

## CHAPTER IV

### WETTING OF POLYMER SURFACES BY AQUEOUS SURFACTANT SOLUTIONS

#### 4.1 Abstract

An important application of surfactants is to improve the wettability of aqueous solutions on hydrophobic surfaces, as indicated by a decrease in the contact angle of the liquid on the solid. The surfactant adsorbs at the liquid/vapor interface, reducing the surface tension and adsorbs at the solid/liquid interface, reducing the interfacial tension. In this work, the reduction of the surface tension and interfacial tension was measured as well as the advancing contact angle and surfactant adsorption as a function of surfactant concentration for three anionic and three cationic surfactants on eight different polymers with varying hydrophobicity. The Zisman equation (cosine of contact angle is a linear function of surface tension) adequately describes all systems studied as the critical micelle concentration is approached. The dependence of contact angle solely on surface tension does not mean that interfacial tension reduction due to surfactant adsorption is not important; rather, interfacial tension reduction mirrors surface tension reduction with increasing surfactant concentration; the ratio of solid/liquid interfacial tension to the liquid/vapor surface tension was shown to be independent of surfactant concentration for all 48 systems studied here. In general, interfacial tension reduction and surfactant adsorption at the solid/liquid interface are less significant as polymer hydrophobicity decreases. The critical surface tension (surface tension at which contact angle is zero as extrapolated from Zisman plots) differs for the different surfactants on a given polymer, emphasizing the limited generic applicability of the Zisman hypothesis for surfactant solutions. A mathematical analysis was developed to calculate the solid/vapor and the solid/pure water interfacial tensions which depend only on the polymer characteristics. The solid/vapor interfacial tension was found to be 33.3 mN/m and does not depend on polymer structure.

**Keywords:** Wettability/Surface tension/Interfacial tension/Zisman plot/Contact angle

## 4.2 Introduction

Wetting improvements on solid surfaces are an important role of a surfactant. A surfactant reduces the surface tension (e.g. liquid/vapor interfacial tension) of the liquid and changes interfacial tension at the solid/liquid interface [1]. The wetting of hydrophobic solid surfaces by liquids, both with and without surfactant, is commonly quantified by the contact angle on flat surfaces and influenced by the surface tension of the liquid ( $\gamma_{LV}$ ) and the interfacial tension between the liquid and the solid [1-14]. A common way to analyze this wetting phenomena is via a Zisman plot [3] which is a linear relationship between the cosine of the contact angle ( $\theta$ ) and  $\gamma_{LV}$ . The critical surface tension is obtained by extrapolation to the surface tension at  $\cos \theta = 1$  ( $\theta = 0^\circ$ ) where complete wetting occurs and has been shown to be independent of the liquid identity and only depend on the chemical nature of the solid surface when pure liquids with different  $\gamma_{LV}$  values were used to generate the Zisman plot. However, solutions containing different surfactant concentrations have been shown to sometimes not exhibit linearity in the Zisman plot and further different surfactants can yield different critical surface tensions. Since the Zisman plot is empirical and has no theoretical basis, this difference is not surprising. Linearity in the Zisman plot implies that surface tension reduction is the only important factor driving decreasing contact angles. However, it has been shown that solid/liquid interfacial tension reduction can also contribute greatly to wettability enhancement – it is just that the interfacial tension reduction mirrors that of  $\gamma_{LV}$ , so surface tension is an effective correlating factor [1].

A common technique to analyze wetting data for surfactant solutions are adhesion plots ( $(\gamma_{LV}\cos \theta)$  vs.  $\gamma_{LV}$ ). As summarized by Rosen [1], the slopes of these plots when linear yield the ratio of surfactant adsorption at the solid/liquid interface

to adsorption at the liquid/vapor surface. For example, on hydrophobic polymers, some studies have found that this slope is nearly -1, indicating that adsorption at the two interfaces is about the same. [1,10-13]. Determination of solid/liquid and solid/vapor interfacial tensions is much more difficult and predictive equations such as the Fowkes equation are often used, but these are generally only valid when dispersion forces dominate which is not the case for surfactants in general. In this work, we have developed a method to calculate the solid/liquid interfacial tension from contact angle and surface tension data. We have also calculated adsorption at the solid/liquid and liquid/vapor interfaces as a function of surfactant concentration rather than just their ratio so do not use adhesion plots here.

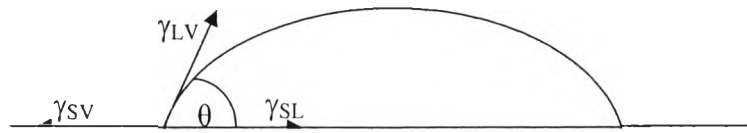
In the present study, wetting of aqueous solutions containing three anionic surfactants and three cationic surfactants (a homologous series) were studied on eight polymers of varying hydrophobicity. The relative importance of adsorption of surfactant at the solid/liquid interface and at the liquid/vapor interface and resulting reduction of interfacial tension and surface tension on wettability improvement are quantified. Applicability of the Zisman approach to wetting of surfactant solutions is analyzed for these 48 systems.

### 4.3 Theory

For a sessile drop on a flat surface, the advancing contact angle is determined by the three surfaces or interfacial tensions (shown in Figure 4.1) as described by the Young's equation [9]:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (4.1)$$

where  $\theta$  is the contact angle,  $\gamma_{SV}$  is the solid/vapor interfacial tension,  $\gamma_{SL}$  is the solid/liquid interfacial tension, and  $\gamma_{LV}$  is the liquid/vapor interfacial tension (which is normally called the surface tension).



**Figure 4.1** Schematic of sessile drop with three interfacial/surface tensions acting on a drop perimeter relating to contact angle shown.

Since at equilibrium, the vapor is saturated with water, adsorption of water vapor onto the surface can cause  $\gamma_{SV}$  to be different than that in vacuum. Berg [15] refers to this  $\gamma_{SV}$  as a “practical surface energy”. Since only dilute surfactant solutions in pure water are considered here,  $\gamma_{SV}$  and the thermodynamic activity of water can be assumed to be constant for different surfactant types and concentrations. The adsorption of surfactant can reduce  $\gamma_{SL}$  and  $\gamma_{LV}$ , improving wettability (causing  $\theta$  to decrease). Surface pressures are useful since they represent the difference between  $\gamma_{SL}$  and  $\gamma_{LV}$  for pure water and the surfactant solution and are defined as follows:

$$\Pi_{SL} = \gamma_{SL}^o - \gamma_{SL} \quad (4.2)$$

$$\Pi_{LV} = \gamma_{LV}^o - \gamma_{LV} \quad (4.3)$$

where the superscript o refers to surfactant-free solution or pure water. The Zisman equation [7,15] assumes that  $\cos \theta$  is a linear function of  $\gamma_{LV}$  from  $\theta = 0^\circ$  ( $\cos \theta = 1$ ) to higher  $\gamma_{LV}$  over a range of surface tensions as expressed by the following:

$$\cos \theta = 1 - \beta (\gamma_{LV} - \gamma_c) \quad (4.4)$$

where  $\gamma_c$  is called the critical surface tension and is defined as  $\gamma_{LV}$  when  $\cos \theta = 1$  (usually obtained by extrapolation) and  $\beta$  is the slope of the so-called Zisman plot.

The Zisman equation is an empirical correlation developed for pure solvents and does not always apply to surfactant solutions [2]. This paper examines the mechanisms responsible for surfactant-induced wettability enhancement and includes

consideration of the applicability of the Zisman equation. For pure water, Equation (4.1) can be written:

$$\gamma_{LV}^{\circ} \cos \theta^{\circ} = \gamma_{SV} - \gamma_{SL}^{\circ} \quad (4.5)$$

where  $\theta^{\circ}$  is the contact angle for pure water and the superscript on the solid/vapor interfacial tension is not written since it is assumed to be constant irrespective of the surfactant concentration. For the surfactant solution; Equation (4.1) can be written as:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (4.6)$$

subtracting Equation (4.5) from Equation (4.6) and using Equation (4.2) defining surface pressure:

$$\Pi_{SL} = \gamma_{LV} \cos \theta - \gamma_{LV}^{\circ} \cos \theta^{\circ} \quad (4.7)$$

Since adsorption of surfactant at interfaces is responsible for reduction of  $\gamma_{LV}$  and  $\gamma_{SL}$ , we are interested in quantifying the adsorption levels. From the Gibbs equation [9] at the solid/liquid interface for an anionic or cationic surfactant with the definition at surface pressure (Equation (4.2)):

$$\Gamma_{SL} = \frac{1}{2RT} \frac{d\Pi_{SL}}{d \ln C_S} \quad (4.8)$$

where  $\Gamma_{SL}$  is the surface excess or relative surfactant adsorption at the solid/liquid interface and  $C_S$  is the surfactant concentration in solution.

Similarly at the liquid/vapor interface, combining the Gibbs equation with the definition at surface pressure (Equation (4.3)), for anionic or cationic surfactant,

$$\Gamma_{LV} = \frac{1}{2RT} \frac{d\Pi_{LV}}{d \ln C_S} \quad (4.9)$$

$\Gamma_{L,V}$  is the surface excess or relative surfactant adsorption at the liquid/vapor interface. Equations (4.8) and (4.9) assume that the surfactant partial fugacity or activity is proportional to concentration, so these equations only apply to dilute solutions below the CMC. The liquid/vapor interface typically exhibits a constant  $\Gamma_{L,V}$ , i.e. constant slope of  $\gamma_{L,V}$  vs.  $\ln C_S$ , from about 20% of the CMC to the CMC as a Gibbs close-packed monolayer is attained [16]. Whether a solid surface becomes saturated as the CMC is approached depends on the nature of the solid.

