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# Specific Interactions and Contact Angle Measurements on Polymer Solids

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The present work examined the susceptibility of contact angle data to specific interactions taking place between solids and contacting liquids. The polymers involved were polystyrene, polyvinyl chloride and polyethylene, representing respectively basic, acidic and neutral substrates. Contacting fluids also were chosen to represent acid and base interaction categories.

Significant time-dependent changes in contact angles were observed when acid/base pairs were involved in the experimental sequence. In specific cases it was possible to identify initial (zero contact time) contact angles, as well as equilibrium values, attained after prolonged contact times. Local solvation, or plasticization, of the polymer by the wetting fluid was postulated as the operative mechanism. The differences between initial and final values of the contact angles were correlated with parameters of specific interaction, calculated from the acceptor/donor numbers for the pertinent materials as measured by inverse gas chromatography. In contrast, when acid/acid or base/base combinations of polymer and wetting fluid were studied, equilibrium values of the contact angle were established rapidly. Since accurate information on acid/base properties of polymers and wetting fluids is not always available, it seems prudent to record contact angles as a function of contact time, and by extrapolation to determine the initial (true) value for further use in surface characterizations of polymers.

**KEY WORDS:** Contact angle; acid/base concepts; time dependence; polystyrene; polyvinyl chloride; polyethylene.

## INTRODUCTION

Among the most basic concepts in the physical chemistry of solid surfaces is the relationship between the surface energy of the solid and the contact angle subtained by a drop of fluid in equilibrium with the surface.<sup>1,2</sup> A knowledge of surface energies and of the wetting characteristics of solids is vital to progress in many fields of endeavor, including the formulation of strong adhesive joints, of material composites, and the evolution of biocompatible materials. It is not surprising therefore that the determination of contact angles has been the subject of much activity. In the case of low energy surfaces, typical of polymeric materials, the contact angle route to surface energies is particularly convenient. The empirical method of Zisman<sup>3,4</sup> serves as an example of that convenience. The apparent simplicity of contact angle determinations, however, is deceptive. Many reviews, for example that of Kinloch,<sup>5</sup> have discussed the factors influencing contact angle measurements. Alternative

routes to polymer surface energy data have been proposed, inverse gas chromatography (IGC), currently enjoying some favor.<sup>6,7,8</sup> Nevertheless, the contact angle datum remains important to the characterization of surface states in polymers, and as such merits efforts to enhance the accuracy of its determination. The present work is intended to contribute to these efforts.

Attention is directed specifically to the potential effect on contact angle and surface energy data of interactions between the polymer solid and the contacting fluid. Clearly, meaningful measurements of surface properties demand that thermodynamic equilibria exist between the contacting materials. Thus, the use of liquids which act as solvents for the polymer would lead to swelling and liquid absorption, compromising the experiment's validity. Another factor which may influence contact angle measurements is the capability of certain polymer molecules to adopt different orientational states at surfaces and at interfaces. This capability has been the subject of recent studies.<sup>9,10,11</sup> They have shown that restructuring at polymer surfaces is demanded by the thermodynamic drives to minimize surface free energies or interfacial surface energies, depending on the medium in contact with the polymer surface. Restructuring rates and mechanisms appear to depend on the medium's non-dispersive surface energy.<sup>12</sup> Contemporary views suggest<sup>12,13,14</sup> that acid-base interactions account for this portion of the surface energy, so that in turn, acid-base interactions between a polymer to be studied and fluids placed on its surface may affect contact angle measurements. The suggestion was tested experimentally, with results reported in this paper.

