

Surfactant Solutions as Test Liquids for Measurement of Critical Surface Tension

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Abstract □ Contact angles of various liquids and surfactant solutions on polytet and paraffin were measured. Critical surface tension values were obtained by extrapolation of plots of cosine of the contact angles versus corresponding surface tension values. Contact angles measured using polyoxyethylene octylphenols produced linear Zisman plots and yielded critical surface tensions that agreed with accepted values. This liquid series provides a reasonable approach to the measurement of critical surface tension for solid drugs that are soluble in organic liquids but relatively insoluble in water.

Keyphrases □ Surfactants, polyoxyethylene octylphenols—test liquids for measurement of critical surface tension □ Surface tensions—analysis, various drugs, solid-liquid mixtures, surfactants □ Structure-activity relationships—surface tension, various surfactants □ Contact angles—wetting of pharmaceutical solids

Critical surface tension, γ_c , was introduced as an empirical index of the wettability of solid surfaces (1) where γ_c represents the liquid surface tension at which liquids just spread over the solid surface. Liquids whose surface tension is below γ_c wet the solid completely, while liquids whose surface tension exceeds γ_c do not. The latter form drops with contact angles greater than 0° on the solid surface.

BACKGROUND

To determine the critical surface tension of a particular solid, a series of liquids with different surface tensions are applied to the surface of the solid and the contact angles, θ , are measured. A plot of cosine of the contact angle versus liquid surface tension is often linear. Extrapolation

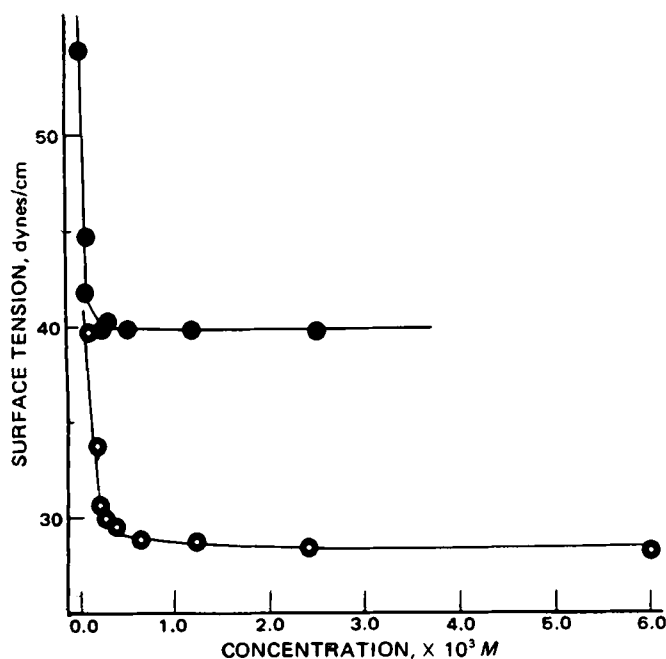


Figure 1—Surface tension as a function of surfactant concentration. Key: O, polyoxyethylene (5) octylphenol; and ●, polyoxyethylene (40) octylphenol.

Table I—Properties of Polyoxyethylene Octylphenols

Average Number of Oxyethylene Groups per Molecule	Average Molecular Weight, daltons	γ_L^a , dynes/cm
5	420	28.5
7	514	28.8
9	596	30.0
12	734	31.1
12.5	756	33.0
16	910	34.7
30	1526	38.8
40	1966	40.0

^a Using $2.5 \times 10^{-3} M$ aqueous solutions.

of this plot to where the cosine of the contact angle equals 1 yields the critical surface tension.

The composition of the liquid mixture influences the critical surface tension (2), possibly due to interfacial interaction (3). Anionic, cationic, and nonionic surfactants in aqueous solution have been used to determine the γ_c values of polytet and polyethylene (4). Experiments were carefully done by using diluted surfactant solutions to vary the surface tension. Zisman plots of the surfactants exhibited discontinuities at points that corresponded to the critical micelle concentration (CMC) of the surfactants. When the surfactant concentrations were higher than the CMC, the plots were linear and indicated the correct values of γ_c .