It will be shown that the empirical Zisman equation (Equation (4)) describes the contact angle data well for all 8 polymers and 6 surfactants studied here as concentrations approach the CMC. In this case, combining Equations (4.1), (4.2) and (4.4):

$$\Pi_{SL} = -\beta\gamma_{LV}^2 + (1 + \beta\gamma_c) \gamma_{LV} + (\gamma_{SL}^o - \gamma_{SV}) \quad (4.10)$$

Since  $\beta$  and  $\gamma_c$  are known for a given system from the Zisman plots ( $\cos \theta$  vs.  $\gamma_{LV}$ ), a quadratic fit of  $\Pi_{SL}$  vs.  $\gamma_{LV}$  from given polymer/surfactant system can yield  $(\gamma_{SL}^o - \gamma_{SV})$  according to Equation (4.10). Note that the values of  $\gamma_{SV}$  and of  $\gamma_{SL}^o$  are independent of the surfactant and depend only on the polymer.

From Equation (4.5),  $\gamma_{SV}^o$  and  $\theta^o$  for pure water yield  $(\gamma_{SV} - \gamma_{SL}^o)$  which can be compared to the value of  $(\gamma_{SL}^o - \gamma_{SV})$  from the best fit of Equation (4.10) to data from each surfactant/polymer system. The Zisman and Young's equations (Equations (4.1) and (4.4)) can be combined to yield Equation (4.11):

$$\cos \theta = \frac{\gamma_{SV}}{\gamma_{LV}} - \frac{\gamma_{SL}}{\gamma_{LV}}. \quad (4.11)$$

Ignoring the specific mathematical relationship between  $\theta$  and  $\gamma_{LV}$  (Zisman equation is just one potential fit), the fact that the Zisman equation can describe all systems studied here implies that  $\theta$  is only a function of  $\gamma_{LV}$  (not of  $\gamma_{SL}$ ). From Equation (4.11), with  $\gamma_{SV}$  constant this is true under two limiting conditions:  $\gamma_{SL}$  is constant or

$\gamma_{SL}/\gamma_{LV}$  is constant. The former is certainly not true in the general case; we will show that for all but the most hydrophilic polymer studied here,  $\gamma_{SL}$  (or  $\Pi_{SL}$ ) depends strongly on surfactant adsorption onto the polymer ( $\Gamma_{SL}$ ) which, in turn, depends on surfactant concentration. So, if we assume that  $\gamma_{SL}/\gamma_{LV}$  is constant, combining with Equations (4.1) and (4.7) yields Equation (4.12):

$$\frac{\Pi_{SL}}{\gamma_{LV}} = \frac{\gamma_{SL}^0}{\gamma_{LV}} - K \quad (4.12)$$

where  $K$  is a constant. So, a plot of  $\Pi_{SL}/\gamma_{LV}$  vs.  $1/\gamma_{LV}$  should have a slope of  $\gamma_{SL}^0$ . This can be combined with  $(\gamma_{SV} - \gamma_{SL}^0)$  from data fits to Equation (4.5) or (4.10) to calculate  $\gamma_{SV}$ .

## 4.4 Experimental

### 4.4.1 Materials

The different types of plastics having various degrees of hydrophobicity were used in this study. Polytetrafluoroethylene (PTFE) was purchased from Chemical Innovation Co., Ltd. High density polyethylene (HDPE) was obtained from Thai Polyethylene Co., Ltd. Polycarbonate (PC), grade Makrolon<sup>®</sup>PC, was obtained from Bayer Thai Co., Ltd. Polyvinylchloride (PVC), grade SG580, was obtained from Thai Plastic and Chemicals Public Co., Ltd. Acrylonitrile butadiene styrene (ABS) was obtained from IRPC Public Co., Ltd. Polymethyl methacrylate (PMMA) was obtained from Diapolyacrylate Co., Ltd. Polyhexamethylene adipamide (PA66), grade A31, was obtained from SY Smile Co., Ltd.. Polycaprolactone (PCL) was purchased from Sigma-Aldrich Co., Ltd. The cationic surfactants – hexadecyl trimethyl ammonium bromide (CTAB, C<sub>19</sub>H<sub>42</sub>NBr), tetradecyl trimethyl ammonium bromide (TTAB, C<sub>17</sub>H<sub>38</sub>NBr), and dodecyl trimethyl ammonium bromide (DTAB, C<sub>15</sub>H<sub>34</sub>NBr) were supplied by Fluka Co., Ltd. (Switzerland) with a purity of 98%. The anionic surfactants – sodium dodecyl sulfate (SDS or C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na, ≥99% purity), 4-octyl benzene sulfonate sodium salt (SOBS

or  $C_{14}H_{21}SO_3Na$ , 97% purity) and sodium octanoate ( $C_8$  or  $C_8H_{15}O_2Na$ , >99% purity) were purchased from Sigma Chemical Company (St. Louis, MO). All chemicals were used without further purification.

#### 4.4.2 Measurements

The surface tensions of surfactant solutions were determined by the pendant drop technique using a drop shape measurement instrument (Krüss, DSA10).

The contact angles of water and surfactant solutions on any studied plastic surfaces were measured using the sessile drop technique by the contact angle measuring instrument (Krüss, DSA10) which does a best fit of contact angle and surface tension to describe the shape of a sessile drop on a flat surface. A fresh plastic surface was prepared by using compression molding. The fresh plastic pellet was first compressed into a smooth sheet beyond the melting point of each plastic, at 10 MPa for 5 min and cooled down to room temperature for 10 min. Finally, the plastic sheet was cut to a size 3 cm x 3 cm for contact angle measuring. A 45  $\mu$ L drop of surfactant solution was then placed onto the plastic sheet put into the chamber and the contact angle was measured after 1 min which was sufficient to allow equilibrium to occur. During the measurement, the chamber was kept at 30°C and saturated with water vapor to prevent liquid drop evaporation effect and to ensure that the dry polymer surface was in equilibrium with saturated air.

### 4.5 Results and Discussion

#### 4.5.1 Critical Micelle Concentrations

Table 4.1 shows the CMC values for the six surfactants studied as determined via surface tension vs. concentration plots. The CMCs of the three cationic surfactants decrease with increasing hydrophobe size from C12 to C16 and permit systematic examination of effect of hydrocarbon chain length. The three anionic surfactants have both dissimilar head groups (sulfate, sulfonate, and carboxylate) and hydrophobe sizes. Of particular note is the CMC of the C8 is much higher than all other surfactants. The Krafft temperature of the carboxylate



surfactants tends to be higher than sulfates or sulfonate, so a small hydrophobe is required for carboxylate solubility at 30°C.

Various parameters reported in this work at the CMC of each surfactant since parameters like contact angle and surface tension plateau at the CMC. So, maximum wettability enhancement occurs at the CMC and levels off at higher concentrations. From a mechanistic viewpoint, comparison of surfactants at their CMC is reasonable, but practically, surfactants are purchased on a mass basis; so for example, at the CMC, the wt. % of surfactant in solution is much greater for C8 than the other surfactants. So, care must be taken in concluding that the most effective wetting agent found here at the CMC is also the most economical wetting agent due to this consideration as well as cost differences.

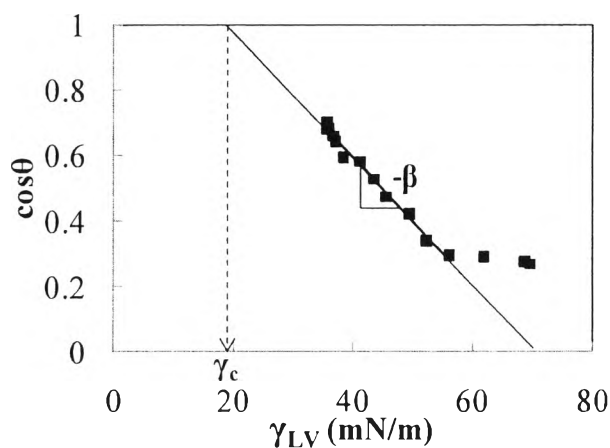
**Table 4.1** CMC values of surfactant solutions

Surfactants	CMC ( $\mu\text{M}$ )
CTAB	$1.0 \times 10^3$
TTAB	$4.0 \times 10^3$
DTAB	$1.4 \times 10^4$
SDS	$8.3 \times 10^3$
SOBS	$1.2 \times 10^4$
C8	$3.5 \times 10^5$

#### 4.5.2 Zisman Plots

Figure 4.2 illustrates a Zisman plot (for the PCL/CTAB system) in detail. The value of  $\gamma_c$  is obtained from extrapolation of the linear region of the curve to  $\cos \theta = 1$  and the slope of this curve equals  $-\beta$ . Note that at high  $\gamma_{LV}$  (low surfactant concentration), deviation from linearity is observed which is of course not unexpected. That is because the surfactant molecule is not sufficiently strong to adsorb at solid/liquid interface, leading to no reduction in solid/liquid interfacial tension and contact angle. At high surfactant concentration, the reduction of

solid/liquid interfacial tension is effective as much as that of surface tension due to surfactant adsorption so, the Zisman plot can show the linearity. Moreover, if the solution surface tension was  $\gamma_c$  for a given system, complete wetting ( $\theta = 0^\circ$ ) would be observed, but the CMC intervenes first and such low surface tension cannot be achieved for these surfactants.



