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Surface free energy characteristics of mixtures

H.A.H. Mohammad and J.T. Fell

Department of Pharmacy, University of Manchester, Manchester M13 9PL (U.K.)

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Summary

The surface free energies of two series of mixtures have been determined indirectly from contact angle measurements and compared with values of the critical surface tension. The values of critical surface tension vary with the liquids used for the determination. For an ideal mixture of spherical particles, the surface free energy values obtained change in a regular manner with mixture composition. For a pharmaceutical system, this was not the case and may be a reflection of the preferential adsorption of one component on the other. The values should, however, represent a value for the mixture as it is used.

Introduction

The surface characteristics of solids are important in a wide variety of pharmaceutical processes. The logical approach to surface characterization would be to determine the surface free energy, a relatively simple problem for liquids, but more difficult for solids. Although several approaches are possible (Adamson, 1960), two methods seem to be particularly applicable to pharmaceutical systems.

Zisman (1963) found that the cosine of the contact angles of a series of liquids on a given solid, when plotted against the surface tensions of the liquids, gives a straight line, the intercept of which, the horizontal line, $\cos\theta = 1$, is designated the critical surface tension. The critical surface tension so determined has been related to the surface energy of the solid (El-Shimi and Goddard, 1974).

Fowkes (1964) has suggested that the total free energy of a surface is the sum of the contributions from the polar and dispersion forces present. Hence:

$$\gamma_a = \gamma_a^P + \gamma_a^D$$

where γ_a is the surface tension of phase a and the superscripts P and D refer to the

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polar and dispersion components, respectively. The interfacial tension is then:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi^P - 2\phi^D$$

where γ_{12} is the interfacial tension between phases 1 and 2, γ_1 and γ_2 are the surface tensions and ϕ^P and ϕ^D are the interaction terms for the polar and dispersion forces, repectively. Wu (1971) found that the interaction terms were best approximated by:

$$\phi^P = \frac{2\gamma_1^P\gamma_2^P}{\gamma_1^P + \gamma_2^P}$$

and similarly for the dispersion forces, giving finally:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^D\gamma_2^D}{\gamma_1^D + \gamma_2^D} - \frac{4\gamma_1^P\gamma_2^P}{\gamma_1^P + \gamma_2^P}$$

To make this general interfacial tension equation specifically of value for solids, it can be combined with the Young equation (where adsorption of vapour from the liquid on the solid is considered negligible).

$$\gamma_S - \gamma_{SL} = \gamma_L \cdot \cos\theta$$

where γ_S is the solid surface tension, γ [illegible] the solid–liquid interfacial tension and γ_L is the liquid surface tension to give

$$(b + c - a)\gamma_S^D\gamma_S^P + c(b - a)\gamma_S^D + b(c - a)\gamma_S^P - abc = 0$$

where

$$a = \frac{\gamma_L}{4}(1 + \cos\theta), \quad b = \gamma_L^D, \quad C = \gamma_L^P$$

Determination of the contact angle with two liquids of known polar and dispersion force contributions allows two simultaneous equations to be written and solved for the dispersion and polar components of the solid surface free energy.

The latter approach has been used by Zografi and Tam (1976) to characterize the surface free energies of several pharmaceutical materials. This report looks at the possibility of extending the approach to mixtures and examines both critical surface tensions and surface free energies.

Materials and Methods

Materials

The solids used were polyethylmethacrylate (Cole Polymers, Croydon, U.K.), a vinyl acetate, vinyl chloride copolymer (Corvic C47/488, I.C.I.), phenobarbitone

(Sigma, London), dicalcium phosphate dihydrate (Emcompress, Forum Chemicals, Reigate, U.K.) and hard paraffin B.P. (Evans, Speke, U.K.). The first 4 materials are powders and were sieved to give a 53–90 μm size fraction. The two polymer powders consist of spherical particles.

The liquids used were isopropylalcohol (Fisons, Loughborough, U.K.), glycerol (MacCarthy, U.K.) and polyethylene glycol 200 (B.D.H., Poole, U.K.). Water was glass-distilled and gave surface tension readings of not less than 70 mN/m at 20°C.

Contact angles

Contact angles were measured directly by projecting the image of a drop of liquid on a compressed disc of the solid, on to a screen. Details of the method have been given earlier (Fell and Efentakis, 1979). Suitable pressures were chosen so that reproducible results were obtained. Saturated solutions were used when necessary. If penetration occurred, the compacts were presaturated with the liquid under test prior to the measurements. Although this method is open to criticism, provided certain precautions are taken, reasonable agreement can be obtained between the results from direct observation and the h–Σ method (Fell and Efentakis, 1979). The method was selected in preference to the h–Σ method as it enabled results to be obtained more rapidly with the use of smaller quantities of materials.