There has been little work on the determination of γ_c values for pharmaceutical substances other than aspirin (5). Such research would be useful because of the importance of wetting in dispersion of powders (6) and dissolution (7). The selection of suitable liquids for the determination of γ_c presents some problems. Hydrocarbons have surface tensions that are too low to be useful with many pharmaceutical powders. Other organic liquids and liquid mixtures may be used, but many drugs

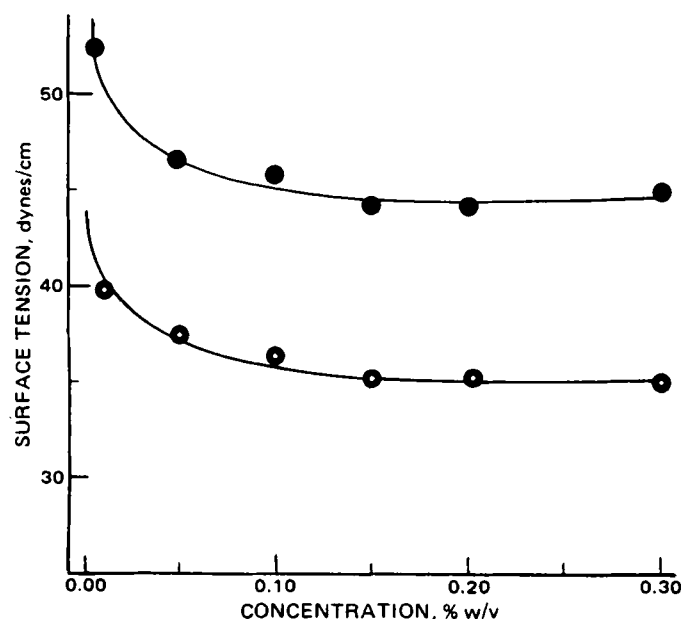


Figure 2—Surface tension as a function of surfactant concentration. Key: O, polyethylene glycol 600 monostearate; and ●, polyethylene glycol 4000 monostearate.

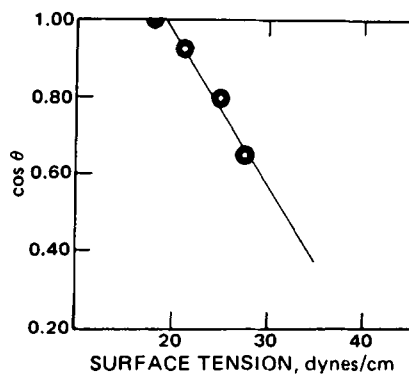


Figure 3—Cosine of contact angle as a function of surface tension for hydrocarbon liquids on polytef.

expected to have low energy surfaces are quite soluble in semipolar liquids, and dissolution complicates contact angle measurement. Drugs that present problems in wetting are likely to be poorly water soluble. Aqueous surfactant solutions should function well in studies of critical surface tension because liquid surface tension may be varied (within certain limits) and solubility problems are minimized.

This study investigated the use of surfactant solutions in the determination of critical surface tension. Nonionic surfactants were chosen since this class is least likely to exhibit specific adsorption effects on solid surfaces. A series of solutions graduated in surface tension was prepared without extreme dilution by using a family of surfactants differing only in polyoxyethylene chain length.

EXPERIMENTAL

Materials—The nonionic surfactants, polyoxyethylene octylphenols¹ and polyethylene glycol monostearates², were used as received. Polytef film³ was used after surface cleaning. Paraffin⁴ was USP grade. Hexane⁵, octane⁵, dodecane⁵, and hexadecane⁵ were reagent grade. Water was double distilled in an all-glass still.

Preparation of Surfaces—Polytef film was cleaned with dichromic acid cleaning solution, rinsed thoroughly with distilled water, and dried. It was then affixed to a glass slide with tape. Molten paraffin was poured onto a clean glass slide on a hot plate. A smooth sheet of cleaned aluminum foil was placed on top of the paraffin, and a plastic scraper was drawn

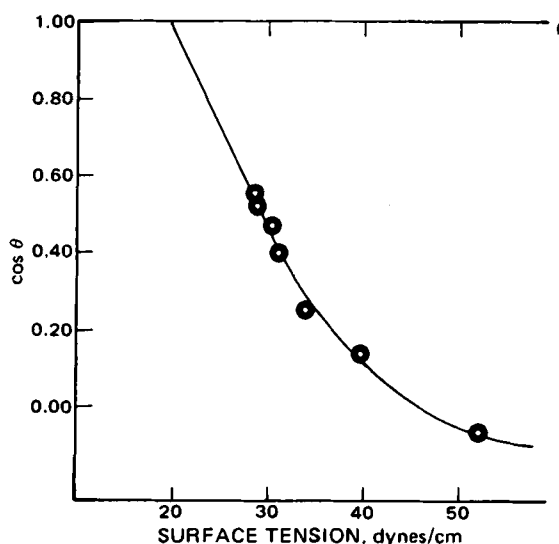


Figure 4—Cosine of contact angle as a function of surface tension for solutions of polyoxyethylene (5) octylphenol on polytef.