## EXPERIMENTAL SECTION

### Materials

Apart from calibration experiments on degreased and vacuum-dried glass slides, contact angle measurements were performed on three polymer surfaces. These were a linear low density polyethylene (LLDPE), polyvinyl chloride (PVC) and polystyrene (PS). The LLDPE was a hexene copolymer, with a melt index of 1.28 and  $M_w = 1.17 \times 10^5$ . The polymer contained no additives. The PVC, obtained from Union Carbide Corp., had a viscosity average molecular weight of  $6.6 \times 10^4$ . The PS, supplied by Amoco Corp., had a viscosity average molecular weight of  $8.7 \times 10^4$ . The PVC and PS again were additive-free. The polymers were chosen as representative of neutral, acid and base categories. The acid-base interaction potentials of their surfaces were evaluated from IGC measurements, using procedures established by Papirer and Schultz,<sup>7,15</sup> and modified by ourselves.<sup>10</sup> In IGC experiments the polymers constitute the stationary phase, while mobile phases were vapors selected on the basis of Gutmann's tabulation<sup>16</sup> of acceptor and donor numbers (AN and DN) for organic liquids. Chloroform (CHL) was the reference acidic probe, diethyl ether (DEE) the base. Their AN and DN indexes, at ambient temperatures, are recorded in Table I along with those for the polymer substrates. Clearly, LLDPE with near zero values of AN and DN may be considered to act as a solid with only dispersion-

TABLE I  
Interaction characteristics of materials

Material	AN	DN	$\gamma_s^d$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_s^{\text{nd}}$
PE <sup>a</sup>	0	0	31.0	0
PVC <sup>a</sup>	8.1	2.6	40.3	1.5
PS <sup>a</sup>	1.7	4.3	38.0	2.5
CHL <sup>b</sup>	23.1	0	—	—
DEE <sup>b</sup>	3.9	19.2	—	—

<sup>a</sup>Determined from retention volumes, IGC procedures.

<sup>b</sup>CHL is chloroform, DEE is diethyl ether. Data taken from Gutmann (ref. 16).

force surface characteristics. The PVC, with an/DN = 3.1 is an acid, while PS, with AN/DN = 0.39 is considered to be basic.

Fluids chosen for contact angle measurements also reflected on acid-base concepts. They are identified in Table II which reports their AN and DN numbers, as given by Gutmann.<sup>16</sup> Water (W), formamide (FM) and benzene (B) display predominantly acid tendencies, pyridine (P) and tetrahydro furan (THF) are bases but with significant secondary capabilities for interacting as acidic electron acceptors. A wide range of acid-base interactions between polymer/liquid pairs is represented by this selection of materials. Efforts to quantify the pair interactions will be discussed later in the paper.

### Contact Angle Measurements

Static contact angle data were collected using the Rame-Hart goniometer. All evaluations were at 30°C. Polymer samples were compression molded at 190°C using Teflon plates from which the specimens were separated readily following quenching in cold, running water. Molded samples were dried thoroughly under vacuum at 40°C. The samples were then placed on a modified stage of the goniometer, designed along lines similar to those reported earlier by Carre and Schreiber.<sup>17</sup> The modification involves shaping a glass dome to fit the goniometer stage, thus housing the polymer specimen in an enclosed dead space. An open vial of the contacting fluid to be used was placed in the enclosure, so that the dead space was saturated with respect to the contact liquid. Calibrated Hamilton syringes containing the liquids at thermal equilibrium with the polymer, were used to dispense 10  $\mu\text{l}$  droplets onto

TABLE II  
Interaction and surface energy data for wetting fluids

Fluid	AN	DN	$\gamma_1^d$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_1^{\text{nd}}$
Water (W)	54.8	18.0	22	50.2
Formamide (FM)	39.8	24.0	32.3	26.0
Benzene (B)	8.2	0.1	29	0.
Pyridine (P)	14.2	33.1	37.2	0.8
Tetra hydrofuran (THF)	8.0	22.5	34.6	14.0

