

WATER AT INTERFACES - SOME RECENT EXPERIMENTAL RESULTS FROM SURFACE SPECTROSCOPY

J. D. Miller, M. R. Yalamanchili, and S. Veeramasoneni

Department of Metallurgical Engineering
University of Utah, Salt Lake City, Utah 84112, USA

Fundamental aspects of interfacial phenomena in aqueous systems are determined by the properties of interfacial water. It has become evident that interfacial water must be characterized spectroscopically in order to explain the recently identified non DLVO forces observed by atomic force microscopy and with the surface force apparatus. In the past little information was available regarding the spectroscopic characteristics of interfacial water due to the difficulty in differentiating between bulk and interfacial water. However, with the advent of FTIR and Raman internal reflection spectroscopy (IRS) and the recent non-linear optical technique, sum frequency generation (SFG), more information on interfacial water is now available as is evident from the results of recent spectroscopic studies. Thus the non DLVO forces eventually may be explained by the extent of hydrogen bonding as revealed by surface spectroscopic techniques.

Podstawowe aspekty zjawisk międzyfazowych w układach zawierających wodę są określone przez właściwości wody międzyfazowej. Ostatnio stało się oczywiste, że woda międzyfazowa musi zostać scharakteryzowana spektroskopowo w celu wyjaśnienia natury sił nie ujętych w teorii DLVO, a zaobserwowanych pod mikroskopem tunelowym oraz z wykorzystaniem wagi powierzchniowej. W przeszłości było dostępnych niewiele informacji na temat spektroskopowej charakterystyki wody międzyfazowej, co wynikało z trudności w rozróżnieniu wody międzyfazowej od wody otaczającej. Wraz z wynalezieniem FTIR i spektroskopii ramanowskiej z detektorem odbić wewnętrznych (IRS), oraz ostatnio techniki optyki nieliniowej sumującej częstotliwość generacji (SFG), dostępnych jest dużo więcej informacji na temat wody międzyfazowej niż przy użyciu tradycyjnych metod spektroskopowych. Tak więc istnienie sił nie ujętych w teorii DLVO może być wyjaśnione przez wiązania wodorowe, które można wykryć technikami spektroskopii powierzchniowej.

Keywords: hydrophobic surfaces, hydrophilic surfaces, interfacial water structure, hydrogen bonding, surface spectroscopy, FTIR/IRS, SFG, spectroelectrochemistry, non-DLVO forces, atomic force microscopy

1. INTRODUCTION

The properties of interfacial water are of great importance in many technological areas including flotation, solid-liquid separation, stabilization of dispersions and emulsions, coalescence, flocculation, adsorption, corrosion, and soil contamination. Recent research suggests that the structural features of interfacial water determine the nature of interaction forces which control the aforementioned phenomena. Thus, it is expected that the fundamental aspects of wetting phenomena are determined to a great extent by the structure and properties of interfacial water. For example, the nature and behavior of thin films during bubble attachment at the surface of a hydrophobic particle and the stability of water films in the froth phase are excellent examples of the importance of interfacial water in the flotation process. Similarly, the phenomenon of film stability is a critical issue in other technological areas, including the treatment of oily waste water.

The characterization of interfacial water is necessary in order to understand the so-called non-DLVO interparticle forces (structural/hydration forces) and their influence on particle dispersion and aggregation in aqueous systems, particularly at high salt concentrations. These non-DLVO forces include both hydrophilic and hydrophobic interaction forces. Several researchers have provided experimental evidence for the existence of these forces and interfacial water structure is believed to strongly influence the nature of these short-range forces (1-4).

