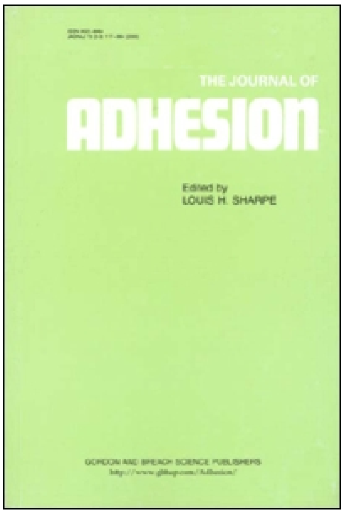

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Limitation of the Young-Dupré Equation in the Analysis of Adhesion Forces Involving Surfactant Solutions

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The atomic force microscope was used to measure adhesion forces between polyethylene particles, serving as model oil droplets, and mineral substrates (fluorite and quartz) in aqueous solutions of ethoxylated alcohols. Also, contact angles were measured in the kerosene–ethoxylated alcohol solution–mineral systems. Correlations obtained between adhesion and surfactant concentration for the polyethylene–aqueous solution–quartz system differs significantly from those predicted by the Young-Dupré equation for the kerosene–aqueous solution–quartz system. Interactions, characteristic for such aqueous systems, which contribute to the pull-off forces measured by atomic force microscopy are not included in the Young-Dupré equation, and are primarily responsible for the inconsistency in the adhesion *versus* surfactant concentration relationship obtained from contact angle measurements.

Keywords: Adhesion; Atomic force microscopy; Contact angle; Ethoxylated alcohols; Work of adhesion; Young-Dupré equation

INTRODUCTION

The *ex-situ* remediation of oil-contaminated soil by flotation and/or washing represents a possible method for the removal of a wide range

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*Corresponding author. e-mail: jwdrelic@mtu.edu of petroleum products from soil, sand and gravel. The efficiency of such a technology is rooted in the nature of the contaminants, the type of soil and the selection of separation reagents. Both flotation and washing technologies utilize interfacial properties to remove contaminants selectively from soil particles suspended in an aqueous solution of surfactant(s). The dual, hydrophobic and hydrophilic, nature of surfactants causes them to adsorb at interfaces, thereby reducing interfacial energies (note that in many systems with a specific adsorption of surfactants to a solid, a value of the solid-water interfacial tension can increase).

The reduction and control of interfacial energies of particulates dispersed in aqueous surfactant solutions are often the keys to optimizing the effectiveness of oil removal from a soil matrix. Controlling the micro-processes such as: (i) the oil roll-up or oil drop necking and release from a mineral, and (ii) the attachment of released oil droplets to air bubbles, are important in the design of oily soil remediation processes. Simply stated, the use of surfactants minimizes the amount of energy required to remove oil and purify the contaminated soil. Ethoxylated alcohol surfactants have been largely overlooked for this application [1,2].

The adhesion forces for oil attachment at mineral particle surfaces are poorly understood at both the microscopic and molecular scale of observation. A common approach in describing the affinity of oil for a solid surface in an aqueous environment is through the measurement of oil–water–solid contact angles (θ) and the measurement of oil–water interfacial tensions (γ_{ow}) [3–5]. The work of adhesion (W_A) is then calculated using the Young-Dupré equation [3–5]:

$$W_A = \gamma_{\mathrm{ow}}(1 + \cos\theta) \tag{1}$$

It follows directly from the above equation that adding surfactant to the aqueous phase can reduce the work of adhesion between an oil drop and a solid surface by changing the interfacial tensions, decreasing the oil–water interfacial tension in particular. Indeed, this approach is typically used in practice.

Although the thermodynamic basis for Eq. (1) is well established, experimental validation, particularly for oil–water–solid systems, has never been accomplished. The lack of appropriate instrumentation is probably the major reason the equation has not been validated for aqueous systems. Recent invention of atomic force microscopy (AFM) [6] and its application to adhesion force measurements certainly has the potential to help in this validation. The principles of the AFM are well described in the literature [7, 8] and will not be repeated here.

In this note, we present the results of AFM pull-off (adhesion) force measurements between polyethylene particles and mineral (fluorite and quartz) surfaces in aqueous solutions of ethoxylated alcohols. The particle – mineral adhesion forces were calculated based on the AFM pull-off results and then compared with the adhesion forces calculated from the measurements of kerosene – aqueous phase – mineral contact angles and kerosene – aqueous phase interfacial tensions. Significant discrepancies in the adhesion forces determined from the AFM study and contact angle/interfacial tension measurements are reported and discussed.