¹ Igepal CA-520, 620, 630, 720, and 897, GAF Corp., New York, N.Y. Triton X-102, 165, and 305, Rohm & Haas Co., Philadelphia, Pa.

² Mapeg 600 MS, 1000 MS, and 4000 MS, Mazer Chemical Inc., Gurnee, Ill.

³ Teflon, Du Pont Co., Wilmington, Del.

⁴ J. T. Baker Chemical Co., Phillipsburg, N.J.

⁵ MC & B Co., East Rutherford, N.J.

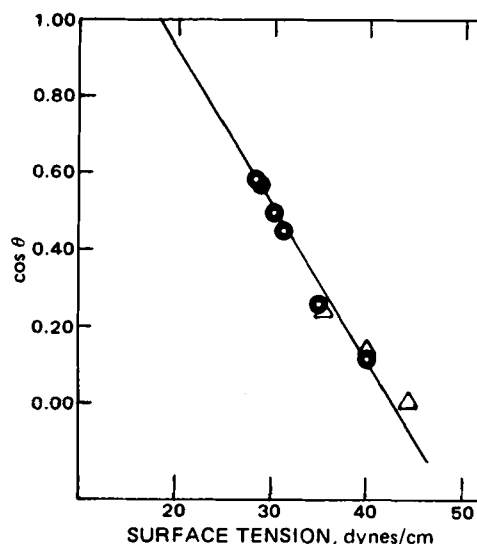


Figure 5—Cosine of contact angle as a function of surface tension on polytef. Key: O, polyoxyethylene octylphenols; and Δ, polyethylene glycol monostearates.

across the covered paraffin film. The slide was allowed to cool, and the foil was removed just prior to use.

Methods—Surface tension was measured by the Wilhelmy plate method⁶. Distilled water was used as the standard.

The advancing contact angles of sessile drops on the flat surfaces were measured directly by a goniometer attached to a telemicroscope⁷. Measurements were made at $25 \pm 1^\circ$ without humidity control. A drop containing $20 \mu\text{l}$ was applied to the surface using a microliter syringe held in place by a supporting rack. After 5 min, more liquid was slowly added (8) and the advancing angle was measured. Contact angle readings were taken from both sides of the drop separately, and at least three individual drops were used for each measurement.

RESULTS AND DISCUSSION

Four different liquid series were used to determine critical surface tensions of paraffin and polytef. The first series consisted of pure liquid hydrocarbons. The second series consisted of aqueous solutions of polyoxyethylene (5) octylphenol in which variations in surface tension

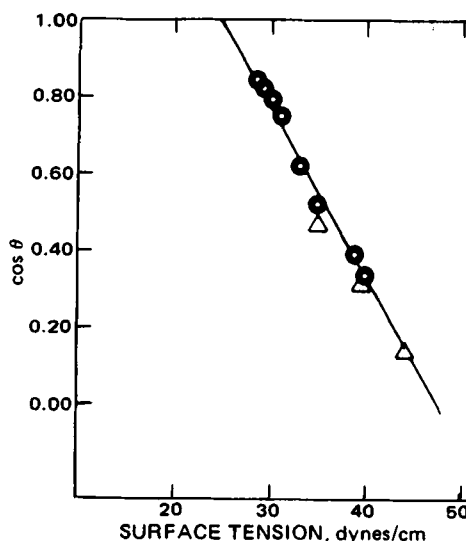


Figure 6—Cosine of contact angle as a function of surface tension on paraffin. Key: O, polyoxyethylene octylphenols; and Δ, polyethylene glycol monostearates.

⁶ Rosano surface tensiometer, Pacific Scientific Co., Newark, N.J.

⁷ Gaertner Co., Chicago, Ill.

Table II—Critical Surface Tensions

Material	γ_c			Literature Value
	Hydrocarbon Series	Diluted Surfactant Series ^a	Polyoxyethylene Octylphenols	
Polytef	19.2	19.5	17.9	18.5 (Ref. 1)
Paraffin	—	—	24.9	25.5 (Ref. 3)

^a Polyoxyethylene (5) octylphenol solutions.

were achieved by dilution. Figure 1 shows the relationship between surface tension and solution concentration for this surfactant, which has the shortest hydrophilic group among the octylphenol derivatives. Also included in Fig. 1 are similar data for polyoxyethylene (40) octylphenol, which has the longest hydrophilic group.