1.1 Hydrophilic Interaction Forces

Model systems such as polystyrene/quartz and silica/sapphire have been studied by atomic force microscopy (AFM) to measure the particle interaction forces prevalent at high ionic strengths. Microspheres of hydrophilic silica and hydrophilic polystyrene (with R-NH₂ surface functional groups)

were glued to an AFM cantilever in order to measure the surface forces involved in these systems as a function of pH and ionic strength (5). In both systems (polystyrene sphere/quartz plate and silica sphere/sapphire plate) repulsive forces were observed at a pH value of 11.5 when the interacting surfaces are similarly charged and attractive forces were observed at a pH value of 3.5 when the interacting surfaces are oppositely charged. Similar results were obtained at different ionic strength values (2M and 4M KCl). The DLVO theory is inadequate to explain the forces observed in these systems at high ionic strengths (5). As a consequence, non-DLVO forces (hydration forces) at small separation distances should be considered in order to explain these observed forces. The hydration forces which are now known to determine the interaction of surfaces at small separation distances were unrecognized until recently. In the past decade there has been significant progress in measuring and characterizing these repulsive hydration forces between hydrophilic surfaces of similar charge (6,7). In addition, attractive forces have been measured between oppositely charged particles. These results suggest that the sign of the surface charge plays an important role and the attractive non-DLVO forces can be present between hydrophilic surfaces of opposite charges. It is evident both from optical and atomic force microscopy studies that there exists both repulsive and attractive forces between hydrophilic surfaces at high ionic strengths depending on whether the surfaces are similarly or oppositely charged. In this regard, the attractive forces observed (optical microscopy) and measured (AFM) between oppositely charged surfaces at high ionic strengths appear to result from an antisymmetric water dipole arrangement near these surfaces. On the other hand, repulsive forces between similarly charged surfaces may be due to the symmetric dipole ordering near the surfaces involved.

1.2 Hydrophobic Interaction Forces

Other attractive non DLVO forces between hydrophobic surfaces have been measured for various systems over the last 10 years (8-10). Direct force measurements were conducted using the surface force apparatus (SFA) of Israelachvili and Tabor (11). Here mica surfaces are hydrophobized by self-assembled amines from aqueous solution (9) or by depositing insoluble, double-chain amines using the Langmuir-Blodgett technique (10). Both short and long range hydrophobic forces have been observed, particularly when neutral surfactants, such as octanol, are coadsorbed in the self assembled monolayer to increase the hydrocarbon chain ordering. Mica surfaces were also hydrophobized by treating them in water plasma, followed by methylation (12). Rabinovich and Derjaguin (13) used a different type of SFA to measure hydrophobic forces between crossed silica fibers methylated with dimethyldichlorosilane (DMDCS). More recently, Rabinovich and Yoon (14) used atomic force microscope (AFM) to measure the hydrophobic forces between silica surfaces methylated with trimethylchlorosilane (TMCS) and octadecyltrichlorosilane (ODTCS).

Many theories have been proposed regarding the origin of the attractive hydrophobic force, including; entropy increase due to configurational rearrangement of water molecules when two hydrophobic surfaces approach each other (15,16), capillary force due to cavitation in the vicinity of hydrophobic surfaces (17), hydrodynamic correlation between fluctuating liquid-solid interfaces (18), and correlation of dipoles associated with molecular domains (19,20).

1.3 Summary

Optical and atomic force microscopy studies of particles have shown that there exist both repulsive and attractive forces between hydrophilic surfaces at high ionic strengths depending upon their surface charge (4). The DLVO theory fails to describe these forces observed at high ionic strengths. Failure of the DLVO theory may be due to the fact that the separating medium (water) is treated as a structureless continuum. While this approach may be applicable at large separation distances, for short distances from the surface, the separating medium may have a distinct structure that varies with distance and is significantly different from that of the bulk. Evidence for this is given by the oscillation of repulsive hydration forces measured on mica surfaces (21). Also, molecular simulations of water dipoles near surfaces suggest that hydration forces arise due to the ordering of interfacial dipoles. The ordering of water molecules depends on many factors such as the geometry and coordination number of aqueous species, the type of interface involved, and the physical and chemical nature of the surface

involved. Marcelja and Radic (16) suggested that a polar surface will perturb interfacial water molecules and the propagation of this perturbation via dipole interaction will result in a force that extends over several molecular layers. The strength of the perturbation of the water structure would depend on the surface charge. Such an approach was favored by Rand and Parsegian (22) to describe the attractive hydration forces between phospholipid bilayers. Recent results from FT-IR/IRS and Raman IRS as well as sum frequency generation techniques for interfacial water characterization indicate that the interfacial water structure is different at hydrophilic and hydrophobic surfaces. These and other spectroscopic features are discussed in the following sections.

