thus, controlling the hydrophobicity of the minerals to be separated from each other is of critical importance in flotation. If one wishes to separate plastics from each other by flotation, however, it would be necessary to render a selected plastic hydrophilic and leave the others hydrophobic. In the present work, the possibility of separating common plastics from each other by flotation has been explored.*

*While water contact angle is the most widely used measure of the hydrophobicity of a solid, it does not give the information on the kinetics of flotation. Therefore, the forces acting between the surfaces coated with different hydrophobic polymers (or plastics) in water were measured using the Atomic Force Microscope (AFM). The results obtained with polystyrene, poly(methyl methacrylate) (PMMA), polypropylene (PP), and Teflon showed the existence of long-range attractive forces (or hydrophobic force) that cannot be explained by the classical DLVO theory. The surface force measurements were conducted in pure water and in solutions of surfactant (alkyltrimethylammonium chloride) and a salt (NaCl). In pure water, the attractive forces were much stronger than van der Waals force. In the presence of the surfactant and NaCl, the long-range attraction decreased with increasing concentration and the alkyl chain length.*

**Keywords:** PMMA, Atomic Force Microscope (AFM), hydrophobic force

## **I. Introduction**

While water contact angle is the most widely used measure of the hydrophobicity of a solid, it does not give the information on the kinetics of flotation. Therefore, the forces acting between the surfaces coated with different hydrophobic polymers (or plastics) in water were measured using the Atomic Force Microscope (AFM). The results obtained with polystyrene, poly(methyl methacrylate) (PMMA), polypropylene (PP), and Teflon showed the existence of long-range attractive forces (or hydrophobic force) that cannot be explained by the classical DLVO theory. The surface force measurements were conducted in pure water and in solutions of surfactant (alkyltrimethylammonium chloride) and a salt (NaCl). In pure water, the attractive forces were much stronger than van der Waals force. In the presence of the surfactant and NaCl, the long-range attraction decreased with increasing concentration and the alkyl chain length.

## **II. Hydrophobic Forces**

The froth flotation is the most widely used method for separating fine particles. In this process, selected hydrophobic minerals are attached to air bubbles to be separated from hydrophilic particles. The control of particle hydrophobic is thus of crucial importance for improving flotation performance. However, the exact nature of the mechanisms involved in hydrophobic, especially the origin of forces between two hydrophobic surfaces in water, is still not completely understood.

In the early days, classical DLVO theory was used to predict the kinetics of coagulation and to describe interactions between particles. The DLVO theory considers two surface forces: the double-layer force and the van der Waals force. However, both the double-layer and the van der Waals forces are repulsive in most of the conditions encountered in flotation, which made it difficult to model fast and spontaneous flotation. The presence of an additional non-DLVO interaction was first recognized by Laskowski and Kitchener. They found that mentholated and pure silica particles had practically the same  $\zeta$ -potentials, and yet only the former floated while the latter did not, which led to the suggestion that a long-range "hydrophobic influence" may be responsible for the rupture of the wetting film, and thus, for the bubble-particle

interactions in flotation. The authors suggested that the hydrophobic influence could be caused by the instability of the water structure in the vicinity of a hydrophobic surface. Later, Blake and Kitchener [3] showed that the thin film of water between a hydrophobic solid and an air bubble ruptures fast and spontaneously and that it does so at separation distances of about 64nm, which was much larger than predicted by the classical DLVO theory. These investigators suggested the presence of a “hydrophobic force” in wetting film between bubble-particle. The term *hydrophobic force* is now widely used to describe the long-range, non-DLVO attractive forces measured between macroscopic hydrophobic solid surfaces immersed in water. The non-DLVO hydrophobic force was first measured experimentally in 1982 using the Surface Force Apparatus (SFA) by Israelachvili and Parsley [4]. The force was shown to decay exponentially in the 0-10 nm range with a decay length of 1 nm. The authors postulated that the force was related to the hydrophobic effect, which is widely used to explain mutual attraction between hydrophobic solutes (e.g. hydrocarbons) in water. Many other investigators conducted follow-up experiments and reported even longer-range of hydrophobic forces, whose decay lengths were shown to vary in the range of 10-30 nm.