The third liquid series contained eight octylphenol derivatives of uniform concentration. From the results in Fig. 1, $2.5 \times 10^{-3} M$ was selected as the concentration to be used because, at that value, small variations in concentration would have a negligible influence on surface tension. Properties of the surfactants in this series are presented in Table I.

The fourth liquid series consisted of some polyethylene glycol monostearates. Only three with sufficient water solubility were available. Figure 2 is a plot of surface tension as a function of concentration for two members of this surfactant family. All solutions for contact angle measurement contained 0.15% (w/v) of the monostearates; γ_L values for polyethylene glycol 600, 1000, and 4000 were 35.3, 39.7, and 44.2 dynes/cm, respectively.

Figure 3 is a Zisman plot for hydrocarbon liquids on polytef. The critical surface tension determined from this plot, 19.2 dynes/cm, is in good agreement with the literature value of 18.5 dynes/cm (1). Results with polytef using the second liquid series, diluted solutions of polyoxyethylene (5) octylphenol, are presented in Fig. 4. The curvature this plot exhibits interfered with the required extrapolation, but γ_c was estimated to be 19.5 dynes/cm.

Contact angles of the two surfactant series on polytef are shown in Fig. 5. A critical surface tension value for the polyethylene glycol stearates was not determined because of the long extrapolation required, but it is evident that results with both sets of surfactants were similar. The plot of $\cos \theta$ versus γ_L is linear. The same is true for contact angles on paraffin (Fig. 6).

The critical surface tension values obtained on polytef and paraffin

are summarized in Table II. In both cases, γ_c values derived from the use of surfactant solutions are quite close to those found using pure nonpolar liquids. Values of critical surface tension are not independent of the properties of the group of liquids used in their determination (2). The agreement in γ_c found with surfactant solutions and hydrocarbon liquids supports the notion that surfactant solutions above the CMC behave as though the liquid surface were a hydrocarbon (4). In the presence of a low energy surface, the adsorbed surfactant film seems to maintain its orientation and arrangement.

The use of a family of surfactants has several advantages over dilution of a single compound to vary surface tension. Diluted surfactant solutions invariably lead to curved Zisman plots, which make extrapolation to γ_c difficult. This may be because dilution below the CMC causes the solution to lose its compact surface film, and the surface tension acquires a larger polar component. Use of a series of surfactants allows maintenance of the surface film in each solution and leads to linear plots (Figs. 5 and 6).

Furthermore, if adsorption of the surfactant molecules by the solid material or a component of the apparatus should occur, the concentration of surfactant in a highly dilute solution may be changed sufficiently to affect the surface tension in the liquid drop whose contact angle is being measured. Thus, the actual surface tension of the liquid would be different from that ascribed to it. Because concentrations of surfactant solutions are well above the CMC for each member of a surfactant family, some adsorption of surfactant would not cause this problem.

To summarize, critical surface tension values for polytef and paraffin determined using a family of solutions containing nonionic surfactants agree well with reported values. This liquid series provides a reasonable approach to the measurement of γ_c values for solid drugs that are soluble in organic liquids but relatively insoluble in water.

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Critical Surface Tensions of Pharmaceutical Solids

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Abstract □ Advancing contact angles measured on compacts of several drugs by the sessile drop method and also by penetration through a column of drug granules were used to find the critical surface tension of the drugs. After liquid was delivered at a very slow rate, the contact angle of sessile drops decreased with time, but use of a consistent method of timing always led to the same value for critical surface tension. Results from penetration studies and work on compacts were in agreement, provided that the surfaces of the compacts were smooth and highly reflective. Critical surface tension of the six drugs, three analgesics and three sulfonamides, ranged from 31 to 33 dynes/cm. The critical surface tension

of mixtures of phenacetin and microcrystalline cellulose was not a linear function of the relative surface fractions of the two materials. If the surface contained 25% or more of phenacetin, the critical surface tension barely differed from that of pure phenacetin.

Keyphrases □ Surface tensions, critical—various pharmaceutical solids analysis, by sessile drop method □ Surfactants, nonionic—used to determine surface tensions of various pharmaceutical solids □ Solids—surface tensions □ Contact angles—wetting of pharmaceutical solids

Wetting of a solid by a liquid is an important step in several pharmaceutical processes including the preparation of suspensions (1) and the adhesion of film coatings to tablets (2). The dissolution rate of powdered phenacetin

was sensitive to the surface tension of the dissolution medium because of differences in wetting (3).

As described previously (4), the critical surface tension, γ_c , of a solid is a measure of its wettability and is related