2. INTERNAL REFLECTION SPECTROSCOPY

2.1 FT-IR Internal Reflection Spectroscopy

Internal reflection spectroscopy (IRS), alternatively referred to as attenuated total reflection (ATR), allows for in-situ real time spectroscopic measurements. Consequently, IRS has become a powerful analytical tool for in-situ surface analysis in many areas of colloid and surface science (23-30).

Total Internal Reflection. Shown in Figure 1 is a schematic representation of a ray of light undergoing total internal reflection in a parallelepiped shaped internal reflection element (IRE). Two requirements must be met before total internal reflection can occur. First, the IRE must be optically denser, that is, have a higher refractive index, than the sample ($n_1 > n_2$). Second, the incident angle of the light beam in the IRE must be greater than the critical angle, θ_c :

$$\theta_c = \sin^{-1}(n_2/n_1) \quad (1)$$

where n_2 and n_1 are the refractive indices of the sample and the IRE respectively. When the incident angle is greater than the critical angle, total internal reflection occurs. As the light is totally reflected at the interface, an exponentially decaying evanescent wave is set up in the rarer outer phase (sample). It is through this evanescent wave that sampling occurs. The exponential decay of the evanescent field into the sample describes the decrease in the electric field perpendicular to the surface, the Z direction. Thus the electric field at some distance Z from the nonabsorbing interface is expressed as (31):

$$E = E_0 \exp((-2\lambda/\lambda_1)(\sin^2 \theta - n_2^2/n_1^2)^{1/2}Z) \quad (2)$$

where E_0 is the electric field amplitude at the surface, $\lambda_1 = \lambda/n_1$ is the wavelength of the radiation in the denser medium, λ is the wavelength in free space, θ is the incident angle, $n_2 = n_2/n_1$, and Z is the distance from the surface.

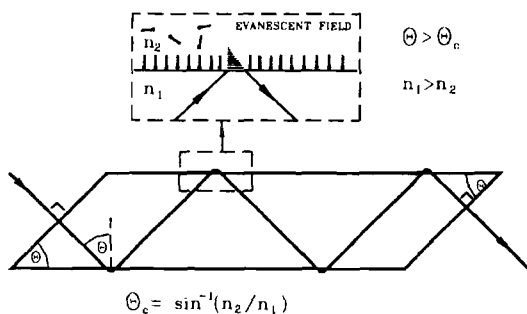


Figure 1. Schematic of light ray undergoing multiple total internal reflections in an IRE.

Depth of Penetration. The depth of penetration of the evanescent field is an important parameter in internal reflection spectroscopy and is particularly significant in the present work. Harrick (32) defined the depth of penetration as the distance from the IRE where the electric field amplitude falls to 1/e of its value at the surface. The depth of penetration, d_p , as defined by Harrick and is given by:

$$d_p = \lambda/(n_1 2\pi(\sin^2 \theta - n_2^2/n_1^2)^{1/2}) \quad (3)$$

As evident from the above, in-situ FTIR/IRS with internal reflection elements should be a powerful

analytical technique to study the spectral characteristics of interfacial water. Specifically, interfacial water present at various distances from the surface can be described based on this in-situ FTIR/IRS spectral information. In other words, spectral characteristics including band position, intensity, and shape can be examined at different distances from a surface by simply varying the incident angle. The incident angle can, in turn, be varied by changing the face angle of the IRE and the optics of the experiment.