When measuring hydrophobic forces, the adsorption of surfactants at the solid-liquid interface involves complex mechanisms and may introduce artifacts. Since the 1990's, direct force measurement between naturally hydrophobic polymer surfaces, without the use of surfactants, has become popular in the study of hydrophobic forces. However, the existence of hydrophobic forces remains controversial, since previous studies provide contradictory results. Measured the forces between polystyrene surfaces in water. The result showed that attractive forces pulled the surfaces into contact, from an initial separation distance as large as 30 nm. No further details regarding the nature of this attractive force were presented. In the same year, Li *et al.* [6] measured forces between 2  $\mu\text{m}$  diameter polystyrene spheres in solutions using a Scanning Force Microscope. The results showed no long-range attraction, but only the existence of a repulsive electrostatic force. In 1994, Meagher and Craig [7] studied the effect of degassing on the surface force between polypropylene surfaces ( $\theta = 90^\circ\text{-}111^\circ$ ) in NaCl solution, using an AFM. The authors postulated the existence an attractive force stronger than the van der Waals force both with and without degassing the solution. The jump distance, particularly significant before degassing, was measured to be as large as  $21.0 \pm 5.2$  nm, indicating the presence of the hydrophobic force. In 1999, no long-range hydrophobic attraction was found in the measurement performed by Schmitt *et al.* [8] on the surface between two fused polystyrene surfaces. In 2001, Vinogradova *et al.* [9] measured the interaction force between polystyrene surfaces and discovered a long-range attraction inconsistent with the DLVO theory. Considine *et al.* [10] investigated the force between polystyrene sphere and plate in aqueous media using an AFM. It was reported

Many investigators showed that mixed plastics can be separated from each other by flotation if the surface properties are modified appropriately. Sisson [17] showed that in 2-15% NaOH (or KOH) and 0.005-0.1% NEODOL<sup>®</sup> 91-6 (a non-ionic surfactant) solutions the contact angle of PET was decreased to below  $25^\circ$ , while that of PVC remained above  $45^\circ$ . Flotation separation under these conditions gave a 93.5% PVC recovery and a 97.5% PET recovery. Shibata *et al.* [18] developed a flow sheet for the flotation separation of a mixed plastic, in which POM and PVC were floated together by depressing PVC with 500 mg/l sodium lignosulfonate. Th POM was then floated from the POM/PC mixture by using 200 mg/t Spooning and 50 mg/l Aerosol OT to depress PC. Singh [19] separated PVC and POM successfully using appropriate wetting agents. Their results showed that sodium lignosulfonate was a good depressant for PVC while Sorbian monolaurate was good for POM. Drelich *et al.* [20] found that the hydrophobic of PET was strongly altered by strong alkaline solutions of sodium hydroxide, while the hydrophobic of PVC remained the same. The PET and PVC recoveries were 95 to 100%, respectively. Le Guern *et al.* [21, 22] studied the adsorption mechanism of lignosulphonate onto PVC and PET surfaces. Results showed that lignosulphonate could selectively interact with PET and render it hydrophilic. Also, the presence of divalent cations such as calcium could enhance the hydrophilization of PET through electrostatic bridge action between the lignosulphonate and the plastics. Both of them were negatively charged before the treatment. Shen *et al.* [23, 24] found that methyl cellulose can depress the flotation of PVC more readily than PET. The authors also investigated the floatability of seven plastics in the presence of an alkyl ethoxylated non-ionic surfactant (15-S-7, for example). The floatability was shown to decrease with addition of the surfactant. Floatability was depressed to a different extent for each plastic (POM < PVC < PMMA < PET < PC < ABS < PS). Dobbin *et al.* [25] separated PET from both PET/ PE and PET/ PP mixtures using either 0.02 kg/m<sup>3</sup> dodecylamine acetate or polyvinyl alcohol. Casanova *et al.* [26] studied the wet ability and floatability of PS in the presence of terpinol, polyethylene glycol dodderly ether (PGDE), tannic acid, and calcium lignosulfonate. The results showed that at concentrations above 60 mg/l, PGDE increased the wettability of PS considerably while at concentrations below 20 mg/l, calcium lignosulfonate strongly

### III. Research Layout

This work was devoted to the experimental investigation of surface forces and wet ability of plastics in the presence of various wetting agents. The overall objective was to better understand the origin of hydrophobic force and identify the

conditions under which different plastics (or hydrophobic polymers) can be separated from each other. In Chapter 2, the results of the AFM surface force measurements conducted between PS, PMMA, PP and Teflon surfaces in pure water and solutions of different surfactants and electrolytes. Chapter 3 describes an experimental study aimed at finding more efficient wetting agents for the separation of PS and PVC by flotation.

#### IV. HYDROPHOBIC FORCES BETWEEN PLASTIC SURFACES IN AQUEOUS SOLUTIONS

The surface forces acting between hydrophobic surfaces play an important role in flotation. In the froth floatation process, the efficiency of separation is largely determined by the interaction between hydrophobic air bubbles and hydrophobic particles. Therefore, it has become increasingly important to achieve a better understanding of the origin of hydrophobic forces. The non-DLVO theory, which takes into account the hydrophobic force, the van der Waals force and the electrostatic force, has been recently applied to explain the phenomena involving hydrophobic interaction. There have been more and more evidences indicating that the non-DLVO theory is a more thorough theory than the classical DLVO theory, for which numerous discrepancies with experiment results have been found.