Contact angles on hard paraffin were obtained by the same method, using glass slides dipped into molten paraffin and cooled to room temperature.

Surface tension measurements

These were carried out by the drop volume method using an Agla syringe with a glass tip, and applying the correction factors of Harkins and Brown (1919) in the calculations.

Results

Isopropylalcohol–water mixtures, and polyethylene glycol–glycerol mixtures were used to determine the contact angles of mixtures of polyethylmethacrylate and Corvic and phenobarbitone and Emcompress. At least 6 liquid mixtures were used on 6 solid mixtures. Plots of the cosine of the contact angles against surface tension were linear with correlation coefficients better than 0.990. Extrapolation to $\cos \theta = 1$ gives the critical surface tensions which are shown in Fig. 1. In both cases, the isopropylalcohol–water mixtures gave lower values of the critical surface tension. Values for Emcompress alone are not shown as all liquid mixtures exhibited zero contact angle against it.

Values of γ_L^D and γ_L^P for water and glycerol are taken from Zografi and Tam (1976). The value for polyethylene glycol 200 was determined by measuring its contact angle against paraffin. Paraffin has a γ_S^P equal to zero; γ_S has been determined as 25.5 ergs/cm^2 (Fowkes, 1964). Hence, only the dispersion forces will interact, and knowledge of the contact angle and the surface tension of the liquid

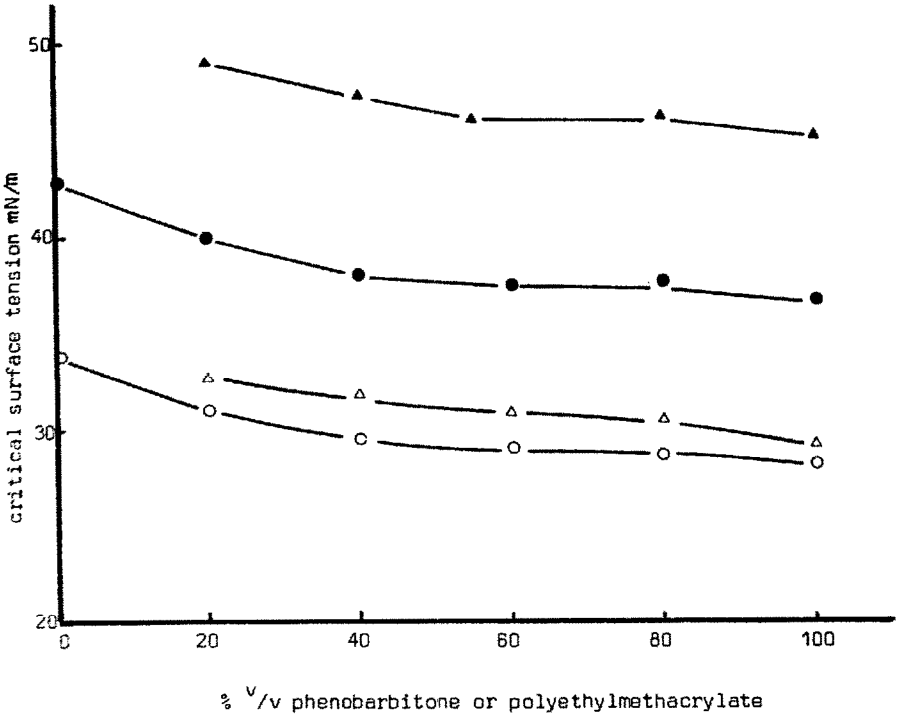

Fig. 1. The relationship between critical surface tension and % v/v phenobarbitone or polyethyl methacrylate. ▲, phenobarbitone–Emcompress determined with polyethylene glycol 200–glycerin mixtures; △, phenobarbitone–Emcompress determined with isopropylalcohol–water mixtures; ●, polyethylmethacrylate–Corvic determined with polyethylene glycol 200–glycerin mixtures; and ○, polyethylmethacrylate–Corvic determined with isopropylalcohol–water mixtures.

allows calculation of γ_L^P and γ_L^D. The values are shown in Table 1, together with those for water and glycerin.