Characterization of Interfacial Water Spectra. The in-situ FTIR/IRS spectra of interfacial water generated at the silicon surface were studied by examining in detail the OH stretching region between 3000 and 3800 cm^{-1} (33). This region of the interfacial water spectrum forms a broad band which can be deconvoluted into several peaks. The origins and the interpretation of the band frequencies in this region still remain somewhat controversial. However, two important regions can be identified in this spectral range without any uncertainty as discussed previously. The spectral features surrounding 3600 cm^{-1} can be assigned to the stretching vibration of non-hydrogen bonded or free OH oscillators (groups), whereas, the spectral features between 3000 and 3500 cm^{-1} can be ascribed to the stretching vibrations of the hydrogen bonded OH (34,35).

The spectral region between 3000 and 3500 cm^{-1} contains two important peaks. The peak centered around 3200 cm^{-1} is generally attributed to the symmetric stretching of OH in tetrahedrally coordinated water molecules (34). This peak dominates the ice spectra and therefore the appearance of this peak would be an indication of the presence of an ice-like structure for water in tetrahedral coordination. The second important peak in this spectral region lies around 3450 cm^{-1} . This peak is attributed to molecular arrangements with a lower degree of hydrogen bonding (incomplete tetrahedral coordination) compared to that indicated by the peak at 3200 cm^{-1} (34).

These peaks in the spectral region from 3000 to 3800 cm^{-1} can be used as indicators of the extent of hydrogen bonding present in interfacial water. The extent, or the degree, of hydrogen bonding then reflects the structure of interfacial water. In view of the above, spectral features in the region from 3000 to 3800 cm^{-1} were used to describe the structure of interfacial water at a hydrophilic silicon surface (33). Similar spectral features were used by other researchers to characterize interfacial water by Raman IRS (36) and sum frequency generation (35,37) near sapphire and quartz surfaces respectively.

Silicon/Water System. Absorbance spectra of water was obtained in the OH stretching region as a function of depth of penetration, d_p , from the silicon surface. Since at smaller d_p values (<262 nm), critical angles can be reasonably well defined for the wavelengths in the OH stretching region (32), water spectra (normalized with respect to the number of reflections) were obtained at d_p values ranging from 153 to 262 nm. The broad peaks were deconvoluted using the Fourier self-deconvolution method. Figure 2 shows the deconvoluted spectrum of water at a d_p of 153 nm along with the original spectrum. Three peaks centering around 3600, 3400, and 3200 cm^{-1} can be clearly seen from this figure. Other deconvoluted spectra of interfacial water are shown in Figure 3 for three different d_p values ranging from 153 nm to 231 nm. The differences in these spectra as d_p is varied from 153 nm to 231 nm are immediately obvious and changes in the relative intensities of the peaks centered about 3600, 3400, and 3200 cm^{-1} can be noticed from this figure. These results suggest that the extent of hydrogen bonding (water structuring-tetrahedral coordination) is higher in the regions closer to the hydrophilic silicon surface than in the regions away from the surface.

It should be noted that the in-situ FTIR/IRS spectra presented in Figure 3 contain information due to the presence of both surface and bulk water. It is evident from these spectra that the extent of water structuring (hydrogen bonding/bond ordering) decreases at greater distances from the silicon surface. Thus spectral results using this in-situ FTIR/IRS technique can be used to distinguish between surface and bulk water as is evident from the distinct changes in the spectra of interfacial water with changes in the depth of penetration. Most importantly, it should be noted that the hydrophilic silicon surface is characterized by an accentuation of the 3200 cm^{-1} peak indicating an increase in hydrogen bonding such as found in the ice structure. In contrast a hydrophobic germanium surface seems to accentuate the 3600 cm^{-1} peak and reduce the extent of hydrogen bonding (38).