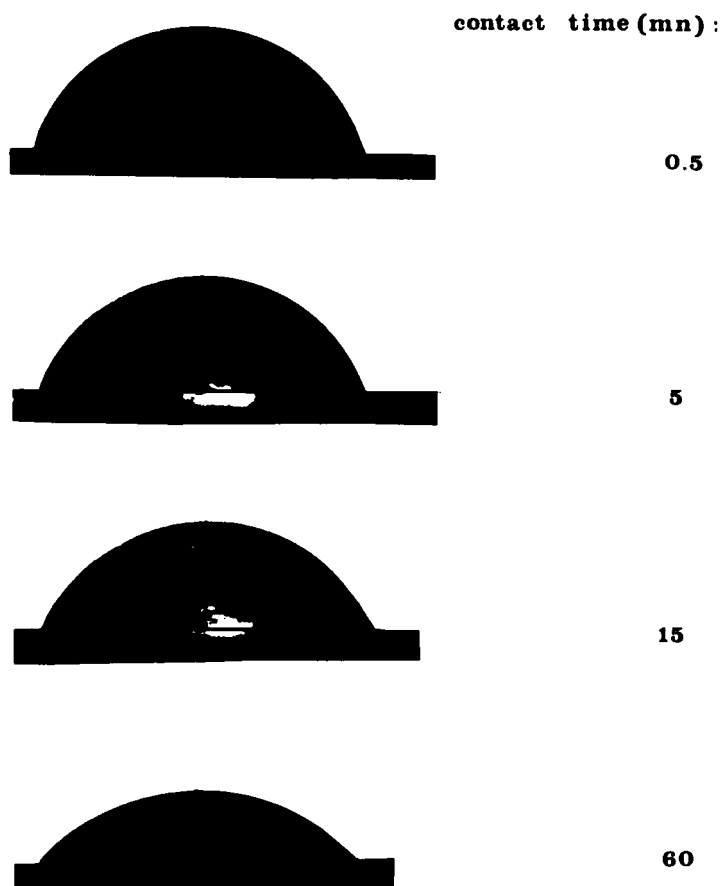


FIGURE 1 Evolution of contact angle of THF on PVC surface.

the polymer surfaces. The droplets were allowed to remain in contact with the solids for up to 90 min. During this period their images were recorded and analysed using the Oculus 300 image captor. A typical example of the results obtained is shown in Figure 1, which traces the changes in contact angle and droplet volume for THF on PVC. Contact times are recorded in the Figure. Observations such as those shown were not due to liquid evaporation, since calibration experiments with glass slide substrates showed invariant droplet sizes and contact angles. Changes in these parameters during the observation period on polymer substrates therefore could be attributed to polymer-fluid interactions.

## RESULTS AND DISCUSSION

The principal findings of this research are to be seen in the series of contact angle vs. contact time plots presented as Figures 2, 3 and 4. In Fig. 2 are shown the results

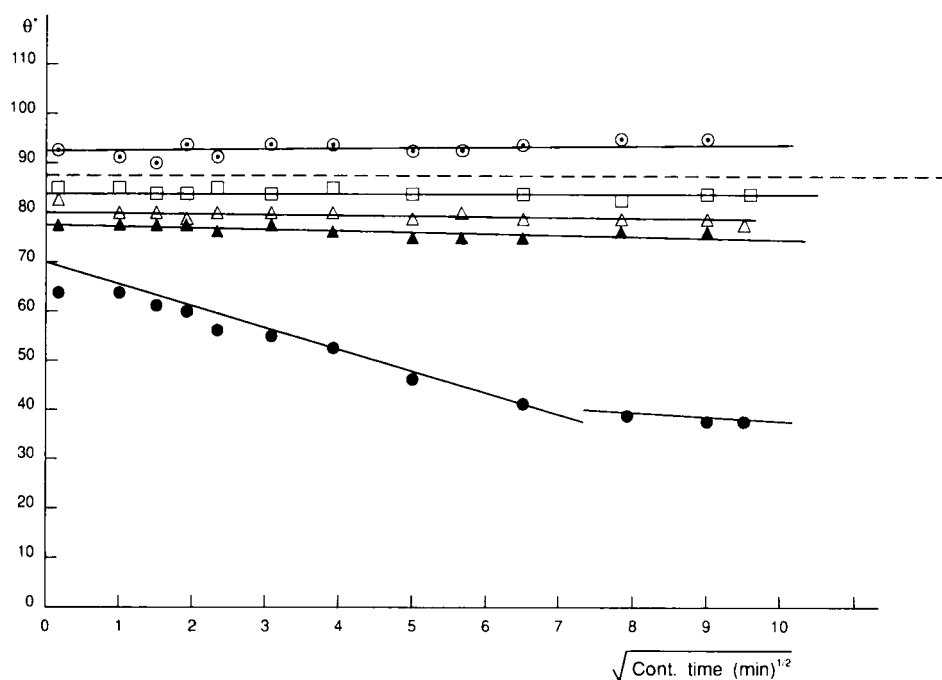


FIGURE 2 Contact angle vs. contact time for wetting fluids on PE surface. Dashed line is for water on glass.  $\circ$  W;  $\square$  FM;  $\bullet$  B;  $\blacktriangle$  THF;  $\triangle$  P.