Values of γ_S, γ_S^D and γ_S^P have been calculated by means of the Wu equation, together with a polarity index,

$$p^0 = \frac{\gamma_S^P}{\gamma_S} \times 100$$

defined by Zografi and Tam (1976). The values shown in Figs. 2 and 3 exhibit

TABLE 1

SURFACE FREE ENERGY TERMS FOR THE LIQUIDS USED IN THE STUDY

Liquid	γ_L	γ_L^D	γ_L^P
Water	72.0	23.2	48.8
Glycerol	63.7	32.0	31.7
Polyethylene glycol 200	48.3	29.3	19.0

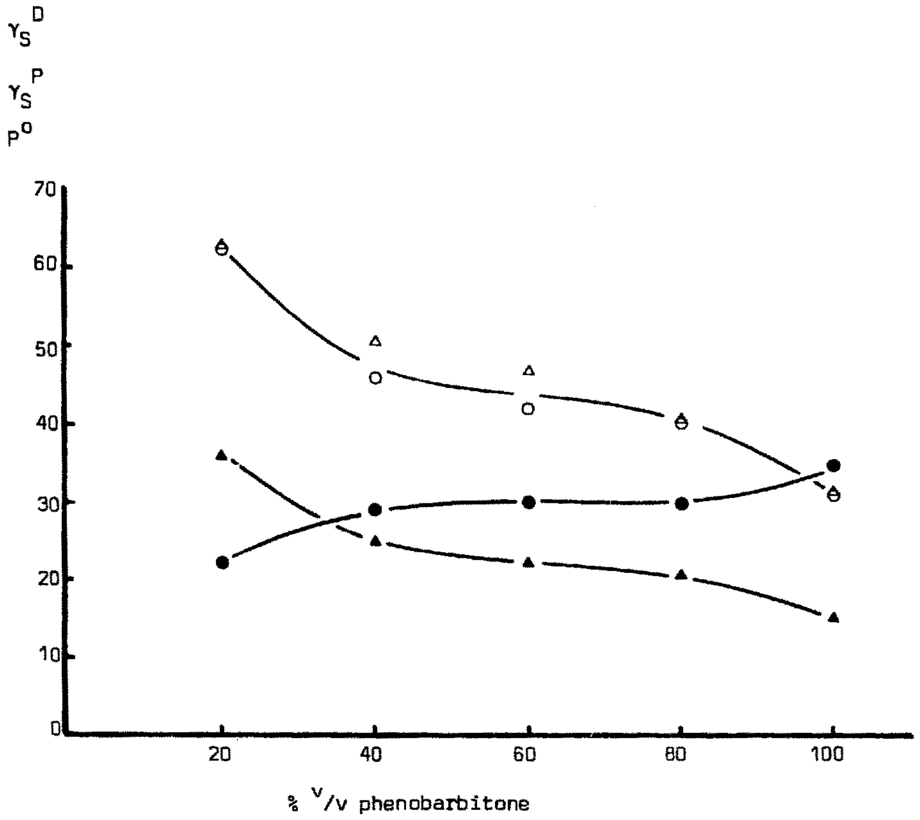

Fig. 2. The relationship between % v/v phenobarbitone in phenobarbitone–Emcompress mixtures and γ_S^P, γ_S^D and the polarity index, P^0. ▲, γ_S^P; ●, γ_S^D; △, P^0 determined with polyethylene glycol 200; ○, P^0 determined with glycerol.

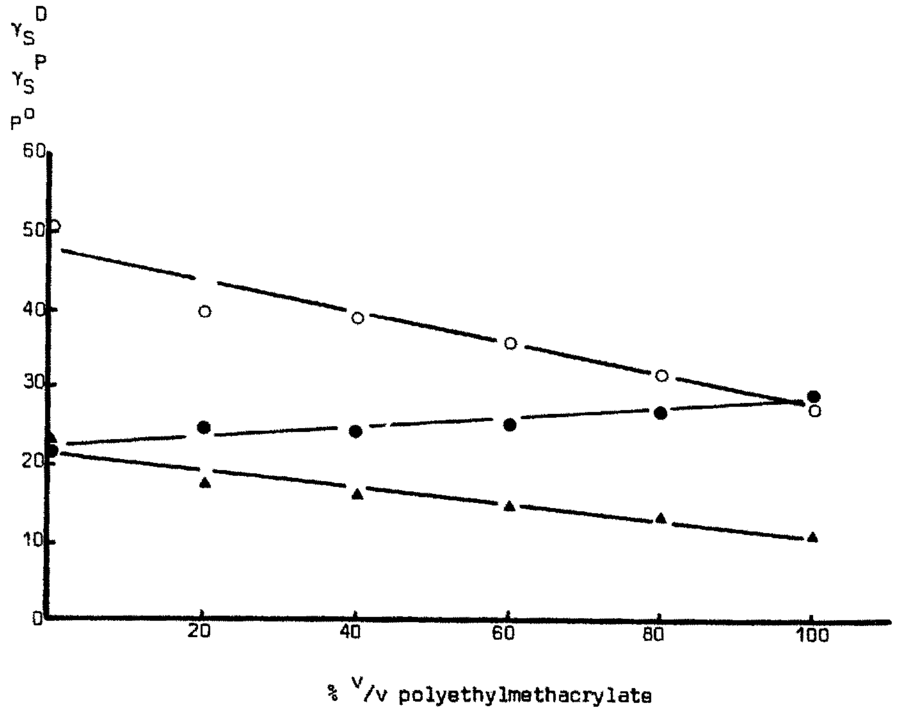

Fig. 3. The relationship between % v/v polyethylmethacrylate in polyethylmethacrylate–Corvic mixtures and γ_S^P, γ_S^D and the polarity index, P^0. Key—see Fig. 2.