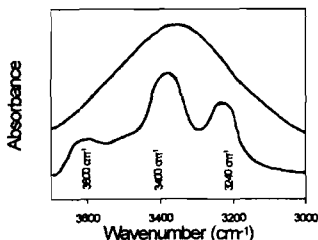


Figure 2. Original and deconvoluted spectra of interfacial water at a silicon surface for a depth of penetration (d_p) of 153 nm in the OH stretching region (33).

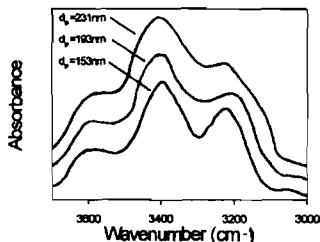


Figure 3. Deconvoluted spectra of interfacial water at various depths of penetration (d_p) in the OH stretching region (33).

2.2 Raman Internal Reflection Spectroscopy

Internal reflection spectroscopy in conjunction with Raman offers an excellent opportunity to further reduce the depth of penetration and as a consequence water structure very close to the interfaces can be investigated. Nickolov et al. (36) used this approach to look at water structure at a hydrophobic sapphire surface using an argon laser with a wavelength of 457.9 nm. The depth of penetration achieved in this work was around 30 nm at the sapphire surface. Of course the OH stretching region was studied in order to investigate the interfacial water structure. However, the extremely weak signals from Raman IRS have to be enhanced by maximizing the efficiency of the collection optics.

3.0 SUM FREQUENCY GENERATION

There has been significant progress in recent years in the development of nonlinear optical spectroscopy techniques for probing interfacial regions. Sum frequency generation (SFG) is one such technique that can be used for the study of interfacial phenomena. SFG is a powerful technique, especially for studying the solid/liquid interfaces, since it can detect the vibrational spectrum of the adsorbed species at the surface. Any effective nonlinear optical method for surface vibrational spectroscopy should satisfy three criteria: it should be a second-order process so that it is surface-specific; input must have a tunable infrared component to excite vibrational transitions; and the output should be in the near-infrared or visible range so that it can be detected by a photomultiplier. Infrared-visible SFG is therefore an excellent candidate for surface vibrational spectroscopy. In SFG, the incoming field, E , is of two frequencies, 1 and 2; the output is no longer 2 but at $1 + 2$. If 1 is in the infrared and 2 in the visible, all three of the above criteria are satisfied by SFG. Thus, SFG is highly surface sensitive and also capable of selective detection of molecules through characteristic vibrational transitions.

The SFG technique was used to study OH stretching vibrations of water molecules at quartz/water and quartz/OTS/water interfaces (35,37). As was the case for the FTIR/IRS results, the SFG results indicate that an ice-like structure prevails at the hydrophilic surface whereas at the hydrophobic surface, the extent of hydrogen bonding is destroyed to a certain extent. Figure 4 presents

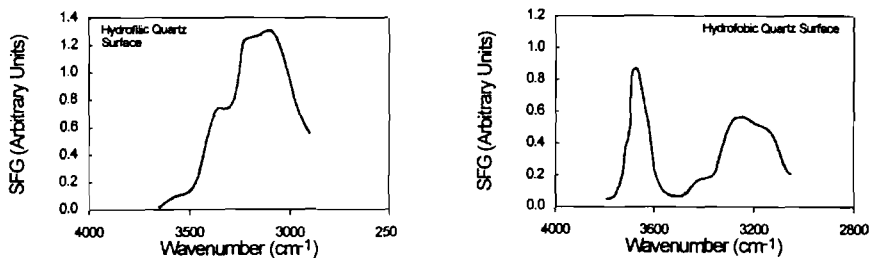


Figure 4. Comparison of SFG spectra from hydrophilic and hydrophobic quartz surfaces in water. It should be noted that spectra similar to the hydrophobic quartz surface were obtained for the air/water interface and the hexane/water interface (37).