for LLDPE surfaces. Expectedly, the polymer is hydrophobic, as indicated by the high ( $94^\circ$ ) contact angle for W. Contact angles for other wetting liquids are generally lower, but with one exception they remain invariant over the period of observation. In this regard the behavior parallels that of wetting fluid on glass. Wetting equilibria are established very rapidly for W, FM, P and THF on LLDPE, and the pertinent contact angles may be used with confidence in computations of surface energy parameters. The exception in this case is benzene, where the contact angle diminishes from a first measurement near  $62^\circ$  to about  $40^\circ$  at the cessation of observation. Benzene, of course, is a mild solvent for olefinic solids, more particularly for amorphous, low molecular weight species. LLDPE, like other members of the polyethylene group, is apt to form weak boundary layers in the surface region, as shown by Sharpe, Schonhorn and coworkers.<sup>18,19</sup> These layers are composed precisely of moieties most susceptible to attack by B. Following a brief "induction" period, seen in Fig. 2, the liquid solvates the amorphous layer and may begin diffusing into the bulk substrate. Both the contact angle and the droplet volume remaining at the surface diminish. Some loss of visible droplet volume also was observed for other contacting fluids without, however, any change in the contact angles, again as shown in Fig. 2. This may be due to the liquids penetrating the loosely structured boundary layer. Only in the case of B, however, is the effect driven by interaction as well as by steric factors. The good linearity of the segment between 1 and about 25 min of contact, permits an extrapolation to be made of the zero-time contact angle,  $\theta_0$ . It

is this value which would most reliably represent the wettability of non-solvated LLDPE by benzene. We will examine the effect of using non-equilibrium values of  $\theta$  on some surface performance parameters later on.

Time variations of  $\theta$  for PVC and PS are shown, respectively, in Figures 3 and 4. Here distinct patterns of behavior become evident. The acidic PVC generates nearly invariant contact angles for W, B and FM, but the variation with the basic fluids P and THF is well marked. Good linearity of segments in root contact time suggests that diffusion phenomena are involved, with apparent equilibrium values of  $\theta$  obtained following about 50 min of contact. In the case of PS, Fig. 4, the pattern is analogous, but now the invariance of  $\theta$  is associated with the basic liquids P and THF, while appreciable time dependent decreases are observed for W, FM and B. The decrease in  $\theta$  is linear in  $t^{1/2}$ , as before, and a steady-state value is attained near 70 min of contact.

Several generalizations follow from Figs. 3 and 4. First, acid-base forces seem to be responsible for the time-dependent changes in  $\theta$ . Second, at room temperatures, the variations seem to follow diffusion-controlled kinetics and third, after adequate contact time it appears possible to identify an equilibrium value of  $\theta$ . Thus, in relevant cases, the two limiting values of contact angle are obtainable. The zero-

