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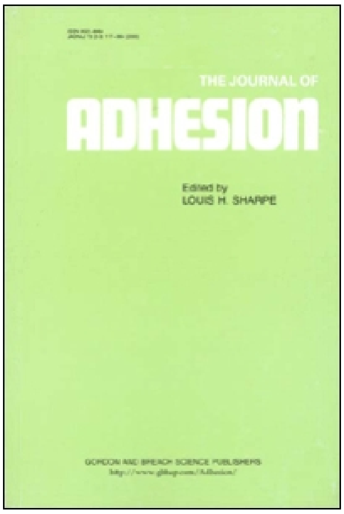

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J. Comyn[a]; D. C. Blackley[a]; L. M. Harding[a]
[a] Department of Chemistry, De Montfort University, Leicester, UK

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The Effect of Lowering the Surface Free Energy of Water on the Thermodynamic Work of Adhesion

J. COMYN,* D. C. BLACKLEY and L. M. HARDING

Department of Chemistry, De Montfort University, P.O. Box 143, Leicester LE1 9BH, UK

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The dispersive and polar force components of surface free energy have been measured for water left in contact with films dried from various emulsion adhesives. The polar component was lowered but the dispersive components were about 28 mJ m^{-2} in each case. From these measurements of thermodynamic work of adhesion in the presence of contaminated water have been calculated for adhesive-polystyrene interfaces. An equation has been derived giving the dependence of thermodynamic work of adhesion upon the total surface free energy of water. It shows that the thermodynamic work of adhesion decreases as the surface free energy of water is lowered, but it eventually reaches a minimum and then may increase slightly.

KEY WORDS dispersion and polar force components of water; films of emulsion adhesives; adhesive/polystyrene interfaces; additives in polymer latices; surfactants; adhesive bond durability.

INTRODUCTION

Emulsion adhesives are based upon polymer latices which are usually compounded with appropriate additives. The latices themselves are colloidal dispersions of polymer particles in a dispersion medium, which is usually aqueous. As well as the polymer, latices contain colloid stabilisers to prevent premature aggregation of the particles. In the case of aqueous latices, these stabilisers are often hydrocolloids and surfactants. An essential requirement of an emulsion adhesive is that it should dry to a continuous film under the conditions of application. Aqueous emulsion adhesives find wide application because they avoid the health and safety hazards which accompany the use of solvent-based adhesives.

Exposure to water generally weakens adhesive bonds.[1] One reason for this is the lowering of the thermodynamic work of adhesion in the presence of water. A positive value of the thermodynamic work of adhesion indicates that the bonded adhesive interface is stable relative to the disbonded state, whereas a negative value indicates that it is unstable relative to the disbonded state. Water is a polar

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*Corresponding author. Present address: 3 Ratcliffe Drive, Huncote, Leicester LE9 6BA, UK.

liquid, and as such has a high value of the polar component of surface free energy; this means that it is able to displace adhesives from many substrates. The surface free energy of water is lowered by surface-active substances. A situation may arise in which an emulsion adhesive/substrate interface is in contact with water and surface-active substances are extracted from the adhesive into the water, thereby modifying the surface properties of the water and changing the value of the thermodynamic work of adhesion. The aim of the work described in this paper was to investigate this phenomenon.

This paper is the third of a series concerned with the durability of the bond between emulsion adhesives and expanded polystyrene (EPS). The two earlier papers dealt, respectively, with the analysis of adhesive film surfaces by fast atom bombardment mass spectrometry (FABMS) and by x-ray photoelectron spectroscopy (XPS),[2] and with characterisation of surfaces by contact-angle measurement.[3]

In the experiments reported here, we have prepared dried films from the various emulsion adhesives, immersed them in pure water, and then measured the surface free energies of these waters after contact with the adhesive films, and also the interfacial free energies of these waters against *n*-hexadecane. The results of these measurements have been used to estimate values of the thermodynamic work of adhesion for each of the adhesive/polystyrene interfaces in the presence of water which has been contaminated by contact with the appropriate adhesive film. Clearly, it is the thermodynamic work of adhesion derived in this way which is likely to provide the best indicator of the probable stability of an adhesive/polystyrene bond in a wet environment. Also, an equation has been derived which relates thermodynamic work of adhesion to the surface free energy of the water in contact with the bond.

