A Research Note

The Effect of Drop Volume on Contact Angle

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ABSTRACT

The effect of drop volume on the equilibrium contact angle, used in evaluation of food contact surface properties, was measured for liquids exhibiting both polar and nonpolar character on six different materials. Drop volumes used ranged from 2 to 40 μl. Contact angles were observed to increase with increasing drop volume in a range below some limiting value, identified as the critical drop volume (CDV). The CDV varied among materials and is explained with reference to surface energetic heterogeneities exhibited by each type of solid surface.

A great deal of attention has been directed toward application of contact angle methods for evaluation of solid surface properties related to surface energy and cleanliness. Over the past decade, researchers associated with the food industry have been particularly interested in application of such methodology to contribute to their understanding of problems including fouling and cleaning of heat exchange equipment as well as packaging material selection, preparation, and sterilization (4,7,10). Additionally, sessile drop techniques and associated equipment are currently used for quality control at plants for the manufacture of food packaging, for example, where polymeric coatings are applied to paper. Still, attempts to compare contact angle results from different laboratories are largely unsuccessful, partially due to measurement under different experimental conditions and with different procedures. The present study was performed in response to a currently popular question, brought up at national meetings and regional sanitation workshops alike, relating to what size drop should be analyzed for a given solid-liquid system.

Good and Koo (3) reviewed several seriously conflicting observations on the relationship between drop size and contact angle, and experimentally established that the contact angle formed by a drop of liquid decreases with decreasing drop diameter for certain solid-liquid systems. Specifically, they observed this effect with water on Teflon FEP and on polymethylmethacrylate for both advancing and receding angles and with ethylene glycol on Teflon FEP for receding angles. Advancing angles of ethylene glycol, and both advancing and receding angles of decane on Teflon FEP, were not observed to vary with drop diameter.

The purpose of this study was to determine the effect of drop volume on the equilibrium contact angle for combinations of solids and liquids of varying polar and nonpolar character, and so recommend an appropriate drop volume for use in contact angle measurement.

MATERIALS AND METHODS

Contact angles formed by a sessile drop on each of six solid surfaces were measured with a contact angle goniometer equipped with an environmental chamber and a microsyringe assembly (NRL Model 100-00, Rame-Hart, Inc., Mountain Lakes, NJ). The contact angle methodology used was identical to that completely detailed by McGuire and Kirtley (10). Drop volumes used ranged from 2 μl to 40 μl. Both sides of the advancing angles were measured at 2 μl increments; reported values are means for at least three drops. The closed sample chamber was maintained at approximately 25°C under water-saturated conditions.

The liquids used in this study included water and aqueous solutions of ethanol (EM Science, Cherry Hill, NJ) prepared at 10%, 20, 30, and 40 volume percentage concentrations. Each liquid had its surface tension measured by the ring method with a DuNoüy tensiometer (CSC Scientific Co., Inc., Fairfax, VA). Measurements were performed at approximately 25°C and were reproducible to within 0.1 mN/m. Solid materials used included four commercial polymers and one metal, each approved and commonly used for food contact: high density polyethylene, nylon, polypropylene, polytetrafluoroethylene (PTFE) (all from Universal Plastics Co., Portland, OR), and #304 stainless steel (Alaskan Copper and Brass Co., Portland, OR). The stainless steel was polished to a mirror finish. Glass surfaces were also studied, but the extensive spreading demonstrated by each liquid made it impossible to detect a definite drop volume effect.

All solid materials had been stored in distilled, deionized water for several months prior to analysis; although advancing angles were measured in the present study, surfaces were thus equilibrated with water. The importance of this practice, particularly if the contact angle data are to be related to biological adhesion, was described with reference to food industry applications earlier (9). Properties related to surface energy have since been measured for a variety of food contact materials by analysis of contact angle data recorded for aqueous solutions of ethanol and methanol on their water-equilibrated surfaces, and successfully correlated with adhesion phenomena of significance to food processing (6,11).
RESULTS AND DISCUSSION

For each solid-liquid situation analyzed, contact angles were observed to increase with increasing drop volume in a range below some limiting value, identified as the critical drop volume (CDV). The CDV varied somewhat among materials, and this observation can be partially explained with reference to representative data recorded on the relatively nonpolar surfaces of PTFE and polypropylene (Fig. 1 and 2) and the relatively polar surfaces of #304 stainless steel and nylon (Fig. 3 and 4).