Plastics are ideal materials to study the hydrophobic force, because they are naturally hydrophobic, and they don't introduce the complexity arising from surfactant adsorption. The existence of hydrophobic attraction between hydrophobic plastic surfaces has been investigated by many researchers. In 1993, Karaman *et al.* [5] measured the forces between polystyrene surfaces in water, and recorded a jump-in distance as large as 30 nm. Li *et al.* [6], in 1993 also measured forces between polystyrene surfaces but observed no long-range attraction force. In 1999, Schmitt *et al.* [8] performed surface force measurement between two fused polystyrene surfaces, but their results showed no long-range hydrophobic attraction. In the same year, Considine [10] observed a much stronger attraction force than the van der Waals force, with a jump-in distance from a quite long range (20-400 nm), between different pairs of polystyrene spheres. In 2001, Vinogradova *et al.* [9] tested the same plastic, and a long-range attraction was also observed.

Force measurements have also been conducted with Teflon and other plastics. In 1994, Meager and Craig [7], using an AFM, investigated the hydrophobic interaction between polypropylene surfaces in NaCl solution. A 30 nm range where they observed the attractive forces was found in solutions both with and without degassing. Nalaskowski *et al.* [27] measured forces between a polyethylene sphere and a polyethylene surface in de-aerated and aerated water. A long-range attractive force between hydrophobic polyethylene surface and sphere was observed.

The Teflon has a very high contact angle ( $\theta=110^\circ$ ). In 1999, Considine *et al.* [28] measured the force between a micron-sized colloidal sphere and a flat plate, both coated with a copolymer of perfluoro (2, 2-dimethyl-1, 3-dioxole) and Teflon AF 1600. It was shown that the surfaces experienced a very strong attraction as two surfaces contact each other. The jump-in distance was about 500 nm in water. In 2005, Hallam *et al.* [29] also observed a long-ranged attraction between hydrophobic amorphous fluoropolymer surfaces. They found that the range of the attraction and its attraction decreased in de-aerated water as compared to normal, aerated water. However, the range and the strength of the attraction in deaerated water remained significantly greater than those of the van der Waals attraction for this system.

In this chapter, the results of the hydrophobic force measured between various hydrophobic polymer-coated surfaces, which included PS, PMMA, PP and Teflon were studied. The measurements were conducted using an Atomic force microscope in water and surfactant solutions. The relationship between surface forces and contact angles has been studied. The objective of this study was to study the nature of hydrophobic forces.

#### V. Conclusion

An atomic force microscope (AFM) was used to measure the surface forces between PS, PMMA PP and Teflon surfaces in pure water and in different concentrations of surfactant and salt (NaCl) solutions. The forces measured in pure water were net repulsive due to the high surface charges, as indicated by their  $\zeta$ -potentials: -30 mV for PS, -67 mV for PMMA, and -80 mV for PP. Nevertheless, two hydrophobic surfaces jump into contact at separation distances much larger than predicted by the classical DLVO theory. The discrepancy can be attributed to the presence of the long-range hydrophobic force between the symmetric PS, PMMA and PP surfaces. In pure water, the hydrophobic forces decrease in the order of PP, PMMA and PS. In the presence of NaCl,

2.4 Figures and Tables

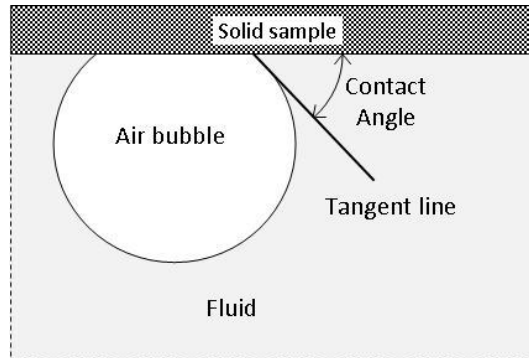


Figure 2.1 Schematic representation of the captive bubble technique.