EXPERIMENTAL PROCEDURE

Materials and Reagents

Polished synthetic quartz and fluorite disks were purchased from Harrick Scientific Corporation. The RMS roughness of the mineral substrates was determined with the AFM, being 20 ± 10 nm for quartz and 10 ± 5 nm for fluorite. The disks of quartz were cleaned with a chromic solution and washed with deionized water before use. Fluorite was water-wet repolished on Chemomet cloth (Buehler) and washed with deionized water before use.

Low-density polyethylene powder (MW 1800 and melting point of 117° C) was purchased from Scientific Polymer Products, Inc., and used to prepare spherical particles according to the procedure presented in previous work [9]. Such prepared PE particles have surface irregularities in the height range from 10 to 50 nm [9]. PE particles with a size from about 10 to 14 μm in diameter were used in the AFM study.

A commercial mixture of ethoxylated alcohols, $(CH_2CH_2O)_6$ $CH_3(CH_2)_{7\ 9}CH_2OH$, known as Rhodasurf 91-6, with a purity of 99.5 wt%, was received from Rhodia Inc. Freshly prepared solutions of Rhodasurf 91-6 in 0.001M KCl were used in all experiments. The pH value of the solutions was pH 6.0 ± 0.2.

Kerosene was purchased from a local gas station. Kerosene was selected for this study because it is non-polar liquid with a value of kerosene–water interfacial tension equal to about 46 mN/m. This is very close to the polyethylene–water interfacial tension that is 45 ± 5 mN/m as discussed in the next part.

Atomic Force Microscopy Study

The interfacial force measurements were performed using a Nanoscope III AFM, with a Nanoscope E scanner, Digital Instruments, Inc. Polyethylene particles were glued to the AFM cantilevers by means of a micromanipulator. V-frame Si_3N_4 tipless cantilevers from Digital Instruments with a spring constant 0.58 N/m were used in this study. The adhesion force measurements were done in a fluid cell, offered by Digital Instruments, using freshly prepared solutions of Rhodasurf 91-6. Loading of the PE particle on the mineral substrate before a pull-off force measurement was nearly constant in all experiments, from 10 to 30 nN for quartz and from 20 to 50 nN for fluorite. Forty to one hundred measurements were carried out for each experimental condition examined.

The deflection in the cantilever was calculated as the horizontal distance from the point where the particle comes into contact with the surfaces (the point of attachment) to the point where the particle is removed from the surface and the cantilever springs back to the undeflected position (point of detachment). The pull-off (adhesion) force was calculated by multiplying the distance (Δz) of cantilever deflection by the force constant (k) of the cantilever.

$$F_A = k \times \Delta z \tag{2}$$

The diameter of the PE particle (R) was determined from scanning electron microscopy (SEM) micrographs after completion of adhesion force measurements.

Contact Angle Measurements

The mineral disk was located in a rectangular polystyrene cell and next covered with kerosene. A 20–40 μl drop of water or surfactant solution was placed on the surface of the mineral disk. A Krüss Drop Shape Analysis System (G10) was used to measure the contact angle for a sessile water drop situated on the mineral surface in kerosene. This contact angle corresponds to the receding contact angle when measured for the oil phase (reported in the next part of the paper), and advancing contact angle when measured for the aqueous phase. Measurements were done in 2–3 minutes from the moment of water drop deposition to the moment the image of the drop was taken by the image analysis system. No detectable change in contact angle was noted after 2–3 minutes.

RESULTS AND DISCUSSION

Figure 1 shows the work of adhesion, calculated from Eq. (1) based on measured oil contact angles and interfacial tensions, for kerosene at quartz and fluorite surfaces for varying concentration of the ethoxylated alcohol surfactant mixture, Rhodasurf 91-6. The decrease in the work of adhesion, for both minerals, was mainly a result of decreasing kerosene–water interfacial tension with increasing concentration of surfactant. The interfacial tension decreased from about 46 mN/m for a kerosene–water system to 29 mN/m for a kerosene –0.01 g/L Rhodasurf solution. On the other hand, the kerosene–water–mineral contact angles remained relatively constant over the