The observed dependence of contact angle on drop volume is likely due to surface energetic heterogeneities exhibited by each of the solid surfaces. For example, PTFE is a nonpolar surface, but surface sites capable of polar interaction had been identified long ago (1). As drop size decreases, the tendency of the three-phase line to distort due to the presence of surface heterogeneities increases; moreover, the local liquid-vapor interfacial tension should be expected to vary from one point to another along the three-phase contact line (8). The three-phase line is defined by the drop boundary at the solid surface, where contact is maintained between the liquid, solid, and vapor phases. In the case of PTFE, the upper curve in Fig. 1 (10% EtOH) falls off the mean line at a value of CDV greater than that for the lower line (40% EtOH). That is, the surface of the 10% EtOH solution is spread by the presence of polar sites on PTFE to a greater extent than the less hydrophilic surface of the 40% EtOH solution. The data for PTFE support the existence of a nonequilibrium surface structure for the liq-
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Figure 4. Contact angle recorded as a function of drop volume on selected solid surfaces: (1) PTFE; (2) polypropylene; (3) #304 stainless steel; and (4) nylon. Upper curves in each plot were constructed from data recorded with 10% EtOH; lower curves, 40% EtOH. Each horizontal line was drawn through the mean value of contact angle corresponding to drops in excess of 20 µl.

TABLE 1. Average drop volume of each liquid under study, formed by a microsyringe with a 22-gauge needle. The associated standard errors are reported in parentheses.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface tension, mN/m</th>
<th>Drop volume, µl</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>71.17</td>
<td>12.39 (0.71)</td>
<td></td>
</tr>
<tr>
<td>10% EtOH</td>
<td>49.86</td>
<td>9.24 (0.30)</td>
<td></td>
</tr>
<tr>
<td>20% EtOH</td>
<td>40.72</td>
<td>7.06 (0.35)</td>
<td></td>
</tr>
<tr>
<td>30% EtOH</td>
<td>35.40</td>
<td>5.69 (0.28)</td>
<td></td>
</tr>
<tr>
<td>40% EtOH</td>
<td>34.22</td>
<td>5.41 (0.34)</td>
<td></td>
</tr>
</tbody>
</table>

(5) observed polyethylene to be polar relative to PTFE and paraffin. This is of interest because the trend observed in Fig. 2 is somewhat similar to that in Fig. 3 and 4, constructed for the more polar surfaces of #304 stainless steel and nylon, respectively. That is, a greater drop size dependence was observed as ethanol concentration was increased.

A less hydrophilic liquid surface, in these cases, might be expected to more readily allow microscopic spreading of the three-phase line over hydrophobic sites on the solid surface; this is analogous to arguments presented in the previous paragraph.

For the liquids considered in this work, Table 1 lists the average volume per drop formed by a microsyringe associated with a 22-gauge needle (0.7 mm o.d.); such an assembly is typically used to produce drops for analysis. These data are particularly important since the single drop volumes produced fall within the range of volumes over which the drop size effect was observed in Fig. 1 through 4. It should also be noted that the manufacturer of the NRL goniometer simply recommends use of a small volume having a diameter of approximately 2.5 mm; this roughly corresponds to the diameter of a single drop of water formed by a 22-gauge needle and placed on a low energy surface. The smallest drop diameter included in construction of the

mean lines of Fig. 1 through 4, i.e., corresponding to a drop volume of 20 µl, is well in excess of 2.5 mm. Moreover, drops of 2.5 mm diameter, in each case, fell within the range over which Good and Koo (3) observed a drop size effect. In other words, a deliberate effort is required to produce drops in excess of the CDV. Considering all materials and diagnostic liquids tested, results suggest that drop volumes in excess of 20 µl should be used. In any event, as expected, the results indicate that a drop size effect exists; most importantly, knowledge and application of this information in practice is currently not satisfactory.

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REFERENCES

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