**Figure 4.2** Zisman plot for PCL and CTAB surfactant illustrating  $\gamma_c$  and  $\beta$ .

The Zisman plots ( $\cos \theta$  vs.  $\gamma_{LV}$ ) are shown in Figures 4.3a - 4.3h for the eight polymers and six surfactants studied. The slopes of lines shown are equal to  $-\beta$  and the extrapolated values of  $\gamma_{LV}$  at  $\cos \theta = 1$  are  $\gamma_c$  (from Equation (4.4)). These values of  $\beta$  and  $\gamma_c$  are shown in Table 4.2 along with the contact angle of pure water ( $\theta^\circ$ ) on each polymer which is indicative of polymer hydrophobicity. The Zisman equation describes all 48 systems well until a high  $\gamma_{LV}$  is reached. In some cases, substantial extrapolation is required to obtain  $\gamma_c$ .

The Zisman equation was originally developed for pure liquids and often was not observed to be valid for surfactant solution [2]. According to the original hypothesis,  $\gamma_c$  should be characteristic of the polymer and independent of the liquid. From Table 4.2, there is substantial variation in the value of  $\gamma_c$  for the six different surfactant solutions on a given polymer and hence the original hypothesis was not observed to be valid. The value of  $\gamma_c$  is expected to decrease as polymer hydrophobicity increases ( $\theta^\circ$  increases); i.e. a lower surface tension solution would

be required to wet a more hydrophobic polymer. From Table 4.2, there is not a good correlation between  $\gamma_c$  and  $\theta^\circ$  for the 48 systems studied here. So, even though the Zisman equation is obeyed for these systems, there is no universal parameter ( $\gamma_c$ ) which is characteristic of a given polymer for the surfactant systems and which correlates to polymer hydrophobicity. This dependence of  $\gamma_c$  on only the surface is a main value of the Zisman correlation; however we are not the first to conclude that the universality is violated for surfactant solutions [5,12-14].

However, the Zisman equation does describe  $\cos \theta$  vs.  $\gamma_{LV}$  for the systems studied here and permits us to calculate fundamental parameters ( $\gamma_{SL}^\circ$  and  $\gamma_{SV}$ ) from Equations (4.10) and (4.12). Our finding that the relationship between  $\cos \theta$  vs.  $\gamma_{LV}$  is linear has not been found universally; others have shown that the Zisman equation is invalid particularly for more hydrophilic polymers [13,17]. Finally, the value of  $\beta$  does generally increase with an increase in  $\theta^\circ$  as would be expected.

#### 4.5.3 Surface Forces and Adsorption –Results and Calculations

In Young's equation (Equation (4.1)),  $\theta$  and  $\gamma_{LV}$  are easily measured while  $\gamma_{SL}$  and  $\gamma_{SV}$  cannot be easily measured; although  $\gamma_{SV}$  only depends on the solid and the pure liquid under the conditions of this experiment. From Equation (4.7),  $\Pi_{SL}$  can be deduced from measurable parameters, which indicates how much the surfactant solution caused the solid/liquid interfacial tension to be reduced below that of pure water. The value of  $\Pi_{LV}$  can be directly calculated for comparison from Equation (4.3). The effect of reduction of  $\gamma_{LV}$  compared to reduction of  $\gamma_{SL}$  (or increase in  $\Pi_{LV}$  and  $\Pi_{SL}$ ) due to the surfactant on wetting ( $\theta$  decrease) will be a focus of our discussion in this paper. These effects are due to adsorption of surfactant at the liquid/vapor and solid/liquid interfaces. The levels of  $\Gamma_{SL}$  and  $\Gamma_{LV}$  can be calculated from  $\Pi_{SL}$  or  $\Pi_{LV}$  vs.  $\log$  (surfactant concentration) data from Equations (4.8) and (4.9). The raw data ( $\theta$  and  $\gamma_{LV}$  vs.  $C_S$ ) are detailed in Appendix A and B.

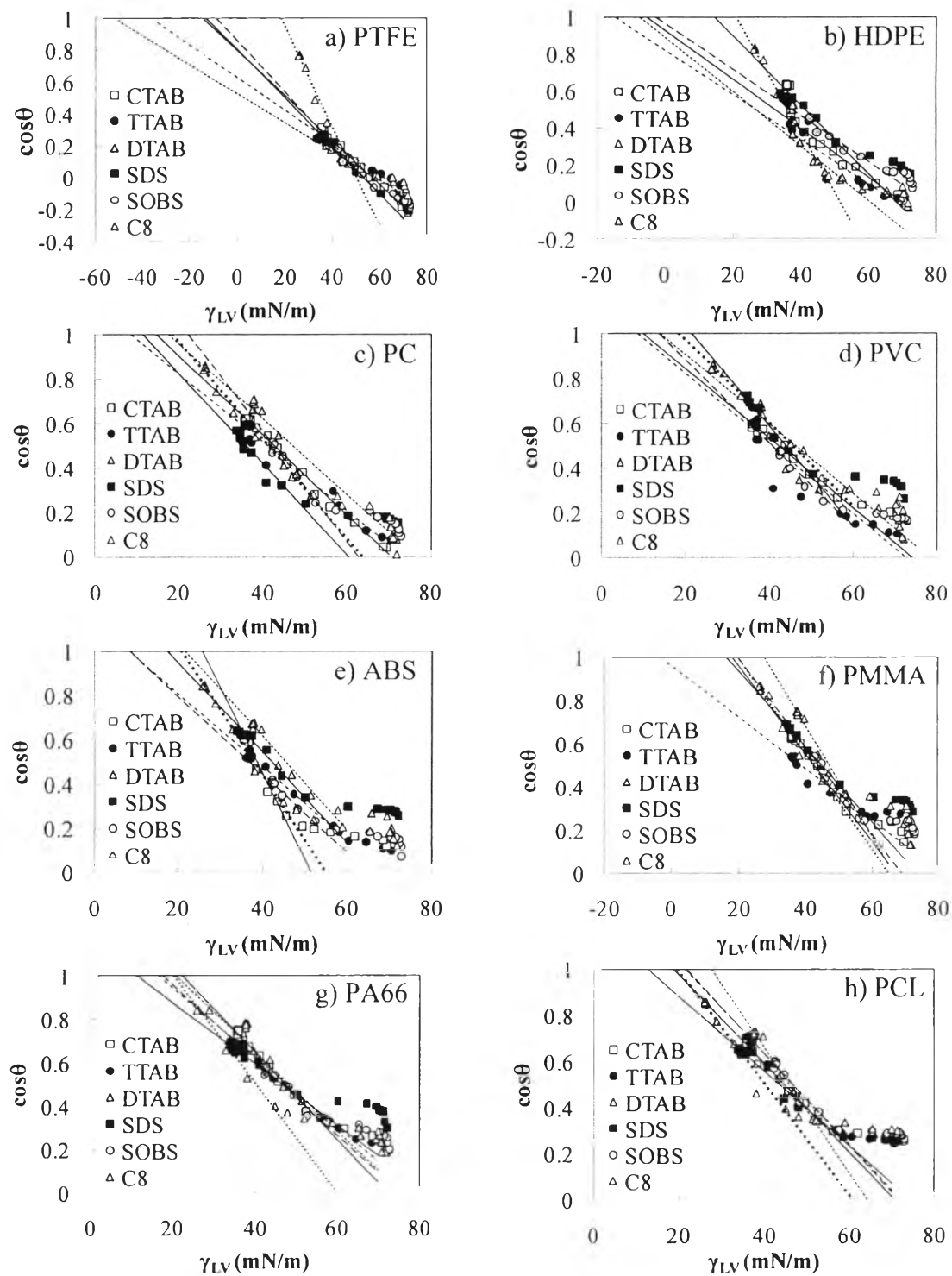


Figure 4.3 Zisman plot for eight polymers with six surfactant types.