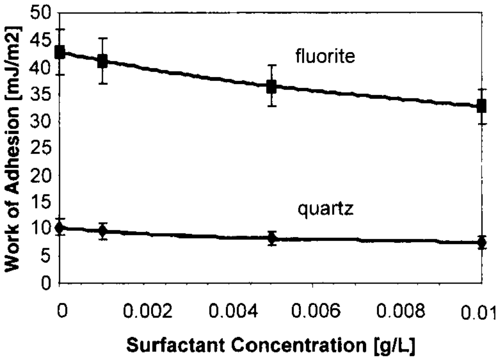

FIGURE 1 Work of adhesion for kerosene at fluorite and quartz surfaces in aqueous solutions of Rhodasurf 91-6 at pH 6 and 20–22° C.

range of surfactant concentration from 0 to 0.01 g/L. In the system with fluorite, the contact angle dropped from 94 degrees to 82 degrees when water was replaced with a 0.01 g/L Rhodasurf solution. In similar experiments, the contact angle dropped from 141 degrees to 138 degrees when measurements were performed on a quartz surface.

Next, the AFM technique was adapted in our laboratory for the examination of oil–water–mineral systems. In this work, we used solid polyethylene particles instead of oil droplets, as we cannot yet overcome the problem of interfacial force measurements for systems involving deformable interfaces. Nevertheless, the selection of polyethylene as a model "oil" particle in the AFM studies should not be questioned. First, in many real-world situations, separated contaminants occur in a solid or semi-solid state. Second, polyethylene has surface properties very similar to those measured for non-polar oils, such as kerosene. In particular, the surface tension of polyethylene is 31–35 mN/m [10]. The polyethylene–water interfacial tension is expected to be 45 ± 5 mN/m, based on available polyethylene surface tension and water-on-polyethylene contact angle data available in the literature [10]. The same properties for kerosene were determined by a pendant drop technique to be 28 mN/m and 46 mN/m, respectively.

Figure 2 shows the values of normalized pull-off forces (force per radius (R) of particle) measured for polyethylene particles on quartz and fluorite substrates in aqueous solutions of ethoxylated alcohols. Both the mineral substrates and Rhodasurf 91-6 solutions were the same as used in surfactant solution–kerosene–mineral contact angle measurements, the results of which are shown in Figure 1.

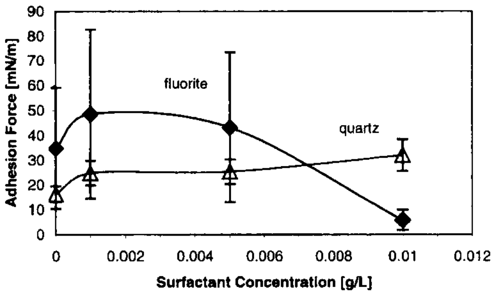

FIGURE 2 Adhesion force measured for a polyethylene particle at the surface of fluorite and quartz in aqueous solutions of Rhodasurf 91-6 at pH 6 and 20–22° C.

Figure 3 shows the comparison between results from Figures 1 and 2. The potential energy of interaction (W_T), per unit area (called the work of adhesion in the next part of the paper), between polyethylene on quartz in Rhodasurf 91-6 solutions was calculated from the adhesion force (F_A) using the following equation [11, 12]:

$$W_T = F_A/(2\pi R) \tag{3}$$

If W_T is assumed to be equal to W_A, an assumption often made in the literature, the relationship between measured adhesion force and concentration of surfactant should be similar to that observed in Figure 1. Because both kerosene and polyethylene demonstrate similar surface properties (see text above), the use of ethoxylated alcohol surfactant solutions should reduce the strength of polyethylene

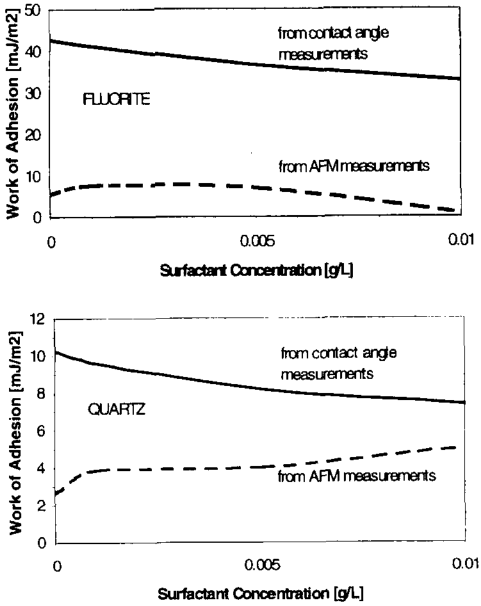

FIGURE 3 The correlation between the work of adhesion and Rhodasurf 91-6 concentration for a kerosene drop (solid line) and a polyethylene particle (broken line) on the fluorite and quartz surfaces. The solid line is the representation of results shown in Figure 1; calculated values from the Young-Dupré Eq. (1) using the results of contact angle and interfacial tension measurements. The broken line is the representation of the experimental results presented in Figure 2; the values are calculated from Eq. (3).

