

The Effect of Roughness on the Values of Contact Angles of Binary Systems Measured at Atmospheric Pressure and Ambient Temperature on Poly(tetrafluoroethylene) Surfaces

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Synopsis

Contact angles are reported for the systems ethanol-water, *n*-propanol-water, and benzene-cyclohexane measured at atmospheric pressure and 25.0°C, in equilibrium with their vapors, on poly(tetrafluoroethylene) surfaces of known roughness. Comparison of the data with those reported by other workers has shown that the discordancy in values can be attributed solely to the various preparation techniques producing surfaces of differing roughnesses.

INTRODUCTION

Much of the theory of wetting suggests an idealized situation where the liquid rests on a uniform, plane, nondeformable solid. For such a system there is a unique equilibrium contact angle. However, in practice such ideal circumstances rarely present themselves, and surface roughness affects the value of the contact angle. The first important contribution to the field was made by Wenzel,¹ who noted that real solids have rough surfaces on the submacroscopic scale. Quantitatively, the average roughness of the surface could be measured by r , the ratio of the real to the apparent surface area:

$$r = A/A'. \quad (1)$$

Gibbs² demonstrated, for a liquid resting on a solid surface, that the drop takes the shape which minimizes the free energy of the system, and this demands that

$$\gamma_{LV}A_{LV} + \gamma_{SV}A_{SV} + \gamma_{SL}A_{SL} \quad (2)$$

is a minimum. If A is replaced by rA' in eq. (2), Wenzel's equation

$$\cos \bar{\theta} = r \cos \theta \quad (3)$$

follows, where $\bar{\theta}$ is the observed angle on a surface having an intrinsic value θ . Wenzel also presented data to support his equation but did not include

TABLE I
Contact Angles of Ethanol-Water Mixtures on a
Poly(tetrafluoroethylene) Surface at 25°C

Dann ⁷		Vergera et al. ⁶		Zisman ⁵	
γ_{LV} , dynes/cm	Contact angle, degrees	γ_{LV} , dynes/cm	Contact angle, degrees	γ_{LV} , dynes/cm	Contact angle, degrees
72.2	112	72.2	108	72.2	114
51.3	107	36.0	83	64.0	111
36.1	83	30.0	70	57.0	107
30.0	69	28.0	66	49.0	101
28.0	55	26.0	60	44.0	96
27.2	53	25.0	56	37.5	86
25.6	51	24.0	50	29.0	67
24.0	45	23.0	48	22.0	41
		22.0	43		

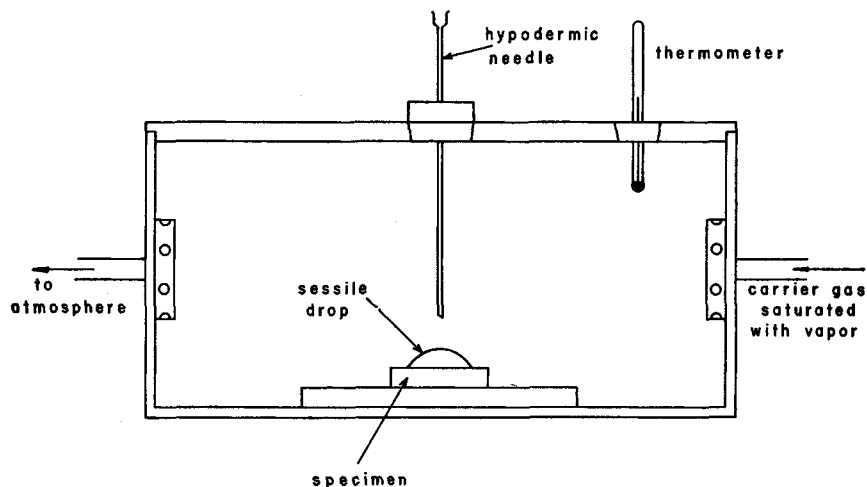


Fig. 1. Equilibrium cell.

a mathematical derivation. This equation has been derived thermodynamically by Good³ and Shuttleworth and Bailey.⁴ Equation (3) suggests that the effect of roughness will be to increase the value of the contact angle with increasing roughness, if the intrinsic angle (on the smooth surface) is greater than 90°. For an angle less than 90°, the effect of roughness is to decrease the resultant contact angle.