**Table 4.2** Contact angle of water and Zisman plot parameters

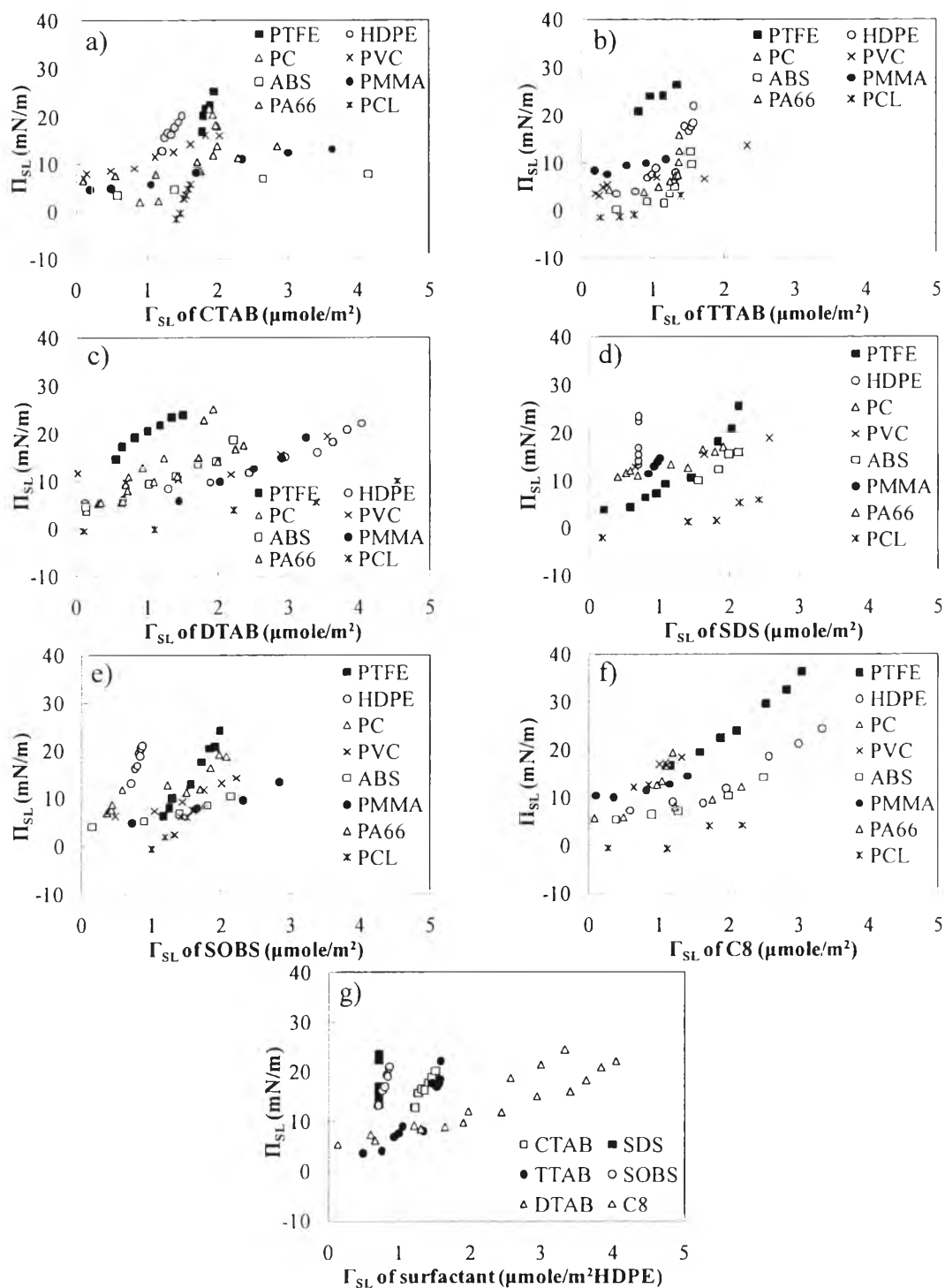
	Surfactant	Polymer							
		PTFE	HDPE	PC	PVC	ABS	PMMA	PA66	PCL
$\gamma_c$	CTAB	-14	-4.9	15	10	26	18	22	19
	TTAB	-36	-14	8.8	8.7	8.5	-3.2	16	21
	DTAB	-52	-7.1	18	14	22	28	21	28
	SDS	-13	15	12	22	18	16	11	13
	SOBS	-9	-2	22	14	9	20	18	22
	C8	19	21	19	18	21	20	20	20
$\beta$	CTAB	0.0140	0.0134	0.0179	0.0156	0.0388	0.0202	0.0199	0.0193
	TTAB	0.0102	0.0122	0.0154	0.0157	0.0165	0.0119	0.0159	0.0198
	DTAB	0.0090	0.0148	0.0170	0.0156	0.0210	0.0256	0.0181	0.0273
	SDS	0.0151	0.0188	0.0204	0.0223	0.0203	0.0175	0.0140	0.0163
	SOBS	0.0159	0.0126	0.0248	0.0187	0.0176	0.0203	0.0172	0.0201
	C8	0.0314	0.0324	0.0222	0.0185	0.0293	0.0221	0.0250	0.0245
$r^2$	CTAB	0.9936	0.9800	0.9927	0.9843	0.9694	0.9893	0.9850	0.9885
	TTAB	0.9536	0.8982	0.9684	0.8887	0.9769	0.9598	0.9956	0.9873
	DTAB	0.9881	0.9324	0.9480	0.9182	0.9678	0.9838	0.9881	0.9849
	SDS	0.9665	0.9801	0.9865	0.9865	0.9715	0.9967	0.9801	0.9664
	SOBS	0.9672	0.9664	0.9529	0.9529	0.9812	0.9866	0.9558	0.9667
	C8	0.9859	0.9964	0.9870	0.9930	0.9928	0.9799	0.9754	0.9682
<b>Contact angle of water (<math>\theta^\circ</math>)</b>		103	91.8	89.2	85.3	84.4	82.7	80.5	75.6

Via Equations (4.7) and (4.8),  $\Pi_{SL}$  is shown as a function of  $\Gamma_{SL}$  for all systems in Figure 4.4. Both  $\Gamma_{SL}$  and  $\Pi_{SL}$  generally steadily increase with increasing  $C_S$  up to the CMC (above which both level off). However, at the liquid/vapor surface,  $\Gamma_{LV}$  plateaus from about 20% of the CMC upward as a Gibbs close-packed monolayer is formed. Since  $\Gamma_{SL}$ ,  $\Gamma_{LV}$ ,  $\Pi_{SL}$ , and  $\Pi_{LV}$  all plateau above the CMC, they

are at their maximum values at the CMC. For comparison between surfactants and between polymers, we tabulate these parameters for all systems in Table 4.3, as well as  $\gamma_{LV}$  and  $\Delta\theta$  ( $\theta^{\circ} - \theta$ ) at the CMC. The parameter  $\Delta\theta$  indicates the maximum contact angle reduction of each surfactant.

From the theory section, a constant ratio of  $\gamma_{SL}/\gamma_{LV}$  was deduced to be consistent with the Zisman equation. The value of  $\gamma_{SL}/\gamma_{LV}$  is plotted as a function of surfactant concentration in Figure 4.5 for all 48 systems with the best fit value for each shown as a horizontal line in the Figures and tabulated in Table 4.4. The value of this parameter will be important to our interpolation of wetting forces later, but constancy of the ratio for a given polymer/surfactant system was assumed in deriving Equation (4.12). As seen in Figure 4.5 and Table 4.4, this ratio is remarkably constant over at least two orders of magnitude concentration range with an average variance of  $\pm 13.5\%$  for all systems. For PA66 polymer with SDS, the average ratio of  $\gamma_{SL}/\gamma_{LV}$  is so close to zero because some  $\gamma_{SL}$  values were slightly negative, leading to a huge relative variance in  $\gamma_{SL}/\gamma_{LV}$  ( $0.01 \pm 0.033$ ). The average variance excludes SDS with PA66 since  $\gamma_{SL}$  is too close to zero to be meaningful.

For pure water, the ratio  $\gamma^{\circ}_{SL}/\gamma^{\circ}_{LV}$  is shown in Table 4.4 excluding the TTAB with PMMA polymer, the SDS with the four most hydrophilic polymers (PVC, ABS, PMMA and PA66) and the SOBS with PVC and PMMA and differs from the average  $\gamma_{SL}/\gamma_{LV}$  (using a range of surfactant concentrations) by an average of 17.9% over the 41 systems analyzed. Based on Equation (4.12),  $\Pi_{SL}/\gamma_{LV}$  is plotted against  $1/\gamma_{LV}$  in Figures 6a – 6h. The slope of the line for each system is  $\gamma^{\circ}_{SL}$  which should be independent of surfactant type for a given polymer; a separated plot is shown for each polymer to visually compare these slopes. The best fit value of  $\gamma^{\circ}_{SL}$  is shown in Table 4.4. The value of  $\Pi_{SL}$  at the CMC in Table 3.3 is subtracted from this  $\gamma^{\circ}_{SL}$  to yield  $\gamma_{SL}$  at the CMC shown in Table 4.3. The average value of  $\gamma^{\circ}_{SL}$  for each polymer with the variance from the values from the six surfactants is shown in Table 4.5.



**Figure 4.4** Surface pressure at solid/liquid interface ( $\Pi_{SL}$ ) of eight polymers and six surfactant solutions as a function of surface excess at solid/liquid interface.

