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An Evaluation of the van Oss–Chaudhury–Good Equation and Neumann's Equation of State Approach with Mercury Substrate

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Extensive studies conducted on wetting and contact angles stem from their importance in varied engineering applications:^{1,2} including froth flotation, adhesives, polymer stability, composite material processing, friction and lubrication, cosmetics and pharmaceuticals, detergents and paints, and nucleation. Our understanding of wetting phenomena has advanced from the macroscopic thermodynamic description developed in Young's era to today's molecular theory.³ A useful expression, derived by combining Young's equation with the extended Fowkes' equation⁴ by including acid/base interactions, is as follows:

$$(1 + \cos \theta)\gamma_L = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}) \quad (1)$$

where θ and γ are the contact angle and the surface tension of the probing liquid, respectively, the subscripts L and S represent the liquid and solid phases, and the superscripts LW, +, and – indicate the apolar (Lifshitz–van der Waals), and Lewis acid and base components of the surface tension, respectively. Equation 1 is often referred to as the van Oss–Chaudhury–Good (OCG) equation.⁵

The OCG equation provides a simple means to characterize a solid surface by using contact angle measurements with three probing liquids, two of which contain different acid and base components of surface tension. The consistent values of surface tension components of a solid, derived from eq 1 by using many different probing liquids serve as a direct confirmation of the approach. Due to its simplicity, contact angle measurement has become a common method for characterizing polymer surfaces and thin films. It should be noted, however, that in deriving eq 1, the equilibrium spreading pressure (π_e) is considered to be negligible, often when the contact angle is greater than 10°. ^{7,8} This approximation is true for low energy surfaces only.

In the present note, we demonstrated, using mercury as novel substrate, that the spreading pressure term cannot be neglected when applying eq 1 to high-energy surfaces even if the contact angle values are greater than 10°.

Experimental Section

Chemicals and Solutions. High-quality mercury (>99.9995%) from Aldrich (USA) was used without further purification. Glycerol and ethylene glycol (Sigma, USA) were above 99% and used as purchased. The water used in this work was triple-distilled and treated using Milli-Q ion exchange

columns followed by organic-Q cartridge (to remove organic contaminants), resulting in a conductivity of 80 μ S/M.

Contact Angle Measurement. Contact angles of probing liquids on a mercury surface were measured at $25 \pm 2^\circ\text{C}$ using the sessile drop method with a contact angle goniometer (Rame-Hart). A square Pyrex container was constructed sufficiently large (20×20 mm) to minimize the curvature of free mercury surface, which arises from the nonwetting nature of mercury on glass. A droplet of approximately 5 μ L probing liquid was placed by gentle touch onto mercury and left for about 5 min to ensure that the measured θ_e represents the true equilibrium contact angle. To minimize the vibration of the liquid surface, the mercury was added to cover just the bottom of the container. The results reported here are the average of six independent measurements with an accuracy of $\pm 1^\circ$.

Interfacial Tension Measurement. The mercury-probing liquid interfacial tension was measured using a drop weight method following the procedures by Harkins and Grafton.⁶ A fine capillary (approximately 2 μ m in diameter) was made by stretching a Pyrex capillary tube of 1.5 mm diameter to control the dropping rate. The mercury drop was drawn by siphon at a rate of about 90 s per drop to ensure the equilibrium. Ten drops of mercury were collected in testing liquid and weighed to calculate the interfacial tension (γ_{mL}) using the following equation

$$\gamma_{mL} = \frac{mg}{2\pi rf} \quad (2)$$

where m is the average mass per drop, g is the acceleration of gravity, r is the radius of capillary tube (0.75 mm), and f is a correction factor. The f value can be calibrated from the measured drop weight of mercury in air and its known surface tension. Using a f value of 0.7436 obtained as such, a value of 425 mN/M was obtained for interfacial tension of mercury in pure water, which is in good agreement with the reported value of 426–427 mN/M.⁷ By use of this procedure, the interfacial tension can be measured to an accuracy of ± 4 mN/M.

Results and Discussion

Contact Angle Measurements. When a water droplet was placed on mercury, a contact angle of 62° was obtained. A similar value (63°) was reported previously.^{8,9} In an attempt to measure advancing and receding contact angles, it was found that the three-phase contact line (mercury–water–vapor) moves spontaneously when water was added to or withdrawn from a droplet by microsyringe, with the contact angle hysteresis being about 4° . No further attempt was made to distinguish between advancing and receding contact angles in the present communication.