In a study of the contact angles of binary liquid mixtures on a low-energy surface, conflicting data have been reported which can be attributed to the effect of roughness. Considering the ethanol-water system, Zisman,⁵ Vergara et al.,⁶ and Dann⁷ have reported contact angles on poly(tetrafluoroethylene) surfaces. Their results are given in Table I. No quantitative

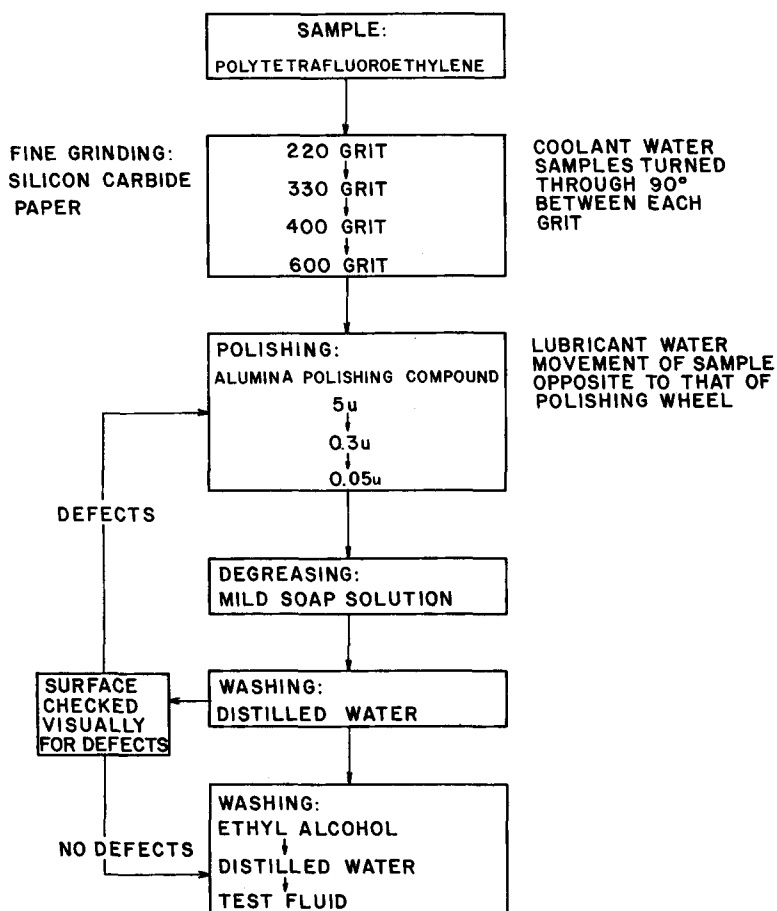


Fig. 2. Surface preparation procedure.

assessment of roughness was reported by any of the workers, but the preparation allowed one to infer the relative smoothness of the specimens involved. A description is now given of experiments repeating the investigations carried out by the above-mentioned workers, together with additional data for the system *n*-propanol-water and benzene-cyclohexane for known surface roughness, care being taken to eliminate the extraneous effects of contamination.

APPARATUS AND PROCEDURE

Contact angles of the binary liquids *n*-propanol-water, ethanol-water, and benzene-cyclohexane were measured in equilibrium with their vapors at atmospheric pressure and 25°C using the equipment shown in Figure 1. The apparatus consisted essentially of an observation cell (3 in. × 3 in. × 6 in.) containing two baffles, to ensure good mixing of the vapors in the cell,

and a removable top, fitted with a thermometer pocket and a septum-covered opening to allow the introduction of a liquid sample using a 10-ml syringe fitted with a stainless-steel hypodermic needle. Four 250-ml flasks were maintained in a constant-temperature bath at $25^\circ \pm 0.1^\circ\text{C}$. The poly(tetrafluoroethylene) surfaces were prepared using the procedure outlined in Figure 2, different surface roughnesses being obtained by following the grinding and polishing procedure to its limit and by terminating the procedure for one of the samples at the 600-grit stage. The surface roughnesses of the specimens (0.44 microinch and 19.64 microinches) were measured as center-line average values using a Talysurf meter and were an average of approximately 15 determinations.

Before each run, the solid specimen was prepared as described, then submerged in the test solution for approximately 30 min before being introduced into the observation cell, and then carefully aligned. Argon of 99.999% purity, used as carrier gas, was contacted with solutions of the same composition as the test liquid in the four cells before entering the observation cell and was finally passed via a vent to the atmosphere. A liquid sample was then introduced onto the poly(tetrafluoroethylene) surface, care being taken to ensure that the drop was formed slowly until the equilibrium drop height had been achieved and that withdrawal of the needle did not disturb the drop. The contact angle was measured using a telescope fitted with a goniometer eyepiece. The reported values, an average of at least five readings, have standard deviations in the range $0.5\text{--}1.0^\circ$. The composition of the liquid was determined using an Abbe refractometer maintained at $25.0 \pm 0.1^\circ\text{C}$.