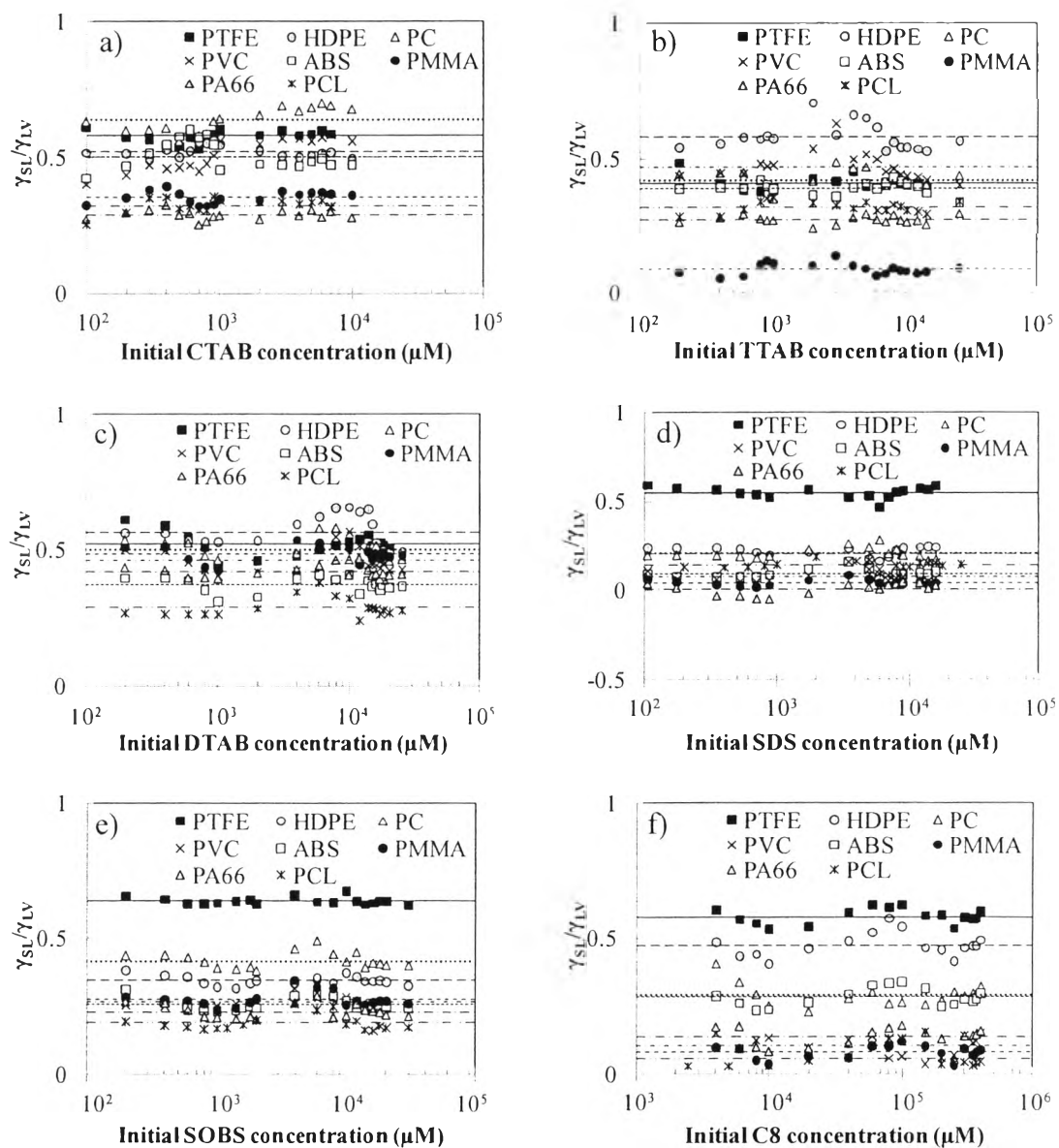
**Table 4.3** Surfactant adsorption, surface pressure, surface/interfacial tension, and fraction of wetting effect due to surface tension reduction at the CMC

Polymer	Surfactant	Contact angle ( $0^\circ$ )		$\Delta\theta^\circ$	$\Pi_{LV}$	$\Pi_{SL}$	$\Gamma_{LV}$	$\Gamma_{SL}$	$\gamma_{LV}$	$\gamma_{SL}^{**}$	$f_{LV}$
		water	surfactant								
PTFE	CTAB	103.0	72.1	30.9	37.0	27.4	3.10	1.67	35.7	21.2	0.29
HDPE		91.8	55.9	35.9		22.1		1.30		18.3	0.48
PC		89.2	51.6	37.6		21.4		1.76		24.4	0.52
PVC		85.3	54.0	31.3		15.5		1.55		20.0	0.58
ABS		84.4	52.3	32.1		15.0		3.15		17.0	0.60
PMMA		82.7	51.0	31.7		13.4		2.04		12.9	0.64
PA66		80.5	42.5	38.0		14.3		1.13		10.7	0.66
PCL		75.6	47.5	28.1		6.25		1.30		12.0	0.80
PTFE	TTAB	103.0	74.4	28.5	36.2	26.2	2.84	0.80	36.7	15.0	0.27
HDPE		91.8	57.6	34.1		21.8		1.25		19.8	0.47
PC		89.2	53.5	35.7		20.8		1.11		14.9	0.51
PVC		85.3	54.5	30.8		15.6		0.92		16.7	0.57
ABS		84.4	58.6	25.9		12.3		1.53		14.9	0.61
PMMA		82.7	57.5	25.2		10.4		0.33		2.92	0.65
PA66		80.5	46.6	33.9		12.9		0.83		10.1	0.66
PCL		75.6	45.4	30.2		7.72		1.15		11.5	0.77
PTFE	DTAB	103.0	75.9	27.0	35.2	25.5	3.23	1.09	37.6	19.3	0.25
HDPE		91.8	58.3	33.4		21.8		1.58		18.6	0.46
PC		89.2	46.8	42.4		24.9		3.64		18.3	0.49
PVC		85.3	47.0	38.3		19.7		0.84		16.5	0.55
ABS		84.4	47.5	36.9		18.3		1.45		13.7	0.57
PMMA		82.7	41.5	41.2		18.9		2.14		17.9	0.58
PA66		80.5	38.4	42.1		17.5		1.37		15.2	0.61
PCL		75.6	43.9	31.8		9.18		2.25		10.4	0.73
PTFE	SDS	103.0	75.7	27.2	38.2	25.0	3.29	2.26	34.7	19.5	0.27
HDPE		91.8	55.4	36.4		22.0		1.87		8.09	0.50
PC		89.2	57.8	31.4		17.8		1.34		6.30	0.53
PVC		85.3	44.9	40.3		18.6		1.45		2.24	0.59
ABS		84.4	51.1	33.3		14.8		1.83		3.10	0.62
PMMA		82.7	47.2	35.5		14.3		0.92		1.27	0.64
PA66		80.5	48.0	32.5		11.4		0.49		0.97	0.69
PCL		75.6	50.0	25.7		4.45		1.25		4.89	0.85
PTFE	SOBS	103.0	79.2	23.7	30.5	24.3	2.52	1.56	42.4	26.7	0.19
HDPE		91.8	63.4	28.3		21.3		0.79		14.3	0.39
PC		89.2	59.3	29.9		20.7		1.65		16.9	0.43
PVC		85.3	61.5	23.8		14.3		1.29		10.4	0.50
ABS		84.4	66.0	18.4		10.2		1.14		10.6	0.55
PMMA		82.7	57.2	25.5		13.7		1.75		11.3	0.55
PA66		80.5	55.3	25.3		12.1		0.50		9.80	0.59
PCL		75.6	53.6	22.0		7.24		1.30		7.31	0.71
PTFE	C8	103.0	39.4	63.5	46.6	36.6	2.93	2.44	26.3	15.3	0.50
HDPE		91.8	34.3	57.5		24.0		2.70		12.4	0.62
PC		89.2	31.8	57.5		21.1		0.90		8.27	0.65
PVC		85.3	31.6	53.7		17.1		1.03		2.85	0.70
ABS		84.4	32.3	52.2		15.0		1.45		7.44	0.72
PMMA		82.7	30.4	52.3		13.4		0.93		1.98	0.75
PA66		80.5	32.5	48.1		10.5		1.33		3.53	0.79
PCL		75.6	31.3	44.3		4.30		1.14		1.45	0.90

$$^* \Delta\theta = \theta_{\text{water}} - \theta_{\text{surfactant}}$$

$$^{**} \gamma_{SL} = \gamma_{SL}^\circ - \Pi_{SL} \text{ with } \gamma_{SL}^\circ \text{ from Table 4.4}$$





**Figure 4.5**  $\gamma_{SL}/\gamma_{LV}$  of eight polymers and six surfactant types as a function of initial surfactant concentration.

Table 4.4 Surface and interfacial forces for each polymer/surfactant system

Polymer	Surfactant	Average $\gamma_{SL}/\gamma_{LV}$	$\gamma_{SL}^0$ (mN/m)	$\gamma_{sv}$ (mN/m)		$\gamma_{SL}^0/\gamma_{LV}^0$
				From Eq. (4.10)	From Eq. (4.5)	
PTFE	CTAB	0.58±0.03	48.6	32.1	32.2	0.67
HDPE		0.52±0.02	40.5	38.2	38.2	0.56
PC		0.64±0.04	45.7	46.8	46.7	0.63
PVC		0.50±0.06	35.5	41.6	41.5	0.49
ABS		0.50±0.05	32.0	39.1	39.0	0.44
PMMA		0.36±0.02	26.3	35.6	35.6	0.36
PA66		0.29±0.02	24.9	36.8	36.9	0.34
PCL		0.32±0.03	18.3	36.3	36.4	0.25
PTFE	TTAB	0.41±0.03	41.2	24.7	24.9	0.57
HDPE		0.58±0.05	41.6	39.4	39.3	0.57
PC		0.42±0.03	35.7	36.7	36.7	0.49
PVC		0.47±0.05	32.4	38.3	38.3	0.44
ABS		0.39±0.02	27.2	34.2	34.3	0.37
PMMA		0.09±0.02	13.3	22.5	22.5	0.18
PA66		0.27±0.02	23.0	35.1	35.0	0.32
PCL		0.32±0.02	19.2	37.4	37.3	0.26
PTFE	DTAB	0.52±0.04	44.7	28.5	28.4	0.61
HDPE		0.56±0.06	40.4	38.3	38.2	0.56
PC		0.50±0.04	43.2	44.2	44.2	0.59
PVC		0.46±0.05	36.2	42.1	42.1	0.50
ABS		0.37±0.03	32.0	39.1	39.1	0.44
PMMA		0.48±0.03	36.8	46.1	46.0	0.50
PA66		0.42±0.02	32.6	44.7	44.6	0.45
PCL		0.29±0.04	19.6	37.6	37.7	0.27
PTFE	SDS	0.55±0.03	44.5	28.1	28.2	0.61
HDPE		0.22±0.02	30.1	27.9	27.9	0.41
PC		0.21±0.03	24.1	25.1	25.0	0.33
PVC		0.07±0.03	20.9	26.8	26.9	0.29
ABS		0.09±0.03	17.9	25.0	24.9	0.25
PMMA		0.04±0.02	15.6	24.8	24.8	0.21
PA66		0.01±0.03	12.4	24.4	24.4	0.17
PCL		0.14±0.02	9.34	27.2	27.5	0.13
PTFE	SOBS	0.64±0.01	50.9	34.6	34.6	0.70
HDPE		0.35±0.02	35.6	33.5	33.4	0.49
PC		0.42±0.03	37.6	38.7	38.6	0.52
PVC		0.27±0.03	24.6	30.6	30.6	0.34
ABS		0.26±0.02	20.7	27.8	27.8	0.28
PMMA		0.28±0.03	25.0	34.2	34.2	0.34
PA66		0.23±0.03	21.9	33.9	33.9	0.30
PCL		0.19±0.03	14.6	32.6	32.7	0.20
PTFE	C8	0.58±0.03	51.8	35.5	35.5	0.71
HDPE		0.47±0.04	36.4	34.1	34.2	0.50
PC		0.29±0.04	29.3	30.3	30.3	0.40
PVC		0.11±0.04	20.0	25.9	25.9	0.27
ABS		0.28±0.03	22.4	29.6	29.5	0.31
PMMA		0.08±0.03	15.4	24.7	24.6	0.21
PA66		0.14±0.04	14.0	26.0	26.0	0.19
PCL		0.06±0.04	5.75	23.7	23.9	0.08