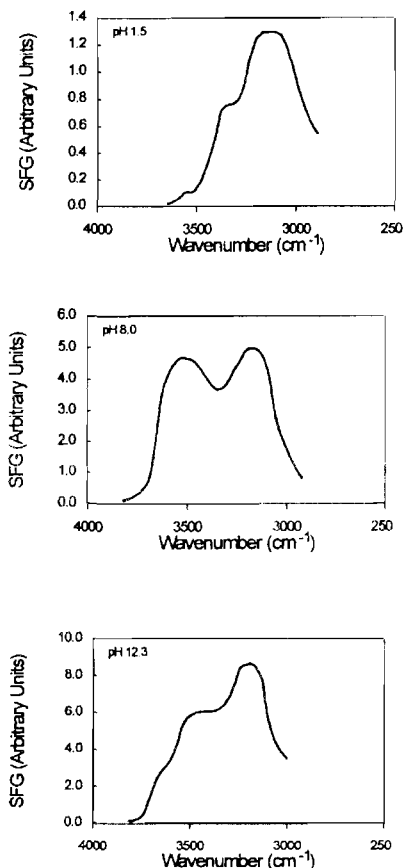


Figure 5. SFG spectra from the quartz/water interfaces with different pH values in the bulk water (35,37).

4.0 SPECTROELECTROCHEMISTRY-FTIR/EXTERNAL REFLECTION

Habib and Bockris (39) studied the possible orientation of water molecule at the surface of platinum electrodes in aqueous NaF solutions. This work was carried out by using FTIR spectroscopy in conjunction with an electrochemical cell having a thin layer of solution in front of the electrode and a reflection attachment to guide the reflected polarized beam from the electrode surface to the detector. Differential IR reflectance spectra for H₂O+D₂O mixtures at various cathodic and anodic potentials were obtained by these authors and the changes in the intensity of the characteristic OH vibration were interpreted as being due to the orientation of the water molecules at the platinum electrode surface. Figure 6 shows the maximum O-H absorbance at wavenumber 3275 cm⁻¹ expressed in percentage as a function of applied potential. Habib and Bockris attributed the observed increase in the intensity of OH stretching band centering around 3250 cm⁻¹ to the differences in hydrogen bonding at the platinum electrode as a function of applied potential. These results were explained in terms of a specific model which describes the dependence of the intensity of OH and OD vibration on potential based on the orientation of water molecules. For example, the results fit a model for water orientation in which water molecules lie flat near the pzc and gradually orient with their oxygen oriented toward the surface with an increase in anodic potential. The results from this work provide excellent information about the nature of water molecules near electrified interfaces. However, these authors failed to describe their results in terms of band positions in the differential spectra of interfacial water at different applied

SFG spectra for the hydrophilic and hydrophobic quartz surfaces in water.

The SFG spectrum for the hydrophilic quartz surface shows a peak at 3200 cm⁻¹, indicating that most of the interfacial water molecules are orderly arranged with tetrahedral coordination. On the other hand, the hydrophobic quartz surface shows a sharp peak at 3680 cm⁻¹ indicating the existence of free OH bonds. Further it was concluded that the OH was oriented with the H atom pointing toward the solid surface. Similar spectral features further supporting the above results were observed by in-situ FTIR/internal reflection spectroscopy (38).

These same researchers have also found that the interfacial water structure can undergo order-disorder changes characterized by the reorientation of water molecules near a hydrophilic surface at different pH values. Figure 5 presents the spectra for the water/quartz interfaces with different pH values in bulk water. The spectra in Figure 5 show how the two peaks at 3200 and 3450 cm⁻¹ vary with pH. At pH 1.5, the spectrum shows a peak at 3200 cm⁻¹, indicating that most of the interfacial water molecules are orderly arranged with tetrahedral coordination. Then, at pH 8.0, two peaks at 3200 and 3450 cm⁻¹ are evident, with the former increasing rapidly. Finally, at pH 12.3, the spectrum resembles that of pH 1.5, but the peak strength is significantly higher. These results can be understood from possible surface-induced ordering and disordering of interfacial water molecules. Note in Figure 5 that for this hydrophilic quartz surface there is no significant peak observed at 3600 cm⁻¹. The free OH peak at 3600 cm⁻¹ seems to be characteristic of hydrophobic surfaces. See Figure 4.