attachment to the mineral surface. As shown in Figures 2 and 3, this tendency was observed for a polyethylene particle at the fluorite substrate surface, although the correlation is slightly different from that for kerosene as shown in Figure 1. A small increase in the polyethylene adhesion force observed at low surfactant concentration is probably associated with wash-off impurities that could slightly contaminate the fluorite surface. Additionally, although we observed a similar effect of surfactant concentration on adhesion of kerosene and polyethylene to a fluorite surface, the relative values of the work of adhesion were significantly different. Specifically, the values of the work of adhesion between polyethylene and fluorite calculated from AFM measurements were about $\Delta W = 32-33\,\mathrm{mJ/m^2}$ smaller that those calculated for kerosene on fluorite from contact angles and interfacial tensions. Surface nano-roughness of the polyethylene particle and the fluorite is probably the major factor causing the presence of this systematic difference in the ΔW value. Surface asperities could reduce the contact area between polyethylene and fluorite surface in our adhesion force measurements and normalized data are probably not true representation of adhesion.

Further, as shown also in Figures 2 and 3, the adhesion force and work of adhesion values follow a different pattern for the polyethylene–solution–quartz system. The force required to pull off the polyethylene particle from the quartz surface increased with increasing surfactant concentration – opposite to what was observed for fluorite. This cannot be attributed to experimental error. We observed the same effect of ethoxylated alcohol on adhesion force between polyethylene and quartz in other experiments [13].

The major problem, not always recognized, is that the condition of $W_T = W_A$ is only applicable to the systems in vacuum and inert gas. In the process of oily soil remediation or detergency, whenever separation takes place in a liquid the value of W_T might differ significantly from the W_A value. This is because the Young-Dupré equation was derived based on consideration of the interfacial free energies of the three-phase system taking into account two states of the system: an initial state corresponding to the contact between bodies, and a final state when interfaces are infinitely separated. The analysis completely neglects the intermediate states of the system at different distances of one interface from another. Specifically, in the system under consideration such as the polyethylene–water–mineral system, the interactions associated with overlapping of electrical double layers around polyethylene (oil) and mineral [14] as well as steric/molecular interactions of ethoxylated alcohols adsorbed on polyethylene and mineral should be taken into account (details of interfacial and molecular forces can be found in [12]). Both the polyethylene and quartz are negatively charged in water and ethoxylated alcohol solutions at pH 6. Consequently, repulsive forces contribute to the work of adhesion for a polyethylene particle at a mineral surface. This effect should be included in the results of AFM measurements but certainly is not included in the Young-Dupré equation. However, the electrostatic interactions cannot be the only factor responsible for the discrepancy of the work of adhesion values shown in Figure 3 for the systems with quartz. Ethoxylated alcohols are non-ionic surfactants and their adsorption at interacting interfaces has no major effect on surface charge. In other words, the electrostatic interactions will approximately equally contribute to the interaction between polyethylene or kerosene and quartz over the entire concentration of Rhodasurf 91-6. As we estimated, a reduction in the work of adhesion between kerosene (polyethyelene) and quartz caused by electrostatic repulsion should be at a level of $0.5-1.5\,\mathrm{mJ/m^2}$ at the conditions of experiments used in this study, over the entire surfactant concentration.

We expect that in the polyethylene–solution–quartz system, molecular interactions between adsorbed surfactants might be important for an interpretation of the experimental data in Figure 2 and 3. The contact angle measurements performed in our laboratory indicate adsorption of ethoxylated alcohols on hydrophobic polyethylene with the hydrophobic part of the molecule attached to the polyethylene surface and the polar group oriented into the aqueous phase (results to be published). It is possible that OH-groups on the quartz surface interact with polar groups of ethoxylated alcohol adsorbed on the polyethylene surface. Increasing adsorption of ethoxylated alcohols on polyethylene increases a number of possible interacting polar groups. As the result, the adhesion force increased with increased concentration of surfactant in the solution (Fig. 2). Obviously, this is only speculation at the moment. The literature [15] indicates, for example, that ethoxylated alcohols also have a tendency to adsorb on silica surfaces. In this regard, other mechanisms for interacting molecular layers cannot be ignored.