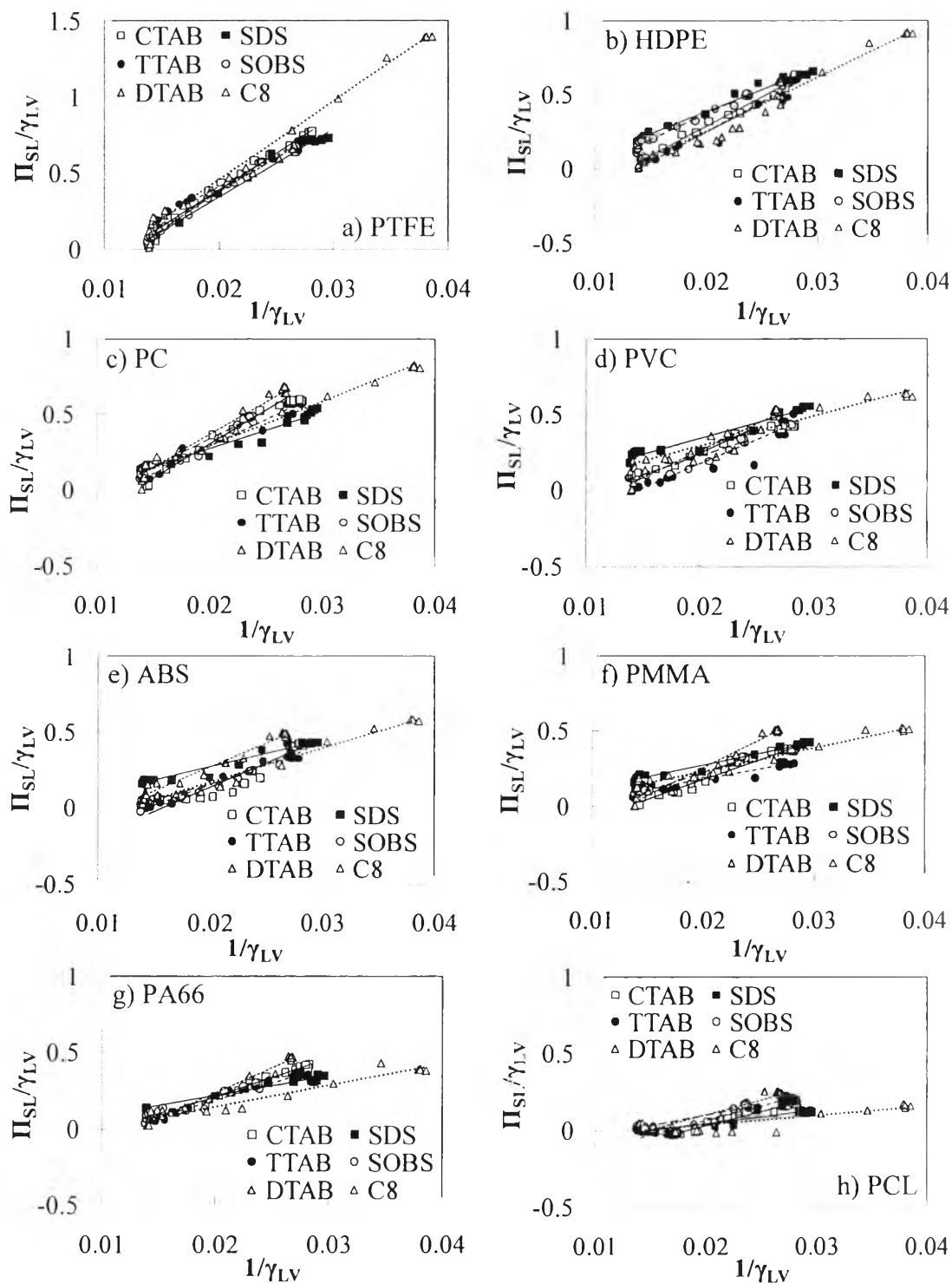
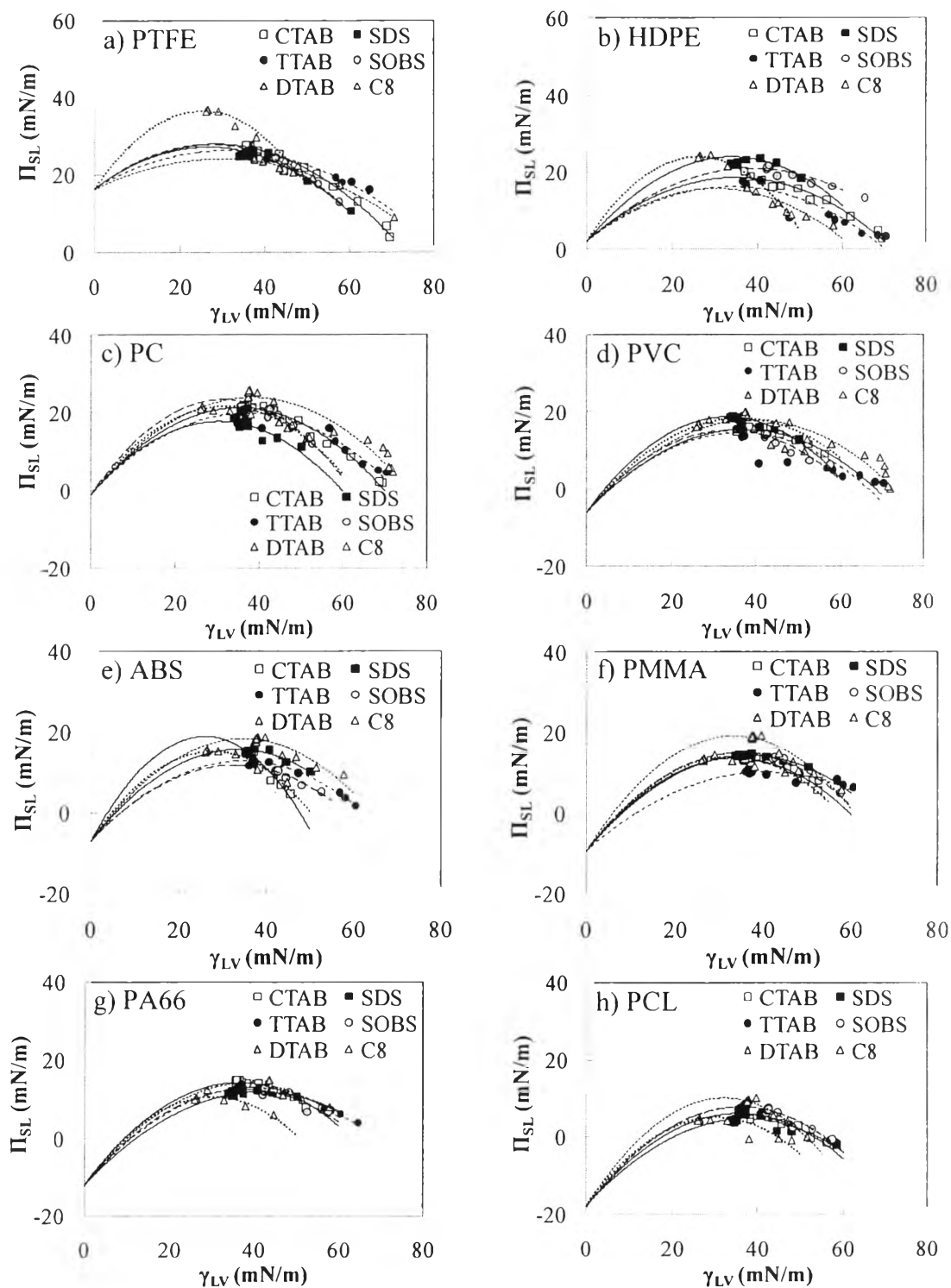


Figure 4.6  $\Pi_{SL}/\gamma_{LV}$  of eight polymers and six surfactant types as a function of  $1/\gamma_{LV}$ .