potentials. The OH stretching band centering around 3250 cm^{-1} in the differential spectra clearly indicates the ice-like structure (complete tetrahedral bonding) near the platinum surface. Additional work certainly needs to be done to further support these findings. Also, it should be mentioned that the external reflection technique can not provide any detailed information with regard to the profile of the water structure near the surface.

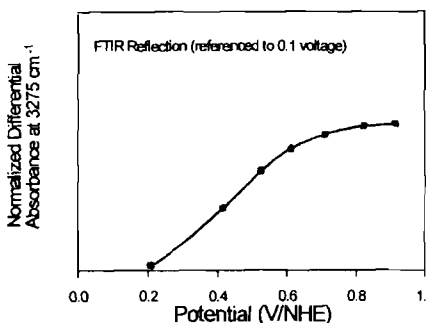


Figure 6. Maximum absorbance expressed in percentage of O-H vibration in adsorbed water molecules on Pt in a solution of 50% H_2O + 50% D_2O + 0.1 M NaF at wavenumber 3275 cm^{-1} as a function of potential obtained from the differential IR spectra with respect to the spectrum at 0.1 V.

5.0 CONCLUSIONS

It is clear that these emerging surface analytical techniques offer excellent opportunities to probe the interfacial regions in many systems. Generally, the preliminary results from these studies indicate that a hydrogen bonded ice-like structure (3200 cm^{-1} and 3400 cm^{-1}) is significant at hydrophilic surfaces and that this structure becomes less significant in regions away from the surface. On the other hand, this interfacial water structure was found to be diminished near hydrophobic surfaces at which surfaces a significant portion of the interfacial water is free (3600 cm^{-1}) and does not exhibit hydrogen bonding. Certainly, further research is warranted, especially, in the area of internal reflection spectroscopy since this technique provides both bulk and interfacial water structure information. Increasing the surface sensitivity of this technique so that the first few layers can be probed is a major challenge and efforts are underway at the University of Utah to meet these goals.

ACKNOWLEDGMENTS

This work, supported by the DOE Basic Science Division, Grant No. DE-FG-03-93ER14315, is gratefully acknowledged.

REFERENCES

1. Israelachvili, J. N.; Adams, G. E., *J. Chem. Soc., Faraday Trans. 1*, 74, 975 (1978).
2. Horn, R. G., and Israelachvili, J. N., *J. Chem. Phys.*, 75, 1400 (1981).
3. Claesson, P. M., *Progr. Coll. Poly. Sci.*, 74, 48 (1987).
4. Israelachvili, J. N., and Wennerstrom, H., *Nature*, 379, 219 (1996).
5. S. Veeramasuneni, M. R. Yalamanchili, and J. D. Miller, Submitted for Publication to *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1996.
6. Israelachvili, J. N., 1992, "Intermolecular and Surface Forces," 2nd Edition, Academic Press, New York.
7. Pashley, R. M., *J. Colloid Interface Sci.*, 83, 531 (1981).
8. Derjaguin, B. V., Kusakov, M. M. *Acta Physicochim. URSS*, 10, 25 (1939).
9. Israelachvili, J. N., Pashley, R. M., *Nature*, 300, 341 (1982).
10. Claesson, P. M., Christenson, H. K., *J. Phys. Chem.* 92, 1650 (1988).
11. Israelachvili, J. N., Tabor, D., *Nature*, 236, 106 (1972).
12. Parker, J. L., Claesson, P. M., Cho, D. L., Ahlberg, A., Blomberg, E. *J. Colloid Interface Sci.* 134, 449 (1990).
13. Rabinovich, Ya. I., Derjaguin, B. V.; Churaev, N. V., *Adv. Colloid Interface Sci.*, 16, 63 (1982).
14. Rabinovich, Ya. I., Yoon, R. H., *Langmuir*, 10, 1903 (1994).
15. Derjaguin, B. V.; Churaev, N. V., *J. Colloid Interface Sci.*, 49, 249 (1974).
16. Marcelja, S., and Radic, N., *Chem. Phys. Lett.*, 42, 129 (1976).