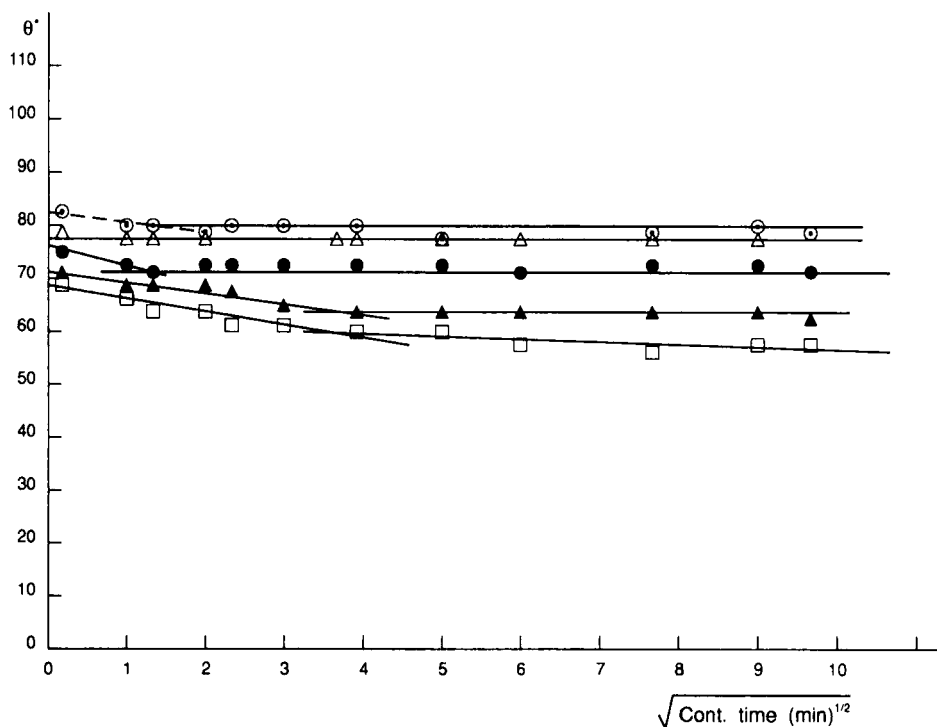


FIGURE 3 Contact angle vs. contact time for wetting fluids on PVC surface.  $\circ$  W;  $\triangle$  FM;  $\bullet$  B;  $\blacktriangle$  THF;  $\square$  P.

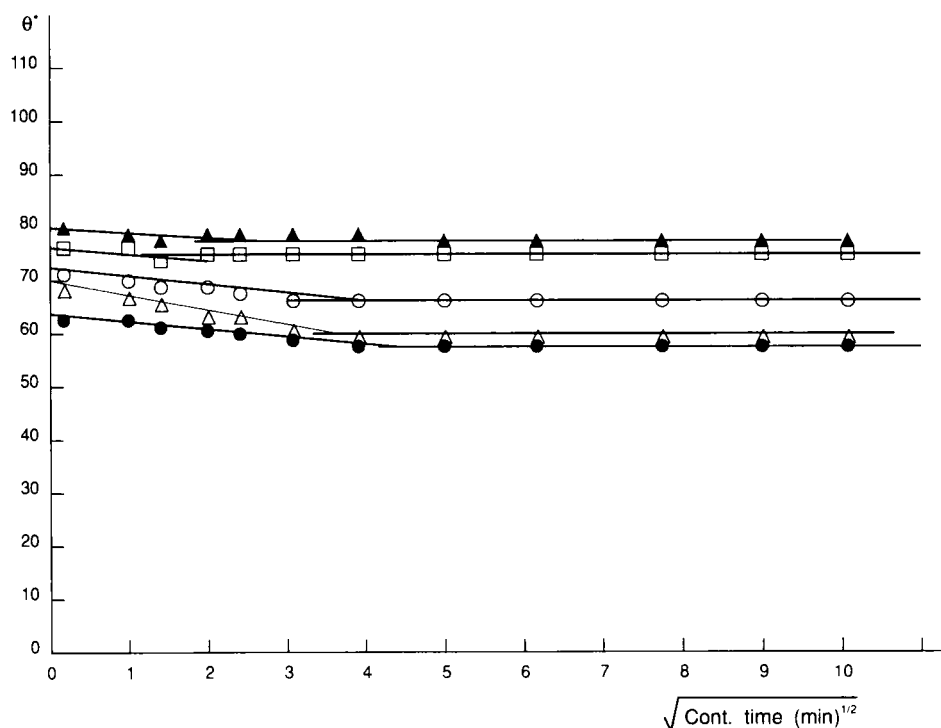


FIGURE 4 Contact angle vs. contact time for wetting fluids on PS surface. ○ W; △ FM; ● B; ▲ THF; □ P.

contact value,  $\theta_0$ , from extrapolations, characterizes the wetting properties of the polymer as conditioned by the sample preparation procedure, and the equilibrium value,  $\theta_e$ , reports on the wettability of a local region of the surface which has responded to the interaction (orienting) strength of the wetting fluid.