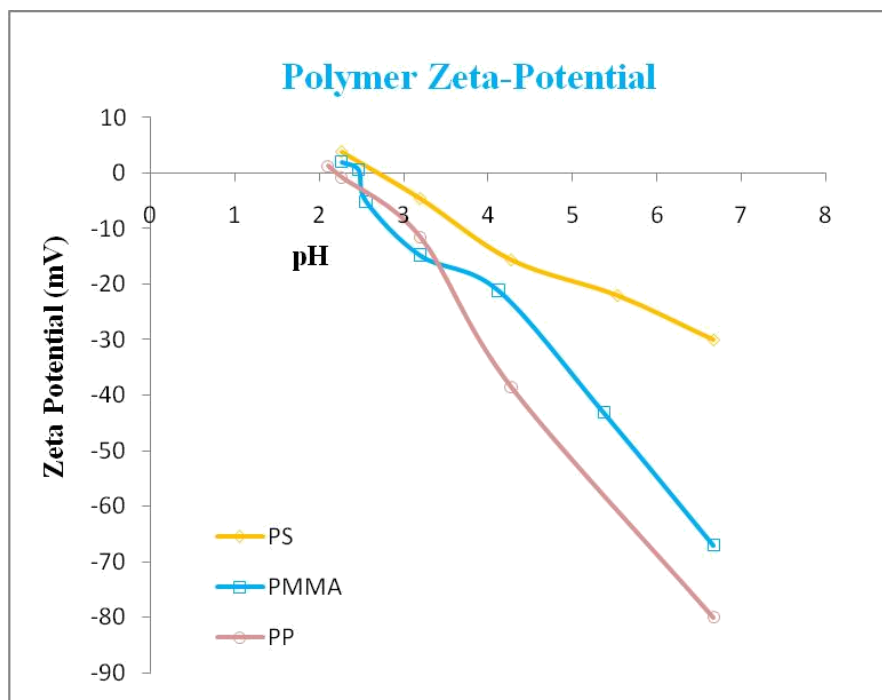
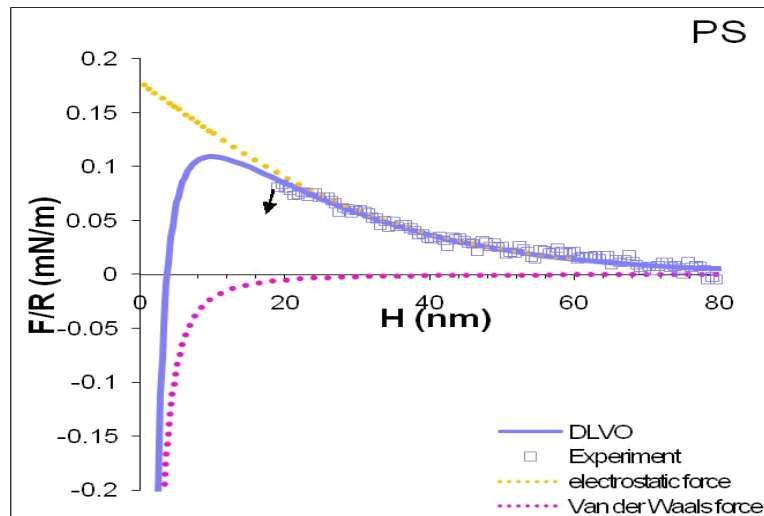


Figure 2.3 Zeta-potential value of PS, PMMA and PP measured at different pH. For PS, at p.c.n., pH = 2.73 and zeta-potential value at natural pH is -30mV. For PMMA, at p.c.n., pH = 2.48 and zeta-potential value at natural pH is -67mV. For PP, at p.c.n., pH = 2.20 and zeta-potential value at natural pH is -80mV.



**Figure 2.4** AFM force measurements conducted between polystyrene (PS) sphere and plate in water at neutral pH:  $A_{131}=1.3 \times 10^{-20}$  J;  $\zeta=-30$  mV;  $\phi_0=-32$  mV;  $\theta=76^\circ$ .

**Table 2.1** Hydrophobic Force Constants of PS, PMMA PP and Teflon

Polymers	$A_{131}$ (J)	Potential (mV)		$\theta$ (deg)	C (mN/m)	D (nm)
		$\phi_0$	$\xi$			
PS	$1.3 \times 10^{-20}$	-32	-30	76	1	4.4
PMMA	$8.0 \times 10^{-21}$	-68	-67	72	3	4
PP	$1.05 \times 10^{-20}$	-82.4	-80	98	3.1	7.6
Teflon	$3.59 \times 10^{-21}$	-86	----	110	3	5.6

**Table 2.2** Effect of  $C_{14}$ TACl concentration on the hydrophobicity ( $\theta$ ) and decay length (D) of PS

Surfactant	Concentration of $C_{14}$ TACl	$\theta$ (degree)	$\phi_0$ (mV)	C (mN/m)	D (nm)
$C_{14}$ TACl	0	76	-32	1.0	4.4
	$8 \times 10^{-5}$ M	84	-19	3.2	4.6
	$1 \times 10^{-4}$ M	96	-4.6	3.4	8.0
	$5 \times 10^{-4}$ M	78	46	1.7	4.0

**Table 2.3** Effect of NaCl concentration on the hydrophobicity ( $\theta$ ) and decaylength ( $D$ ) of PMMA

Salt	Concentration of NaCl	$\theta$ (degree)	$\phi_0$ (mV)	$C$ (mN/m)	$D$ (nm)
NaCl	0	72	-68	3.0	4.0
	$1 \times 10^{-3}$ M	78	-36	3.1	4.1
	$3 \times 10^{-3}$ M	82	-1.8	3.4	4.5
	$6 \times 10^{-3}$ M	89	-19	3.6	5.1

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