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An Algorithm for Estimating Contact Angle

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Abstract

Contact angles of a variety of hydrophobic and hydrophilic liquids on polymer surfaces are correlated with surface tension and the interfacial free energy between solid and liquid. It is assumed that intimate molecular contact between and the polymer surface is made. The interfacial free energy is represented by the residual infinite dilution activity coefficient of the liquid monomer as computed by the UNIFAC equation. Estimated contact angles are within an average of 7° of measured values.

Zisman and coworkers (1) found a nearly linear dependence of contact angle with liquid surface tension when a homologous series of liquids were placed on a given polymer surface. The intercept of the linear plot with $\text{Cos } \theta = 1$ has been referred to as the Zisman critical surface tension σ_c . Zisman noted that the value of the critical surface tension was dependent on the specific surface chemistry of the solid surface. van Oss, Chaudhury, and Good (2) recently separated surface tension into components based on London dispersion forces and Lewis acid-base interactions. While valuable for gaining insight into the origins of contact angle, the approach does not provide for general contact angle estimation.

The relationship between contact angle and basic physico-chemical properties can be understood in terms of surface thermodynamics. Recalling the Young equation

$$\sigma_{sv} - \sigma_{sl} = \sigma_{lv} \text{Cos } \theta \quad (1)$$

and noting that at $\text{Cos } \theta = 1$, the liquid surface tension σ_{lv} is just the Zisman critical surface tension, σ_c , it follows that

$$\sigma_c = \sigma_{sv} - \sigma_{sl} \quad (2)$$

Recalling further that the work of adhesion W_a is related to interfacial tensions via the following relationship

$$W_a = \sigma_{sv} + \sigma_{lv} - \sigma_{sl} \quad (3)$$

Thus,

$$W_a = \sigma_c + \sigma_{lv} \quad (4)$$

or

$$\sigma_c = W_a - \sigma_{lv} \quad (5)$$

The empirical Zisman equation may be written as

$$\cos \theta = 1 - \beta(\sigma_{lv} - \sigma_c) \quad (6)$$

Recalling the relationship between W_a and σ_c , the Zisman equation can be rearranged to

$$\cos \theta = 1 + \beta W_a - 2 \beta \sigma_{lv} \quad (7)$$

Equation 7 expresses contact angle in terms of two fundamental parameters: the liquid vapor surface tension, and the adhesion energy. In order to evaluate eq. 7, it is necessary to estimate W_a .

We have chosen the UNIFAC residual activity coefficient for the solute (in this case, the liquid) at infinite dilution in the monomer of the solid polymeric material as a measure of the interaction between the liquid and the polymeric surface. UNIFAC is a group contribution method used principally in the chemical engineering community (3). It represents activity coefficient as the product of a combinatorial component that reflects differences in size and shape between the components in the mixture, and a residual contribution that measures heat effects. Since the surface is approximated by a monomer, the combinatorial component is unnecessary. The residual component of the activity coefficient was calculated using the interaction parameters listed by Hansen et al. (4).

Contact angle and surface tension data were taken from the literature; the former are listed in Table 1. The surfaces were generally hydrophobic (ranging from paraffin to polytetrafluoroethylene), and the liquids covered a wide range of hydrophobicity from water to hexadecane. Regression of contact angle against $\ln \gamma_r$ and surface tension (σ) led to the equation

$$\cos \theta = 1.42 - 0.102 \ln \gamma_r - 0.0115 \sigma \quad (n=54, r=0.95) \quad (8)$$

which is of the form of eq 7. The relationship is illustrated in Figure 1. The sign of the $\ln \gamma_r$ coefficient is correct, since $\ln \gamma_r$ increases with increasing solute-surface incompatibility, which, in turn results in larger contact angles. Not surprisingly, $\ln \gamma_r$ and σ are weakly correlated at $r=0.43$.

In summary, equation 8 appears to be able to handle a variety of liquids and surfaces. Estimates are within 7° of measured values which compares quite well with the precision reported for measurements made across several laboratories.

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Table 1. Contact angles and residual activity coefficients of some liquids

	$\ln \gamma_r$	contact angle
polyethylene (20C) (ref.6)		
diiodomethane	2.44	52
dibromomethane	2.17	27.5
1,2-dibromoethane	1.93	47
pyridine	1.18	32
N,N-dimethylformamide	4.15	41
dimethylsulfoxide	4.75	60
water	7.37	107
polyethylene (20C) (ref.7)		
water	7.48	96.1
bromoform	3.65	36.7
diiodomethane	2.48	52.8
1,1,2,2-tetrabromoethane	4.77	50.9
1,2,3-tribromopropane	3.09	43.1
iodobenzene	1.48	33.1
1-bromonaphthalene	1.71	41.1
1-chloronaphthalene	0.67	36.3
bromobenzene	1.55	21.8
chlorobenzene	0.51	10
2-nitrotoluene	2.46	39.2
nitromethane	4.00	55
nitrobenzene	2.20	47.3
3-nitrotoluene	2.46	40.8
carbon disulfide	0.54	0