If it is true that acid-base forces drive variations in  $\theta$ , then correlations should be found linking the difference between the limiting values,  $\Delta\theta$ , with acid-base interaction parameters. Relevant parameters may be calculated from available AN

TABLE III  
Specific interaction parameters for polymer-liquid pairs

Parameter	Isp			Pab		
	PE	PVC	PS	PE	PVC	PS
Liquid						
W	0	24.0	20.9	0	-3.00	1.65
FM	0	24.1	19.5	0	-1.32	0.80
B	0	5.5	6.0	0	-0.62	0.31
P	0	22.4	15.3	0	1.51	-0.81
THF	0	18.1	12.0	0	1.24	-0.63



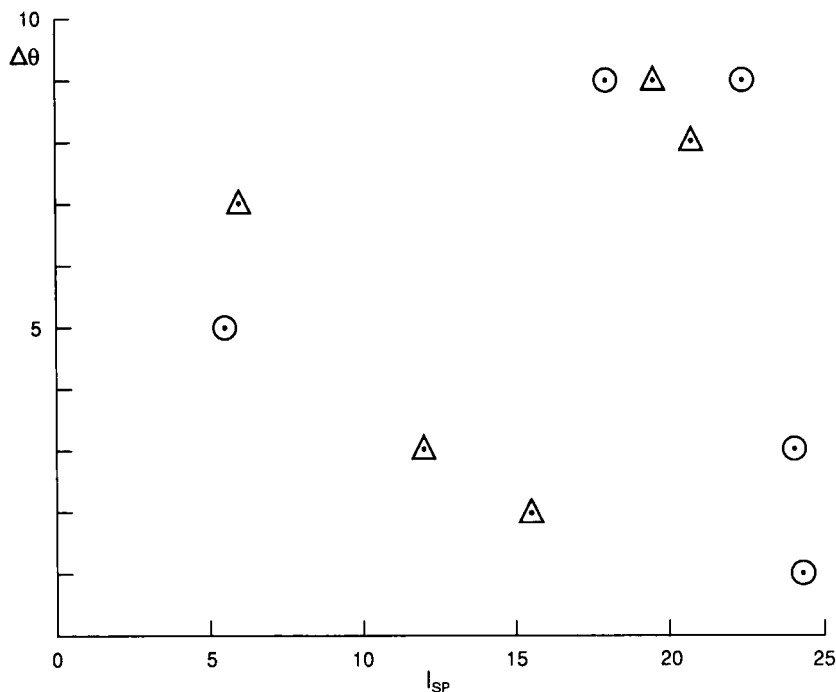


FIGURE 5 Difference between initial and equilibrium contact angles vs. acid/base interaction parameter  $I_{SP}$ .

and DN numbers, but the procedure is not clearly defined by theory. One option, suggested by Schultz,<sup>15</sup> was modified recently<sup>20</sup> to define an interaction parameter,  $I_{ab}$ , as follows:

$$I_{ab} = (AN_s \cdot DN_L)^{1/2} + (AN_L \cdot DN_s)^{1/2} \dots \quad [1]$$

Here the subscripts relate to the relevant liquid and solid components of the case. Table III presents values of the parameter for the polymer/liquid pairs of this work. In past reports,  $I_{ab}$  was found to be helpful in defining the contribution of interfaces to the performance of carbon fiber-reinforced composites,<sup>15</sup> and to the adsorption of polyesters onto a variety of pigment surfaces.<sup>20</sup> As shown in Figure 5, however, it is notably unsuccessful in correlating acid-base and contact angle variables. Alternative approaches may be suggested to quantify acid-base interactions. For example a net attractive potential  $P_{ab}$ , may be obtained from:

$$P_{ab} = (0.01)\{(AN_1 \cdot DN_2) - (AN_1 \cdot AN_2), \text{ or } -(DN_1 \cdot DN_2)\} \quad [2]$$

Here the interaction number for dominant characteristics of any pair (1,2) is reduced by the product of the dominant *like* characteristics. For example in the pair PVC/W, water is a dominant acid, and the interaction product becomes  $AN_w \cdot DN_{pvc}$ ; this quantity is reduced by the AN products of the materials, so that  $P_{ab} = -3.0$ . This value is also entered in Table III, along with those for the other polymer/liquid systems. The empiricism of  $P_{ab}$  is evident. As shown in Figure 6, however, it corre-

TABLE IV  
Comparison of  $W_a$  obtained from limiting contact angles

Polymer	PE		PVC		PS	
	$\theta_0$	$\theta_c$	$\theta_0$	$\theta_c$	$\theta_0$	$\theta_c$
For						
W	70	70	81	84	92	104
FM	64	64	70	72.0	79	88
B	40	>51	36	39	42	45
P	45	45	50	56	47	50
THF	42	43	47	57	61	73