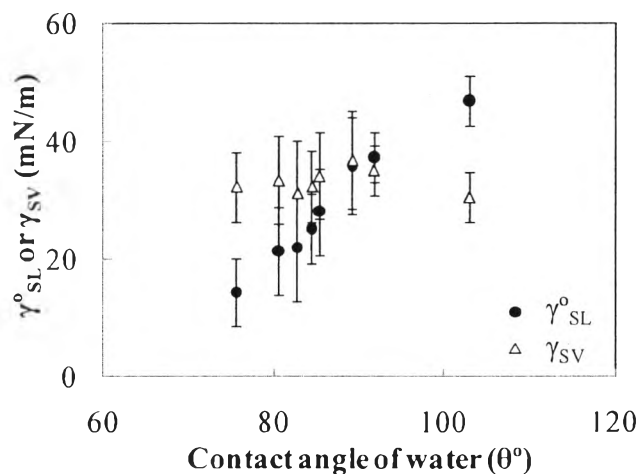
**Table 4.5** Surface and interfacial forces for each polymer averaged from all six surfactants

Polymer	Contact angle of water ( $\theta^\circ$ )	$\gamma_{SL}^\circ$ (mN/m)	$\gamma_{SV}$ (mN/m)
PTFE	103.0	47.0 $\pm$ 4.13	30.6 $\pm$ 4.18
HDPE	91.8	37.4 $\pm$ 4.31	35.2 $\pm$ 4.30
PC	89.2	35.9 $\pm$ 8.21	37.0 $\pm$ 8.21
PVC	85.3	28.2 $\pm$ 7.32	34.2 $\pm$ 7.35
ABS	84.4	25.4 $\pm$ 5.96	32.5 $\pm$ 5.94
PMMA	82.7	22.0 $\pm$ 9.02	31.3 $\pm$ 9.04
PA66	80.5	21.5 $\pm$ 7.46	33.5 $\pm$ 7.47
PCL	75.6	14.4 $\pm$ 5.75	32.5 $\pm$ 5.85

Figures 4.7a - 4.7h show  $\Pi_{SL}$  vs.  $\gamma_{LV}$ . The values of  $\beta$  and  $\gamma_c$  from the Zisman plots in Table 4.2 are used to fit the quadratic equation (Equation (4.10)) to the data as shown in Figures 4.7a - 4.7h with the intercept ( $\gamma_{SL}^\circ - \gamma_{SV}$ ) as the adjustable parameter for best fit. This value was then combined with  $\gamma_{SL}^\circ$  from Equation (4.12) to calculate  $\gamma_{SV}$  as tabulated in Table 4.4. Equation (4.5) uses pure water ( $\gamma_{LV}^\circ$  and  $\theta^\circ$ ) to calculate ( $\gamma_{SV} - \gamma_{SL}^\circ$ ) which can be combined with  $\gamma_{SL}^\circ$  from Equation (4.12) to give an alternate value of  $\gamma_{SV}$  also shown in Table 4.4. The values of  $\gamma_{SV}$  calculated with the two different approaches compare very well with an average difference of 0.19% for all 48 systems giving some confidence in the assumptions made (e.g. use of the Zisman equation to derive Equation (4.10)). The average values of  $\gamma_{SL}^\circ$  and  $\gamma_{SV}$  for each polymer with the variance from the values from the six surfactants are shown in Table 4.5 and are plotted against the contact angle of pure water for each polymer in Figure 4.8 to show the effect of polymer hydrophobicity. Since the value of  $\gamma_{SV}$  obtained from Equation (4.10) is a best fit to numerous data instead of a single measurement as from Equation (4.5), we will use this former value of  $\gamma_{SV}$  in further discussions and calculations.



**Figure 4.7** Surface pressure at solid/liquid interface ( $\Pi_{SL}$ ) of eight polymers with six surfactant types as a function of surface tension.



**Figure 4.8** Average  $\gamma_{SL}^\circ$  and  $\gamma_{SV}$  for all studied systems as a function of contact angle of pure water on eight polymers.

The values of both  $\Pi_{SL}$  and  $\Pi_{LV}$  at the CMC are substantial, particularly for more hydrophobic polymers where they are comparable in value as shown in Table 4.3. Clearly adsorption of surfactant at both the solid/liquid and liquid/vapor interfaces is important to wetting enhancement by surfactants. In order to quantify the relative importance of changes at the two interfaces, we calculate the horizontal force component at the CMC contributed from each surface (see Figure 4.1) which must balance to force from the solid/vapor ( $\gamma_{SV}$ ) pulling in the opposite direction. The difference in this horizontal force between pure water and the surfactant solution for the solid/liquid ( $F_{SL}$ ) and liquid/vapor ( $F_{LV}$ ) interfaces are:

$$F_{SL} = \Pi_{SL} \quad (4.13)$$

$$F_{LV} = \Pi_{LV} \cos \theta \quad (4.14)$$

The fraction of the surfactant effect attributable to surface tension reduction ( $f_{LV}$ ) is:

$$f_{LV} = \frac{F_{LV}}{F_{SL} + F_{LV}} \quad (4.15)$$

with  $(1 - f_{LV})$  being the fraction attributable to solid/liquid interfacial tension reduction. The value of  $f_{LV}$  at the CMC is shown in Table 4.3.

#### 4.5.4 Most Effective Wetting Agent

For a given system, the lowest contact angle occurs at the CMC. From Table 4.3, the C8 results in the lowest contact angle (highest  $\Delta\theta$ ) at the CMC while the SOBS yields the highest contact angle. The primary reason for the improved wetting by C8 is the lowest surface tension attained as seen in Table 4.3. Also from Table 4.3, the fraction of the wetting improvement due to surfactant attributable to surface tension reduction compared to interfacial tension reduction is the highest for C8 compared to the others while this fraction is similar for studied cationic surfactants.

From Table 4.3, the contact angle at the CMC is still lower for more hydrophilic polymers, but the decrease in contact angle due to the C8 surfactant causes the gap between hydrophilic and hydrophobic polymers to shrink while the other surfactants do not reduce this gap as much. At the CMC, the C8 surfactant is most effective at improving wetting of the most hydrophobic polymer, which is where the effect is most needed.

#### 4.5.5 Overview of Surfactant Effects on Wettability

The fundamental question is what forces are causing contact angle to decrease as surfactant concentration increases below the CMC and how these are affected by surfactant type and polymer characteristics. Of course, hydrophobicity is only one characteristic of the polymer, but is a convenient first approximation of its nature and is determined here via the contact angle of pure water.

The Zisman equation implies that  $\theta$  is only a function of  $\gamma_{LV}$  and it was shown in the Theory section that this is true under two limiting conditions:  $\gamma_{SL}$  is constant or  $\gamma_{SL}/\gamma_{LV}$  is constant. From Tables 4.3 and 4.4,  $\gamma_{SL}$  can be reduced by more than a factor of 2 at the CMC compared to  $\gamma_{SL}^0$  for pure water. So clearly,  $\gamma_{SL}$  depends on surfactant concentration. From Table 4.4 and Figures 4.5a - 4.5f, the ratio of  $\gamma_{SL}/\gamma_{LV}$  is remarkably constant for all systems studied with varying surfactant

concentrations. Hence, the contribution of the liquid/vapor surfactant adsorption to reduction of surface tension ( $\gamma_{LV}$ ) or increase in liquid/vapor surface pressure ( $\Pi_{LV}$ ) mirrors the contribution of the solid/liquid surfactant adsorption to reduction of solid/liquid interfacial tension ( $\gamma_{SL}$ ) or increase in solid/liquid surface pressure ( $\Pi_{SL}$ ) to contact angle decrease with increasing surfactant concentration. The ratio of  $\gamma_{SL}/\gamma_{LV}$  tends to increase with increasing hydrophobicity of the polymer, but there is not a clear correlation to surfactant type. For pure water, the solid/liquid interfacial tension ( $\gamma_{SL}^0$ ) increases with increasing hydrophobicity of the polymer (Tables 4.4 and 4.5 and Figure 4.8) since incompatibility of the solid and liquid phases becomes greater. For more hydrophobic polymers, the value of  $\gamma_{SL}$  decreases more rapidly with increasing surfactant concentration, resulting in a constant ratio of  $\gamma_{SL}/\gamma_{LV}$ .

The relative importance of surface tension reduction due to the surfactant compared to that of the interfacial tension reduction on wettability improvement, as indicated by  $f_{LV}$ , decreases with increasing polymer hydrophobicity as shown in Table 4.3. For the more hydrophobic polymers, the solid/liquid surface pressure can be as much as 80% of the liquid/vapor surface pressure at the CMC, indicating the danger of ignoring the contribution of the surfactant adsorption on the polymer to wettability enhancement.

C8 exhibits the best contact angle reduction at the CMC primarily due to its low plateau surface tension. The contribution of solid/liquid surface pressure increases to the reduction in contact angle tends to be lower for C8 than the other surfactants, but the trend is not valid for all polymers. There are no particularly general conclusions about effect of hydrophobe size for the cationic surfactants. Since the CMC is lower for the longer hydrophobe, practically the longest hydrophobe possible without solubility limitations would be most effective on a weight basis.