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EXPERIMENTAL

The liquids used were triply distilled water and "Gold Quality" *n*-hexadecane (n-HEX) obtained from the Aldrich Chemical Company. The surface free energies of these liquids were measured using the ring-pull technique described below; they were found to be very close to the literature values.[3]

The emulsion adhesives used are described in a previous paper.[2] Summary descriptions of the adhesives are as follows:

i) VAVV is the latex of a copolymer of vinyl acetate and vinyl neodecanoate.
ii) VAE1, VAE2 and VAE3 are latices of copolymers of vinyl acetate and ethylene.
iii) VABA is the latex of a copolymer of vinyl acetate and *n*-butyl acrylate which is supplied as both a summer and a winter grade, denoted as VABA/S and VABA/W respectively. The winter grade of VABA contains 2-propanol as an antifreeze.

Average particle diameters were 0.75–1.15 μm for VAVV, 1–2 μm for VAE1, 0.5–2.0 μm for VAE2 and *ca.* 2 μm for VABA.

Samples of water contaminated with extractables from the dried adhesive films were prepared as follows. A layer of emulsion was spread on a glass microscope slide and allowed to dry for several days. The dry adhesive film was then placed in a small glass container with about 7 cm^3 of water. In some cases, the procedure was repeated with twice the amount of adhesive and slightly less water (5 cm^3). Checks showed that the surface free energy of pure water was not changed by contact with the glassware, or with EPS beads.

Surface and interfacial free energies were measured by the ring-pull method using a torsion balance which had been calibrated with a 1-g weight; using this technique, values could be reproduced to ±0.1 mNm^{-2}. Measured values were corrected by the method of Harkins and Jordan,[4] which has been justified theoretically by Freud and Freud.[5] The correction factor (F) is a function of R^3/V and R/r, where R is the radius of the ring from its centre to the centre of the wire, r is the radius of the wire, and V is the volume of liquid raised above the free surface or interface at the time when the surface breaks. V can be obtained from the expression $V = M/(\rho_1 - \rho_2)$, where M is the mass of liquid raised above the free surface at the time of breaking, ρ_1 is the density of the liquid, and ρ_2 is either the density of air saturated with the vapour in measurements of surface free energies, or the density of *n*-hexadecane in measurements of interfacial free energies. As $\rho_1 \gg \rho_2$ in surface free energy measurements, the latter density has been taken as zero in these measurements. A fairly thick layer of *n*-hexadecane (about 10 mm) was required to give reproducible results for interfacial free energies. The layer needed to be sufficiently thick to contain the relatively large volume of water raised above the interface, due to the buoyancy of water in *n*-hexadecane.

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RESULTS AND DISCUSSION

For a liquid, the surface tension and surface free energy are numerically the same but dimensionally different. Surface free energies of water (γ_W) after being in contact with adhesive film (one microscope-slide casting of adhesive in about 7 cm^3 of water) for various times are given in Table I. It can be seen that surface free energies decreased from the value for pure water (72.8 mJ m^{-2}) within the first hour, and then remained fairly constant for the next month. A possible exception to this is the water which had been kept in contact with the film from VAE3; this was the only sample to show an overall downward trend in surface free energy.

TABLE I
Surface free energy of water after contact with adhesive films for various times

Adhesive film	γ_W (mJ m^{-2}) after contact for time indicated			
	1 hour	23 hours	52 hours	720 hours
ex VAVV	47.3	49.9	48.5	48.8
ex VAE1	38.9	37.0	36.5	37.3
ex VAE2	45.7	42.9	44.0	43.9
ex VAE3	53.2	50.6	47.9	45.4

Measurement error ±0.1 mJ m^{-2}

Results for a second experiment using double the amount of adhesive film and 5 cm^3 of water are given in Table II. Surface free energies with both amounts of adhesive film after 23–24 hours are in close agreement, indicating that the surface free energy lowering is not particularly dependent upon the amounts of adhesive and water used. Table II also includes values of interfacial free energies of the aqueous phases against *n*-hexadecane (γ_{HW}). Reported values of F[4] do not extend down to $R^3/V = 0.155$, which is the value obtained for the measurements of interfacial free energies; a value of F obtained by graphical extrapolation was used in these cases.