Table 1. (cont.) Contact angles and residual activity coefficients of some liquids		
	$\ln \gamma_r$	contact angle
polyethylene terephthalate (20C, ref. 7)		
water	2.16	76.5
bromoform	0.29	21.4
diiodomethane	1.14	40.8
1,1,2,2-tetrabromoethane	0.35	37.8
1,2,3-tribromopropane	0.14	26.1
iodobenzene	0.46	19.2
1-bromonaphthalene	0.21	22.7
1-chloronaphthalene	0.10	18.5
bromobenzene	0.16	14.8
nitromethane	0.14	30
polytetrafluoroethylene (ref. 5)		
hexadecane	4.56	46
tetradecane	4.03	44
n-dodecane	3.49	42
undecane	3.23	39
decane	2.97	35
nonane	2.70	32
n-octane	2.43	26
n-heptane	2.17	21
n-hexane	1.90	12
n-pentane	1.33	0
benzene	1.33	46
t-butyl/naphthalene	2.78	65

Table 1. (cont.) Contact angles and residual activity coefficients of some liquids		
	ln γ_r	contact angle
paraffin (25C, ref. 8)		
water	7.37	108
propanol	3.05	36
α -bromonaphthalene	1.68	42
polyethylene (25C, ref. 8)		
water	7.37	109
α -bromonaphthalene	1.68	15
polystyrene (25C, ref. 8)		
water	5.45	84
α -bromonaphthalene	0.21	10
polymethylmethacrylate (25C, ref. 8)		
water	2.18	79
propanol	1.02	13
α -bromonaphthalene	0	14

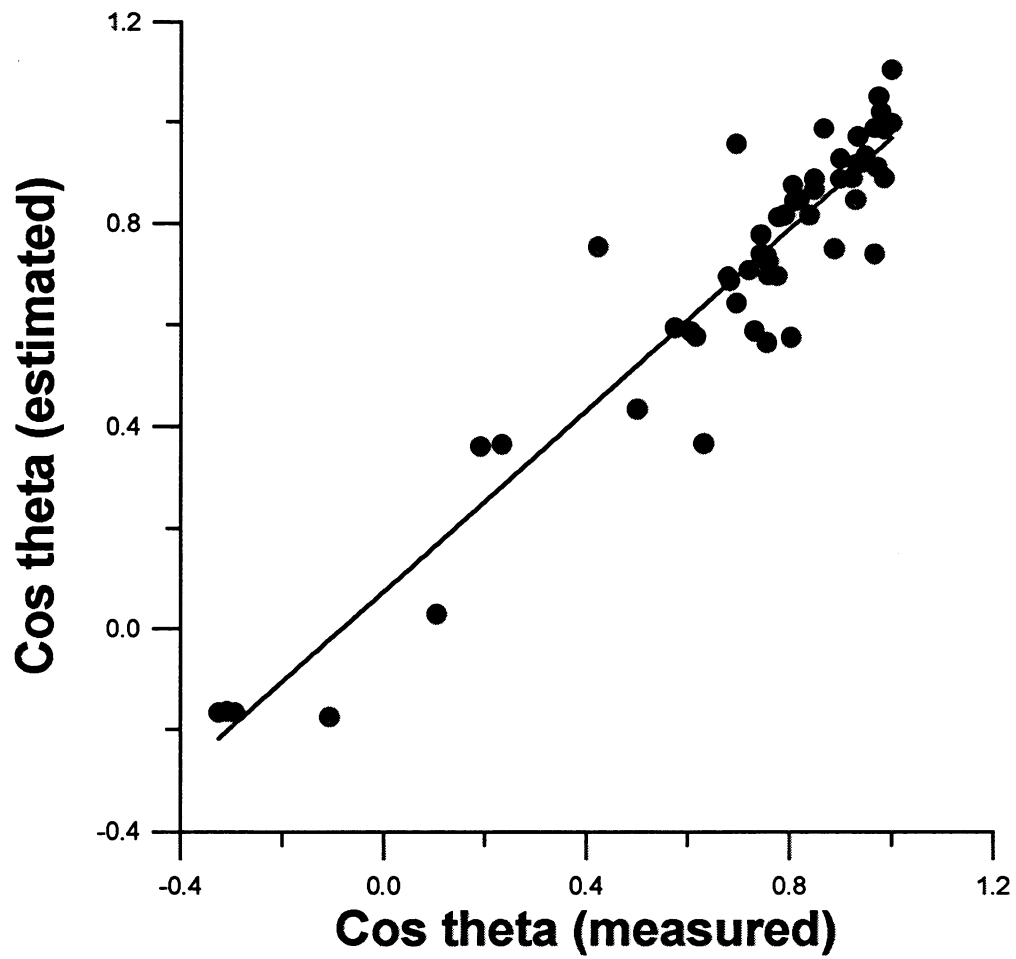


Figure 1: Comparison of contact angles estimated by equation (8) to measured values.