RESULTS

The values of contact angle obtained by the authors for the ethanol-water system are compared with those of other workers in Figure 3. It would appear that the results of Vergara et al.⁶ indicate a very smooth sur-

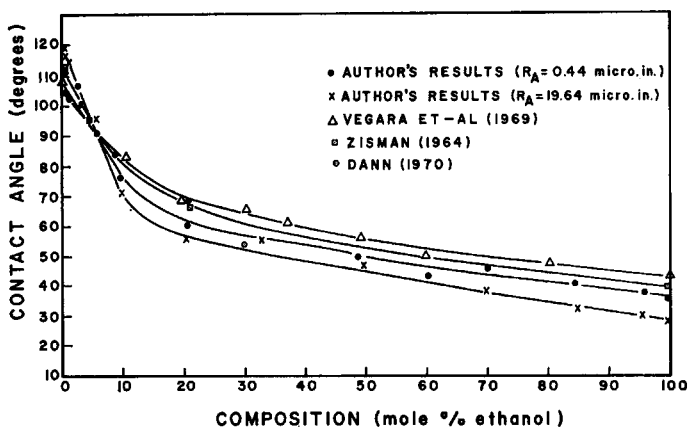


Fig. 3. Comparison of contact angle vs. concentration data for the system ethanol-water.

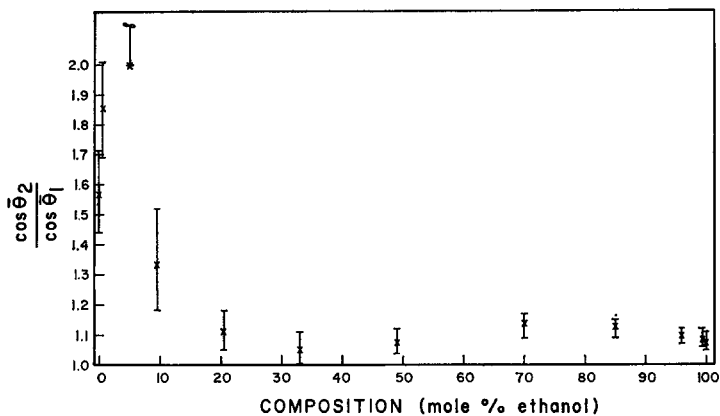


Fig. 4. $\cos \bar{\theta}_2 / \cos \bar{\theta}_1$ vs. concentration for the system ethanol-water.

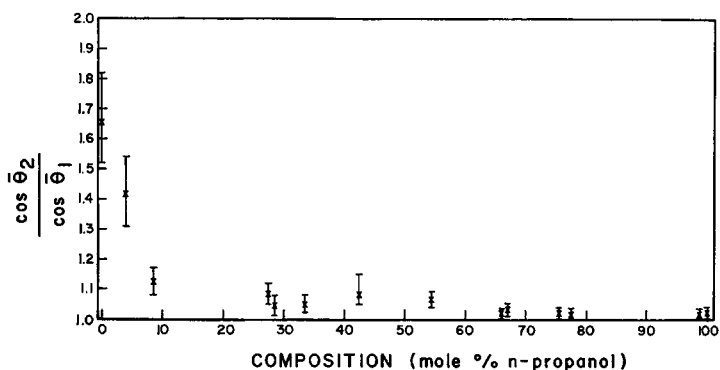


Fig. 5. $\cos \bar{\theta}_2 / \cos \bar{\theta}_1$ vs. concentration for the system *n*-propanol-water.

face; and, in fact, in their experimental procedure it is pointed out that the surface was obtained by melting the solid with subsequent cooling. Two poly(tetrafluoroethylene) surfaces have been studied with surface roughnesses of 19.64 microinches and 0.44 microinch. Denoting the smoother surface by the subscript 1 and the rougher by 2, we have, from eq. (3),

$$\cos \bar{\theta}_1 = r_1 \cos \theta \quad (4)$$

and

$$\cos \bar{\theta}_2 = r_2 \cos \theta. \quad (5)$$

Thus,

$$\frac{\cos \bar{\theta}_2}{\cos \bar{\theta}_1} = \frac{r_2}{r_1} = \text{constant}. \quad (6)$$

Figures 4-6 show plots of $\cos \bar{\theta}_2 / \cos \bar{\theta}_1$ versus composition for the three binary systems. The range of values of the ratio has also been plotted for a variation of $\pm 1^\circ$ on the experimental values of $\bar{\theta}$.