The surface free energy of a liquid is assumed to be the sum of a contribution from dispersive intermolecular forces (denoted by superscript D) and a contribution from polar intermolecular forces (denoted by superscript P). Thus for *n*-hexadecane and water we have, respectively:

$$\gamma_H = \gamma_H{}^D + \gamma_H{}^P \tag{1}$$

$$\gamma_W = \gamma_W{}^D + \gamma_W{}^P \tag{2}$$

The interfacial free energy between *n*-hexadecane and water (γ_{HW}) is assumed to be related to the surface free energy of water and that of *n*-hexadecane by equation (3) below. This is based upon Fowkes's assumption that the dispersive and polar components of interfacial free energy are the geometric means of the corresponding components of the surface free energies for the two liquids.[6]

$$\gamma_{HW} = \gamma_H + \gamma_W - 2(\gamma_H{}^D\gamma_W{}^D)^{1/2} - 2(\gamma_H{}^P\gamma_W{}^P)^{1/2} \tag{3}$$

n-hexadecane is a nonpolar liquid. It is widely assumed that the value of $\gamma_H{}^P$ for this liquid is zero. If so, then equation (3) becomes

$$\gamma_{HW} = \gamma_H + \gamma_W - 2(\gamma_H{}^D\gamma_W{}^D)^{1/2} \tag{4}$$

Values of $\gamma_W{}^D$ calculated from equation (4), together with the consequent values of $\gamma_W{}^P$ from equation (2), are given in Table II. The values obtained for these components for pure water are very close to the literature values of 21.8 and 51.0 mJ m^{-2} respectively. The values of $\gamma_W{}^D$ for the waters contaminated by contact with the various adhesive films are close together and probably the same within experimental error; the mean value and standard deviation are 27.7 ± 1.6 mJ m^{-2}. Our values are very similar to those obtained by Owens[7] for aqueous solutions of sodium alkyl sulphates.

The following equation gives the relationship between the thermodynamic work of adhesion, W′, for an interface in a wet environment in terms of the thermodynamic work of adhesion, W, for the same interface in a dry environment:

$$W' = W + 2\{\gamma_W - (\gamma_P{}^D\gamma_W{}^D)^{1/2} - (\gamma_P{}^P\gamma_W{}^P)^{1/2} - (\gamma_A{}^D\gamma_W{}^D)^{1/2} - (\gamma_A{}^P\gamma_W{}^P)^{1/2}\} \tag{5}$$

In this equation, $\gamma_P{}^D$ and $\gamma_P{}^P$ are, respectively, the dispersive and polar components of the surface free energy of the substrate (in our work polystyrene), $\gamma_A{}^D$ and $\gamma_A{}^P$ are those of the adhesive film, and $\gamma_W{}^D$ and $\gamma_W{}^P$ are those of water.

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TABLE II
Interfacial free energies between *n*-hexadecane and water which has been in contact with adhesive films for 24 hours, together with values of $\gamma_W{}^D$, $\gamma_W{}^P$ and W derived from these results

Aqueous phase	γ_W (mJ m^{-2})	F	γ_{HW} (mJ m^{-2})	$\gamma_W{}^D$ (mJ m^{-2})	$\gamma_W{}^P$ (mJ m^{-2})	W (mJ m^{-2})
pure water	74.1	1.14	51.9	22.5	51.6	
water contacted with film *ex* VAVV	47.4	1.008	18.8	28.6	18.8	6.8 ± 11.7
water contacted with film *ex* VAE1	33.6	0.910	6.5	27.1	6.5	−6.4 ± 7.2
water contacted with film *ex* VAE2	42.9	0.970	13.2	29.7	13.2	−6.2 ± 5.5
water contacted with film *ex* VAE3	47.5	1.016	19.8	27.7	19.8	−28.2 ± 10.3
water contacted with film *ex* VABA/W	34.4	0.940	9.4	25.1	9.3	−15.4 ± 8.3
water contacted with film *ex* VABA/S	36.7	0.930	8.4	28.3	8.4	−13.5 ± 8.7