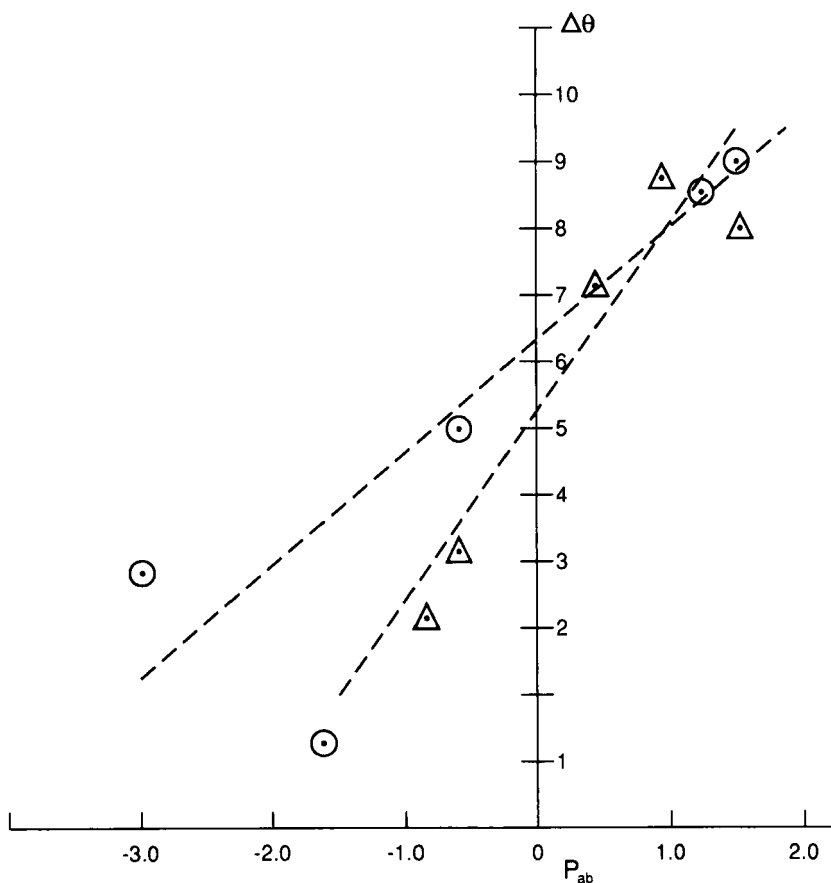


FIGURE 6 Difference between initial and equilibrium contact angles vs. acid/base interaction parameter  $P_{ab}$ .

lates with  $\Delta\theta$  in a satisfactory manner, supporting the thesis of the present argument.

Variations in contact angles of as much as  $10^\circ$  will exert an obvious influence on surface property functions obtained from the measurement. For example, the work of adhesion at a liquid/solid interface,  $W_a$ , will vary with  $\theta$ , according to:

$$W_a = \gamma_L (1 + \cos\theta) + \pi_{eq} \cdot \cdot \cdot \quad [3]$$

where  $\pi$  is the equilibrium spreading pressure. Values of  $W_a$  have been calculated using both  $\theta_0$  and  $\theta_c$ , and reported in Table IV. Results from LLDPE, where only dispersion forces are involved, are within the range of experimental uncertainties of  $\theta$  measurements. In strongly interacting systems, however, such as PVC/P, PVC/THF, PS/W and PS/FM, the range of values exceeds experimental error significantly. It then becomes essential to take the interaction forces into account, if reliable determinations of functions dependent on the contact angle are to be secured. Evidently, as a general rule, it will be advantageous routinely to measure  $\theta$  as a function of contact time, and estimate  $\theta_0$  from constructions such as those indicated in the present work.

## SUMMARY

Specific interactions between polymer solids and wetting liquids have been evaluated from data obtained by inverse gas chromatography, and their influence on static contact angle measurements has been examined. On solids, such as PE, able to interact through dispersion forces only, contact angle equilibria tend to establish rapidly provided non-solvent fluids are used in the measurements. However, acid-base coupling between solids and fluids, exemplified for PVC and PS substrates, can lead to appreciable time-dependent variations in the contact angle, with significant consequences on parameters calculated from the contact angle datum. In such cases contact angles may be monitored as a function of contact time, with extrapolations to zero time of contact yielding a more reliable contact angle value.

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