Broadly speaking, the CTAB, TTAB, DTAB, and SDS have similar wetting properties (e.g., for HDPE,  $\Delta\theta$  varies from 33.4° to 36.4° at the CMC). The values of  $\Pi_{LV}$  and  $\Pi_{SL}$  at the CMC are also similar. The poorest wetter at the CMC is SOBS and the best is C8 ( $\Delta\theta$  of 28.3° and 57.5°, respectively on HDPE). These also have the highest and lowest plateau surface tensions, respectively. While the



solid/liquid surface pressure trends vary from polymer to polymer, they do not vary systematically with surfactant structure. So, the solid/liquid surface pressure contribution to contact angle reduction does not vary with surfactant structure as much as liquid/vapor surface pressure.

#### 4.5.6 Surface Forces and Adsorption –Discussion

From the previous section, we have shown that both the surface tension reduction and the solid/liquid interfacial tension reduction due to the surfactant are important to wettability enhancement. The relationship between surfactant adsorption at the liquid/vapor interface and surface tension reduction is well understood [18]. But, since the solid/liquid interfacial tension is generally unavailable, how surfactant adsorption reduces it is less well understood, so it is discussed here. Detailed surfactant adsorption isotherms (adsorption vs. surfactant concentration) for the 48 systems studied here are presented in Figure 4.9. It is difficult to obtain the kind of detailed adsorption isotherms from analysis of surface tension and contact angle data (Equation (4.8)) compared to that from a solution depletion method. However, the latter requires a surface area of at least about  $1 \text{ m}^2/\text{g}$ , so is only useful for porous materials or those with very small particle sizes. From the adsorption isotherms derived from Equation (4.8), important conclusions are that a plateau is generally not reached before the CMC so saturation (either a monolayer or bilayer) is not attained. Consistent with not achieving saturation, adsorption levels for the different polymers at the CMC in Table 4.3 are generally below the adsorption at the liquid/vapor interface (Gibbs close-packed monolayer). In some cases, plateau adsorption levels are between a monolayer and a bilayer, indicating bilayer or admicelle formation [19] on at least some fraction of the surface.

Figures 4.4a - 4.4f show the solid/liquid surface pressure as a function of adsorption at the solid/liquid interface for each surfactant. The surface pressure increases monotonically with adsorption. Surfactant adsorption clearly drives the reduction in solid/liquid interfacial tension. The value of  $\Pi_{\text{SL}}$  appears to increase more rapidly with surfactant adsorption for the more hydrophobic polymers, one reason for higher values of  $\Pi_{\text{SL}}$  and lower  $f_{\text{LV}}$  at the CMC with higher polymer hydrophobicity (Table 4.3). While surfactant adsorption does not show a clear trend

at the CMC with polymer hydrophobicity, it induces a greater reduction in solid/liquid interfacial tension for more hydrophobic polymers.

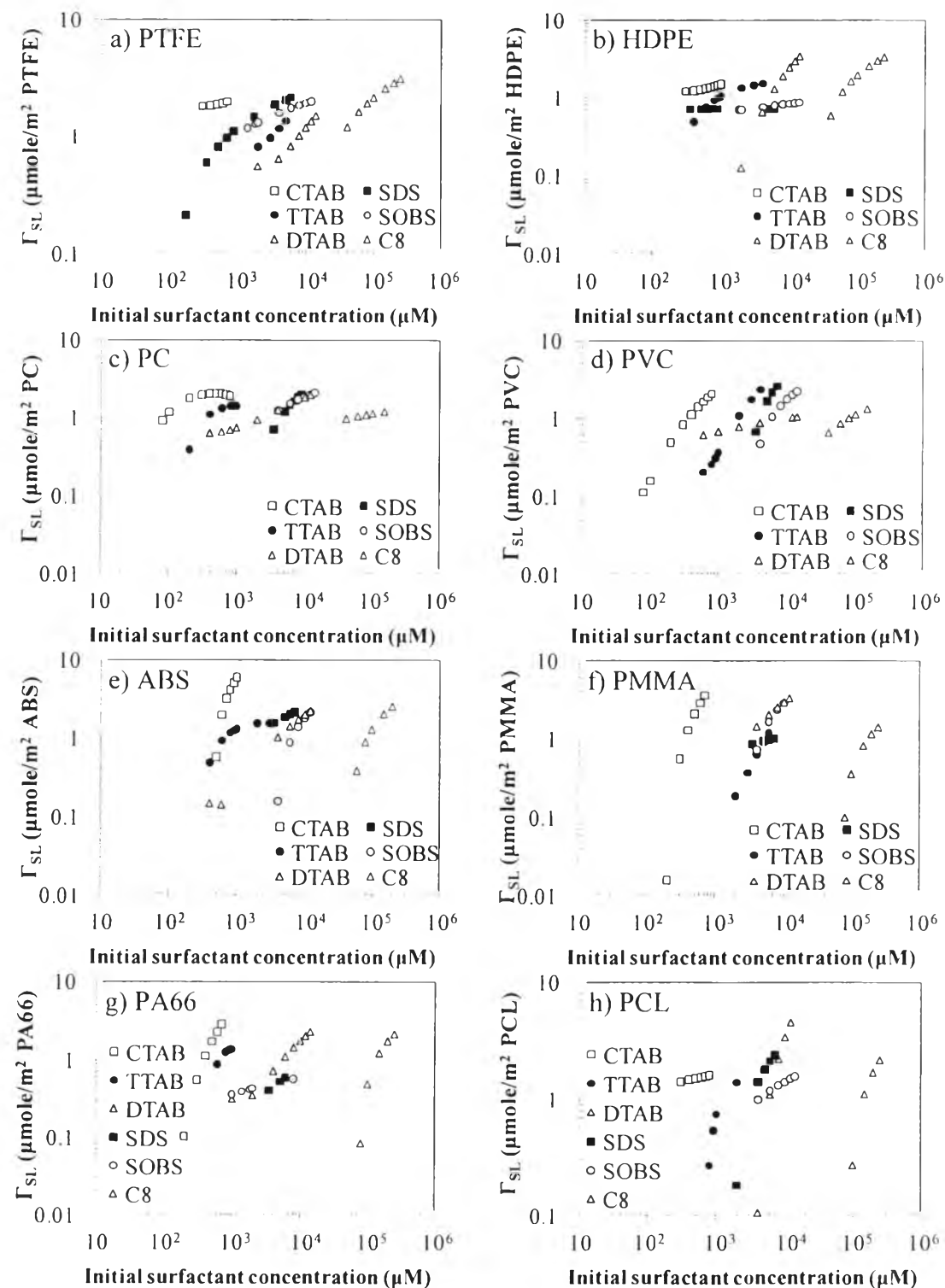


Figure 4.9 Surfactant adsorption isotherm of six surfactant types on eight polymers.

To illustrate the effect of surfactant structure, Figure 4.4g shows  $\Pi_{SL}$  as a function of surfactant adsorption for HDPE. There is less dependence of  $\Pi_{SL}$  on surfactant adsorption for the higher CMC surfactants (C8 and DTAB). However, from Table 4.3 at the CMC, the solid/liquid surface pressure varies less with surfactant structure than surfactant adsorption. For surfactants with higher plateau adsorption, there is less dependence of  $\Pi_{SL}$  on surfactant adsorption.

As polymer hydrophobicity increases, the reduction in contact angle at the CMC compared to pure water is greater, solid/liquid surface pressure is greater, and the fraction of contact angle reduction attributable to solid/liquid interfacial tension reduction increases (compared to surface tension reduction effects).

#### 4.5.7 Calculation of $\gamma^{\circ}_{SL}$ and $\gamma_{SV}$

From Equation (4.12),  $\Pi_{SL}/\gamma_{LV}$  vs.  $1/\gamma_{LV}$  should have a slope of  $\gamma^{\circ}_{SL}$  as shown in Figure 4.6 and Table 4.4. All systems show good linearity in Figure 4.6.  $\gamma^{\circ}_{SL}$  should be independent of surfactant type and the slopes in Fig. 6 are similar with the variance of  $\gamma^{\circ}_{SL}$  (from Table 4.5 and shown in Figure 4.8) averaged over all eight polymers is  $\pm 26.0\%$ . From Figure 4.8 and Tables 4.4 and 4.5, the value of  $\gamma^{\circ}_{SL}$  increases with increasing water contact angle, which is expected since the water is increasingly incompatible with more hydrophobic polymers. The value of  $\gamma_{SV}$  (Table 4.4) should be also independent of surfactant structure. The values of  $\gamma_{SV}$  and the variances for the eight polymers are shown in Table 4.5 and Figure 4.8 averaged over the six surfactants studied. The average variance ( $\pm 19.6\%$ ) is similar to that for  $\gamma^{\circ}_{SL}$  ( $\pm 26.0\%$ ). Berg [20] summarizes models for  $\gamma_{SV}$ , but these are generally useful when dispersion forces dominate and for solids in vacuum.

From Figure 4.8, the value of  $\gamma_{SV}$  was found to be fairly invariant with polymer type over a wide range of polymers ( $\gamma_{SV} = 33.3 \pm 6.5$  mN/m) at 30°C. This consistency indicates that the surface energy of a polymer in vacuum is substantially different than one saturated with water since certainly the surface energy in vacuum (or dry air) will be depend strongly on the polymer. If this value of  $\gamma_{SV}$  is a universal constant for polymer surfaces saturated with water, evaluation of the modification of surface energies at the solid/liquid interface due to surfactant adsorption could be

enhanced via calculation of  $\gamma_{SL}$  from easily measured contact angles and surface tensions of surfactant solutions. A wider range of surfactants, added electrolyte levels, temperatures, etc. would need to be evaluated to give a fair evaluation of the universality of this use of the Young's equation.

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