17. Yushchenko, V. S., Yaminsky, V. V., Shchukin, E. D., *J. Colloid Interface Sci.* 96, 307 (1983).
18. Ruckenstein, E., Churaev, N. V., *J. Colloid Interface Sci.* 147, 535 (1991).
19. Rabinovich, Ya. I., Guzonas, D., Yoon, R. H., *Langmuir*, 9, 1168 (1993).
20. Tsao, Y. H., Evans, D. F., Wennerstrom, H. *Langmuir*, 9, 779 (1993).
21. Pashley, R. M., *Adv. Colloid Interface Sci.*, 16, 57 (1982).
22. Rand, R. P., and Parsegian, V. A., *Biochimica et Biophysica Acta*, 988, 351 (1989).
23. Miller, J. D.; Kellar, J. J. *Challenges in Mineral Processing*; Sastry, K. V. S., Fuerstenau, M. C.; Eds.; AIME/SME: Littleton, CO, 1989, p.109.
24. Kellar, J. J.; Cross, W. M.; Miller, J. D. *Separation Science and Technology*. 25, 33 (1990).
25. Yalamanchili, M. R.; Kellar, J. J.; Miller, J. D., *Proceedings of the XVII International Mineral Processing Congress; Polygraphischer Bereich; Dresden, Germany: 1991, Vol. VI, p. 131.*
26. Sperline, R. P.; Muralidharan, S.; Freiser, H. *Langmuir*. 3, 198 (1987).
27. Parry, D. B.; Harris, J. M. *Applied Spectroscopy*. 42, 997 (1988).
28. Fu, F.; Fuller, M. P.; Singh, B. *Applied Spectroscopy*. 47, 98 (1993).
29. Higashiyama, T.; Takenaka, T. *J. Phys. Chem.* 78, 941 (1974).
30. Kellar, J. J.; Cross, W. M.; Miller, J. D. *Applied Spectroscopy*. 44, 1508 (1990).
31. Mirabella, F. M. *Internal Reflection Spectroscopy: Review and Supplement*; Harrick, N. J.; Ed.; Harrick Scientific Corporation: New York, 1985, p. 195.
32. Harrick, N. J. *Internal Reflection Spectroscopy*; Harrick Scientific Corporation: New York, 1987.
33. Yalamanchili, M. R., Atia, A. A., and Miller, J. D., *Langmuir*, in press, 1996.
34. Scherer, J. R. *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Heyden: London, 1978, Vol. 5, 149.
35. Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* 15, 2313, (1993).
36. Nickolov, Z. S.; Earnshaw, J. C.; McGarvey, J. J. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 76, 41(1993).
37. Du, Q.; Freysz, E.; Shen, Y. R. *Science*. 264, 826 (1994).
38. Yalamanchili, M. R., Atia, A. A., and Miller, J. D., "Characterization of Interfacial water at Hydrophilic and Hydrophobic Surfaces by In-Situ FTIR/IRS," in: *Proceedings of the 34th CIM Conference of Metallurgists, Vancouver, British Columbia, August, 1995.*
39. Bockris, J. O'M.; Habib, M. A. *Electrochim Acta*. 22, 41 (1976).



INTERNATIONAL CONFERENCE
ANALYSIS AND UTILISATION OF OILY WASTES
AUZO'96

8-12 September 1996, Gdańsk, Poland

Proceedings of the Conference

Volume II



Faculty of Chemistry
Technical University of Gdańsk