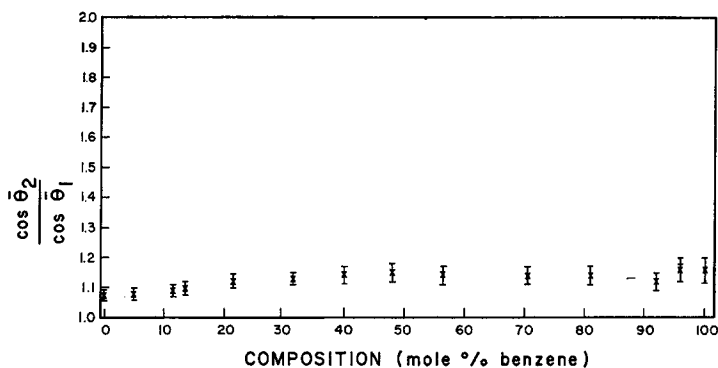


Fig. 6. $\cos \bar{\theta}_2 / \cos \bar{\theta}_1$ vs. concentration for the system benzene-cyclohexane.

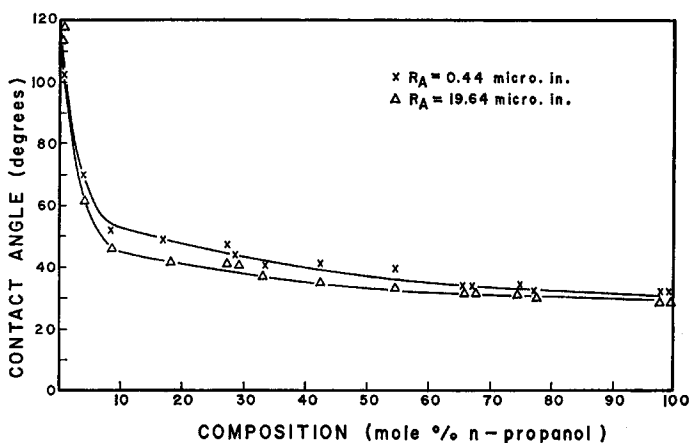


Fig. 7. Contact angle vs. concentration for the system *n*-propanol-water at 25.0°C on poly(tetrafluoroethylene) surfaces.

It can be seen that the ratio $\cos \bar{\theta}_2 / \cos \bar{\theta}_1$ is a constant for the benzene-cyclohexane system over the entire concentration range but only over the range 10–100% for the ethanol-water system and 5–100% for the propanol-water system. The regions where the ratio deviates from the constant corresponds to contact angles in the vicinity of 90°. As θ approaches 90°, the ratio $\cos \bar{\theta}_2 / \cos \bar{\theta}_1$ becomes sensitive to small variations in $\bar{\theta}$, a variation of $\pm 1^\circ$ resulting in a very large change in $\cos \bar{\theta}_2 / \cos \bar{\theta}_1$. For example, at 5.5% ethanol, the ratio changes from 1.9 to infinity for a $\pm 1^\circ$ change in $\bar{\theta}$. Thus, neglecting the regions 0–5% for the *n*-propanol-water system and 0–10% for the ethanol-water system gives a value for the ratio r_2/r_1 of 1.09 ± 0.08 for these three systems.

The relationship between contact angles and roughness for angles above and below 90°, formulated by Wenzel¹ and described above, is demonstrated in Figures 3, 7 and 8. Equation (3) also suggests that at 90° all experimental lines presented in Figure 3 should coincide. This is clearly evident and

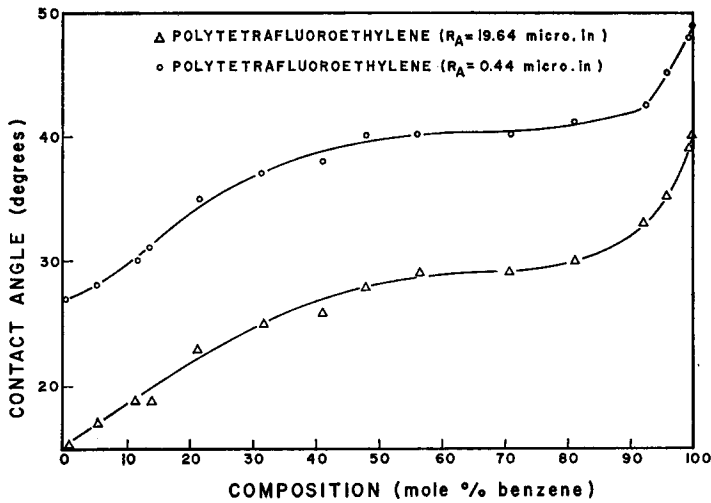


Fig. 8. Contact angle vs. concentration for the system benzene-cyclohexane at 25.0°C on poly(tetrafluoroethylene) surfaces.

shows that the variation in contact angles presented in the literature for the ethanol-water system is attributable to this roughness factor. Data for the *n*-propanol-water system (Fig. 7) support this conclusion.

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