The contact angle values obtained by using other probing liquids (glycerol and ethylene glycol) are given in Table 1 along with the literature values of surface tension components of these liquids.¹⁰ This table shows that with decreasing surface tension of probing liquid, contact angle decreases as expected. The $\cos \theta$ values are 0.47, 0.7, and 0.8 for water, glycerol, and ethylene glycol, respectively. In an attempt to fit these values into eq 1 in which the surface tension of mercury is set to be 484 mN/M and its LW component, 200 mN/M,⁷ it was found that the values of $\cos \theta$ are 0.81, 1.57, and 2.17 for water, glycerol, and ethylene glycol, respectively, even without considering the acid/base interactions, which gives the lowest value of $\cos \theta$. A much higher calculated $\cos \theta$ value for water and unrealistic $\cos \theta$ values (greater than 1) for glycerol

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Table 1. Contact Angle Values of Probing Liquids on Mercury and Surface Tension Components of Probing Liquids¹⁰ (Surface Tensions Are in mN/M)

	water	glycerol	ethylene glycol
θ (deg)	62	46	37
γ_{LV}	72.8	64	48
$\gamma_{LW}, \gamma_{L^+}, \gamma_{L^-}$	21.8	34	29
$\gamma_{LW}, \gamma_{L^+}, \gamma_{L^-}$	25.5	3.92	1.92
$\gamma_{LW}, \gamma_{L^+}, \gamma_{L^-}$	25.5	57.4	47

Table 2. Measured Interfacial Tensions and Calculated Spreading Pressure of Probing Liquids on Mercury Using Equation 3

	water	glycerol	ethylene glycol
γ_{mL} (mN/M)	425	382	385
π_e (mN/M)	25	58	61

and ethylene glycol suggest that an additional term has to be included in eq 1 for these systems.

Interfacial Tension Measurements. In spite of finite contact angle of these probing liquids on mercury ($> 35^\circ$), it is expected that a thin film of probing liquid may exist on mercury, due to the high surface energy of liquid mercury. Therefore, the spreading pressure term needs to be included in eq 1. As a liquid, the interfacial tension between mercury substrate and probing liquids can be measured separately which allows the equilibrium spreading pressure to be calculated using the following equation.¹¹

$$\pi_e = \gamma_m - \gamma_{mL} - \gamma_{LV} \cos \theta_e \quad (3)$$

where interfacial tensions between mercury and its vapor (γ_m), mercury and probing liquid (γ_{mL}), and liquid and its vapor (γ_{LV}) can be measured accurately.

The measured interfacial tensions are given in Table 2 along with equilibrium spreading pressure values as calculated using eq 3. It is evident that the measured spreading pressures are significant, ranging from 25 to 61 mN/M and increasing with decreasing surface tension of probing liquids.

By inclusion of the equilibrium spreading pressure, eq 1 becomes¹²

$$(1 + \cos \theta_e) \gamma_L = 2(\sqrt{\gamma_s^{LW} \gamma_L^{LW}} + \sqrt{\gamma_s^+ \gamma_L^+} + \sqrt{\gamma_s^- \gamma_L^-}) - \pi_e \quad (4)$$

By fitting the measured contact angle values to eq 4, values of 192, 0.1, and 0 mN/M were obtained for γ_m^{LW} , γ_m^+ , and γ_m^- , respectively. It is clear that the acid and base components of surface tension for liquid mercury are negligible, and interactions between mercury and these probing liquids are LW type in nature. The LW component of surface tension obtained in this work (192 mN/M) is in the range of reported values (200 ± 7 mN/M).⁷ The above discussion suggests that even if the substrate is lyophobic ($\theta > 0^\circ$) and interacts with liquids by LW forces only, the equilibrium spreading pressure may still be significant, which may result in errors in derived surface tension components using eq 1. This is expected for a high-energy substrate with $\gamma_s > \gamma_{sl}$ (e.g., mercury) because the formation of a liquid film on such substrate is energy-favorable. The equilibrium spreading pressure was also reported to be significant for water on carbon (142 mN/M), graphite (64 mN/M), and polyethylene (14.4 mN/M)

although these substrates are hydrophobic with contact angles ranging from 65° to 85° .⁸ This clearly demonstrates that caution has to be taken when using eq 1 to characterize some polymer surfaces.

A further test was conducted using reported values of interfacial tension of mercury and other probing liquids, including apolar (carbon tetrachloride), electron donor (Lewis base) type (ethanol and benzene), and electron acceptor (Lewis acid) type (chloroform). The interfacial tension values were taken from Harkins and Grafton⁶ and the values of surface tensions and their components from van Oss.¹⁰ By fitting these values to the following well-known fundamental interfacial tension equation:^{11,12}

$$\gamma_{mL} = \gamma_m + \gamma_L - 2(\sqrt{\gamma_m^{LW} \gamma_L^{LW}} + \sqrt{\gamma_m^+ \gamma_L^+} + \sqrt{\gamma_m^- \gamma_L^-}) \quad (5)$$

the values of 195, 1.4, and 5.3 mN/M were obtained for γ_m , γ_m^+ , and γ_m^- , respectively. These results are in good agreement with those obtained above using other probing liquids based on contact angle measurements. It also confirms that the acid and base interactions between mercury and these various types of liquids are small and the LW interactions dominate.