changes as the proportion of the solid components is varied. Excellent agreement between the calculated values was obtained for the phenobarbitone–Emcompress system using either polyethylene glycol and water as the two liquids, or glycerol and water. Only the two sets of values for the polarity index are shown on the figures, for clarity. Comparative results could not be obtained for the polymer system due to difficulties in measurement using glycerol alone with this system.

Discussion

Isopropylalcohol–water mixtures and polyethylene glycol–glycerol mixtures represent two liquid series with different polarities, the isopropylalcohol system being the more polar. The critical surface tension values obtained are higher when using the polyethylene glycol–glycerol system and for the polymer systems are more in keeping with literature values (e.g. polyvinylchloride, 39 mN/m; Girafalco and Good, 1957). Based on the concept of the independent interaction of forces across an interface, Dann (1970) has shown that different values of the critical surface tension should be obtained when using different liquid series, and higher values would be obtained when using liquids with a greater dispersion force contribution. The cirtical surface tension values obtained with the polyethylene glycol–glycerol system are close to the values of γ_S determined by the technique of Wu (1971) (Table 2). An alternative explanation to the difference in values obtained from the two systems is based on adsorption of ispropylalcohol onto the solids, changing γ_{SL} and γ_S. Murphy et al. (1972) showed that the critical surface tensions obtained for a variety of polymers using various alcohol–water mixtures were independent of the solid and a similar result for pharmaceutical powders using methanol–water mixtures was obtained by Fell and Efentakis (1979).

The addition of a second component would be expected to alter the polar and

TABLE 2

CRITICAL SURFACE TENSIONS AND SOLID SURFACE FREE ENERGIES FOR MIXTURES OF POLYETHYLEMETHACRYLATE AND CORVIC AND PHENOBARBITONE AND EMCOMPRESS

% v/v P.E.M. or phenobarbitone	P.E.M. in Corvic			Phenobarbitone in Emcompress		
	γ_c PEG/Gly.	γ_c isoprop.	γ_s	γ_c PEG/Gly.	γ_c isoprop.	γ_s
0	42.7	33.8	44.9	–	–	–
20	39.8	31.0	41.9	45.1	29.1	51.4
40	37.9	29.5	40.3	46.1	30.4	50.4
60	37.4	29.0	39.6	46.0	30.9	52.2
80	37.5	28.6	39.8	46.1	30.4	50.4
100	36.5	28.1	40.5	45.1	29.1	51.4

γ_c PEG/Gly and γ_c isoprop. are the critical surface tensions determined with polyethylene glycol 200–glycerol mixtures or isopropyl alcohol–water mixtures, respectively.

dispersion forces of the original surface in proportion to the amount added. The results in Fig. 3 from the Corvic, polyethyl methacrylate mixtures show that this is the case, the calculated values changing linearly with composition. This system is ideal in that both materials consist of spherical particles of similar size, and compaction takes place by similar mechanisms not involving fracture of the particles. Hence, the surface on which the contact angles are measured should accurately reflect the composition of the mixture. This may not be the case for other systems. For example, the spreading of magnesium stereate during mixing (Bolhuis et al., 1975) or the formation of an ordered mix (Staniforth, 1982) could lead to surfaces which do not bear a resemblance to the original mixture composition. In the case of the phenobarbitone–Emcompress mixtures, the polarity of the system is reduced by the addition of phenobarbitone to a greater degree than would be expected on a simple proportional basis. This could be a reflection of the preferential coverage of one component with the other, or a difference in compaction mechanisms leading to an increased surface area of one component. The values obtained, however, will be representative of the 'as compacted' material and may be useful in understanding surface-controlled processes such as dissolution and adhesion of film coating materials.

A problem that arises with the determination of the surface polarity of mixtures by contact angle measurements is the variation of contact angle with the particle size of the material comprising the mixture. This has been reported by Lerk et al. (1976) and Mohammed and Fell (1982) and discussed theoretically by Johnson and Dettre (1964). The results of Mohammed and Fell show that the effect is not an artefact of the measuring technique. Although not measured in this study, these results would lead to different values of polarity for identical mixture compositions of different particle size. This effect and its practical consequences are currently being investigated.

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