In conclusion, we expect that the following equation should be valid in general:

$$W_T = W_A + \Sigma W_i \tag{4}$$

where W_i represents the contribution of forces characteristic for systems in a liquid such as electrostatic interactions, specific molecular and/or steric interactions (see [12, 14] for review of interfacial and molecular forces). Some researchers have already recognized [14, 16, 17] that electrostatic interactions must be included in the analysis of adhesion between solids and liquids suspended in a liquid. The results presented here indicate that adsorption of surface-active compounds at these interfaces would require consideration of molecular interactions in the analysis of adhesion forces.

CONCLUSIONS

We found that the work of adhesion of kerosene at mineral surfaces, calculated using kerosene – water – mineral contact angles and kerosene – water interfacial tensions, decreases in the presence of ethoxylated alcohol. Direct AFM measurements of the pull-off force (adhesion force) in the model oil (polyethylene) – water – quartz system showed the reverse correlation, *i.e.*, the ethoxylated alcohol might improve the strength of attachment of oil at the quartz surface. This unexpected result shed important light on the mechanisms of oil release from mineral surfaces. In view of this discovery it is clear that the Young-Dupré equation should be used with care in the analysis of three-phase systems involving liquid(s). The Young-Dupré equation has limited application to systems that involve suspended matter in liquids. Simply, the effects associated with overlapping of interfacial regions have not been included in the original Young-Dupré equation which limits its application to only a few systems of practical importance, and probably not to the removal of oil from mineral surfaces in the presence of natural or artificial surface-active compounds.

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References

[1] Abdul, A. S. and Gibson, T. L., *Environ. Sci. Technol.* **25**, 665 (1991).
[2] Verma, S. and Kumar, V. V., *J. Colloid Interface Sci.* **207**, 1 (1998).
[3] Cutler, W. G. and Davis, R. C. Eds., *Detergency: Theory and Test Methods* (Marcel Dekker, Inc., New York, 1972).
[4] Drelich, J. and Miller, J. D., *Fuel* **73**, 1504 (1994).
[5] Carroll, B. J., *Colloids Surf. A: Physicochem. Eng. Aspects* **74**, 131 (1993).
[6] Binnig, G., Quate, C. F. and Gerber, C., *Phys. Rev. Lett.* **56**, 930 (1986).
[7] Sarid, D., *Scanning Force Microscopy* (Oxford University Press, New York, 1991).
[8] Wiesendanger, R., *Scanning Probe Microscopy and Spectroscopy: Methods and Applications* (Cambridge University Press, Cambridge, 1994).
[9] Nalaskowski, J., Drelich, J., Hupka, J. and Miller, J. D., *J. Adhesion Sci. Technol.* **13**, 1 (1999).
[10] Wu, S., *Polymer Interface and Adhesion* (Marcel Dekker, Inc., New York, 1982).
[11] Cappella, B. and Dietler, G., *Surface Sci. Rep.* **34**, 1 (1999).
[12] Israelachvili, J., *Intermolecular and Surface Forces* (Academic Press, San Diego, 1992).
[13] Beach, E., Gosiewska, A., Fang, Ch., Dudeck, K. and Drelich, J., In: "*The Proceedings of US United Engineering Foundation Conference on Environmental Technology for Oil Pollution*" (Hupka, J. and Miller, J. D. Eds), pp. 89–93, Technical University of Gdansk, Gdansk, Poland, 1999.
[14] Van Oss, C. J., *Interfacial Forces in Aqueous Media*, (Marcel Dekker, Inc., New York, 1994).
[15] Tiberg, F., Jonsson, B. and Lindman, B., *Langmuir* **10**, 3714 (1994).
[16] Van Oss, C. J., *Colloids Surf. A: Physicochem. Eng. Aspects* **78**, 1 (1993).
[17] Ontiveros, A., Duran, J. D. G., Gonzalez-Caballero, F. and Chibowski, E., *J. Adhesion Sci. Technol.* **10**, 999 (1996).