Test of Neumann's Equation of State. Another often used approach to characterize solid films from the measured contact angles is derived from Neumann's equation of state (EQS).¹³ A phenomenological form of this equation is given by¹⁴

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_{LV} \gamma_{SV}} e^{-\beta(\gamma_{LV} - \gamma_{SV})^2} \quad (6)$$

where β is a fitting parameter. A β value of 0.0001247 (M^2/mJ^2) has been obtained from contact angle data for most polymer systems (usually low energy surfaces).¹⁴ By fitting the experimental results obtained from the mercury-probing liquid system to eq 6, a β value of 3.52×10^{-6} (M^2/mJ^2) was obtained, which is 2 orders of magnitude smaller than the reported value. The detailed discussion on this empirical parameter is beyond the scope of this communication.

It is, however, interesting to compare the goodness of the best fitting of these two different approaches. Figure 1 shows the correlation between measured and calculated interfacial tensions using the parameters from the best fit. For a perfect fit, all the points should lie on the diagonal line (i.e. $\gamma_{mL}^M = \gamma_{mL}^C$, where superscripts M and C indicate measured and calculated interfacial tensions). The closeness of the points to this line indicates the goodness of the fit. This figure shows that the OCG approach, eq 4, gives better fit (open square) than the EQS approach, eq 6, (open circle), for the mercury substrate, suggesting that the OCG approach is more general and provides a more representative description of interactions across various interfaces. (The square point for ethanol is off the line, which may be due to the experimental error or the existence of other specific interaction(s) between mercury and ethanol that has not been recognized yet.) One additional advantage to use OCG approach is that the components of surface tensions derived provide the information regarding the nature of the interactions with other liquids or solids across the interface.

The lack of the fit of EQS approach to our results may be due to the presence of traces of impurities in mercury (the best quality of the mercury we can get is $> 99.9995\%$),

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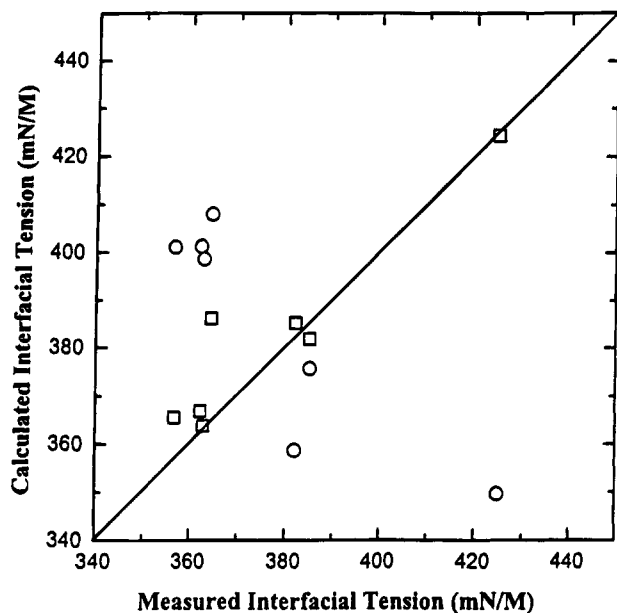


Figure 1. Correlation between measured and calculated interfacial tensions using the fitted parameters from the van Oss-Chaudhury-Good's (open square) and Neumann (open circle) methods.

which breaks down the assumptions included in the EQS approach. However, this is unlikely the case since our contact angle and interfacial results agree with other published data⁷⁻⁹ (in the case of water) and fit the OCG equation nicely. The lack of fit for the EQS approach to other liquid-liquid systems has been recognized and reported previously.¹⁵ There is, however, no satisfactory

explanation as to why the EQS approach does not apply to a liquid-liquid-vapor system if it works in some solid-liquid systems.¹⁵⁻¹⁸ The limitations of EQS in other solid-liquid systems were also reported recently.^{19,20} The use of the geometric mean combining rule (Berthelot combining rule) alone in the EQS approach may not be sufficient for describing the general interactions across an interface. Refinement is therefore needed in choosing the proper form of the equation to extend the approach to more general systems.

In summary, the present work clearly demonstrates that the equilibrium spreading pressure has to be considered even when the high surface energy substrates are lyophobic and interact with liquids mainly by dispersion forces. It was confirmed that mercury interacts with various (nonmetallic) liquids mainly by Lifshitz-van der Waals forces. A sufficient condition for using eq 1 is $\gamma_s < \gamma_{sl}$; i.e., the formation of film is energetically unfavorable. It is also found that the approach proposed by van Oss-Chaudhury-Good is more suitable for the interactions between mercury and other liquids than that of Neumann's equation of state.

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