We have used equation (5) to calculate thermodynamic work of adhesion for the interfaces between EPS and the various adhesive films in the water which they have contaminated. The values are given in Table II, together with standard errors calculated in a manner which we have described previously.[3] It can be seen that only the interface with VAVV adhesive has a positive value of W′. This interface is, therefore, predicted to be stable in the presence of both pure water and water which has been contaminated by contact with the adhesive film. The other interfaces all have negative values of W′ and are, therefore, predicted to have a tendency spontaneously to disbond in the presence of water which has been contaminated by contact with the adhesive film. However, the standard errors are high and the experimental procedure used in this work probably represents a very severe case, in that a relatively small amount of water was contacted with the adhesive films. In some practical applications, the effect of water may be to wash away the surface-active substances which cause the surface free energy of water to be reduced by contamination.

We have previously measured the breaking strengths of blocks of EPS beads bonded with the various adhesives[3] after immersion in water. The blocks bonded with VAE3 adhesive all disintegrated in water, but the others held together and had measurable strengths. The data given in Table II show that VAE3-EPS interfaces in an environment of water contaminated by contact with the adhesive film are predicted to be much less stable than interfaces between EPS and the other adhesives.

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THEORETICAL RELATIONSHIP BETWEEN WORK OF ADHESION AND SURFACE FREE ENERGY OF AN AQUEOUS SOLUTION

It is assumed that any lowering of the surface free energy of water is due to a reduction in the polar component, with the dispersive component remaining essentially constant. Equation 5 can then be written as

$$W' = W + 2\{\gamma_W - (\gamma_P^D\gamma_W^D)^{1/2} - (\gamma_P^P[\gamma_W - \gamma_W^D])^{1/2} - (\gamma_A^D\gamma_W^D)^{1/2} - (\gamma_A^P[\gamma_W - \gamma_W^D])^{1/2}\} \tag{6}$$

Written in this way, the dependence of W′ upon the surface free energies of water is expressed in terms of the single variable γ_W. The assumption that γ_W^D is constant seems justified because molecules of surface-active substances have a polar hydrophilic head and a hydrophobic non-polar tail, and it is the latter moiety which will be orientated towards any organic phase, such as an adhesive film or a polymer substrate which is placed in a solution of a surface-active substance.

Values of W′ as a function of γ_W have been calculated for the various EPS-adhesive bonds using the values of the dispersive and polar components of surface free energy which are shown in Table III. These latter values were determined by us from measurements of contact angles.[3] The calculated values of W′ are plotted against γ_W in Figures 1 and 2. For Figure 1, a value of 21.8 mJ m^{-2} has been used for the dispersive component of the surface free energy of water; for Figure 2, a value of 27.7 mJ m^{-2} has been used. These are, respectively, the literature value for pure water and the average value which we obtained for the waters contaminated by contact with the adhesive film. The differences in the values of W′ calculated using the two values of γ_W^D are not very great, and are probably less than the uncertainties arising from errors in the quantities used from Table III.

The loci in both figures are curves. All the interfaces have their highest value of W′, and are therefore most stable, in pure water (for which $\gamma_W = 72.8$ mJ m^{-2}). The value of W′ falls as γ_W is lowered, until a minimum is reached. There is then a small increase in W′. Bonds formed between EPS and VAVV, VAE1, VAE2 and VABA are thus predicted to be thermodynamically stable as long as γ_W exceeds a certain critical value, but are thermodynamically unstable for values of γ_W below this value. Bonds with VAE3 are predicted to be always thermodynamically unstable in contact with an aqueous phase.

TABLE III
Dispersive and polar components of surface free energy of air-cast adhesive films and of EPS

Surface	γ^D (mJ m^{-2})	γ^P (mJ m^{-2})
VAVV film	16.5 ± 5.5	12.4 ± 2.7
VAE1 film	15.8 ± 2.8	18.6 ± 1.7
VAE2 film	11.9 ± 0.4	24.4 ± 1.1
VAE3 film	4.8 ± 2.2	69.2 ± 4.8
VABA/S film	6.4 ± 2.1	38.5 ± 6.3
VABA/W film	6.4 ± 2.1	38.5 ± 6.3
EPS	25.5 ± 2.9	0.4 ± 0.4

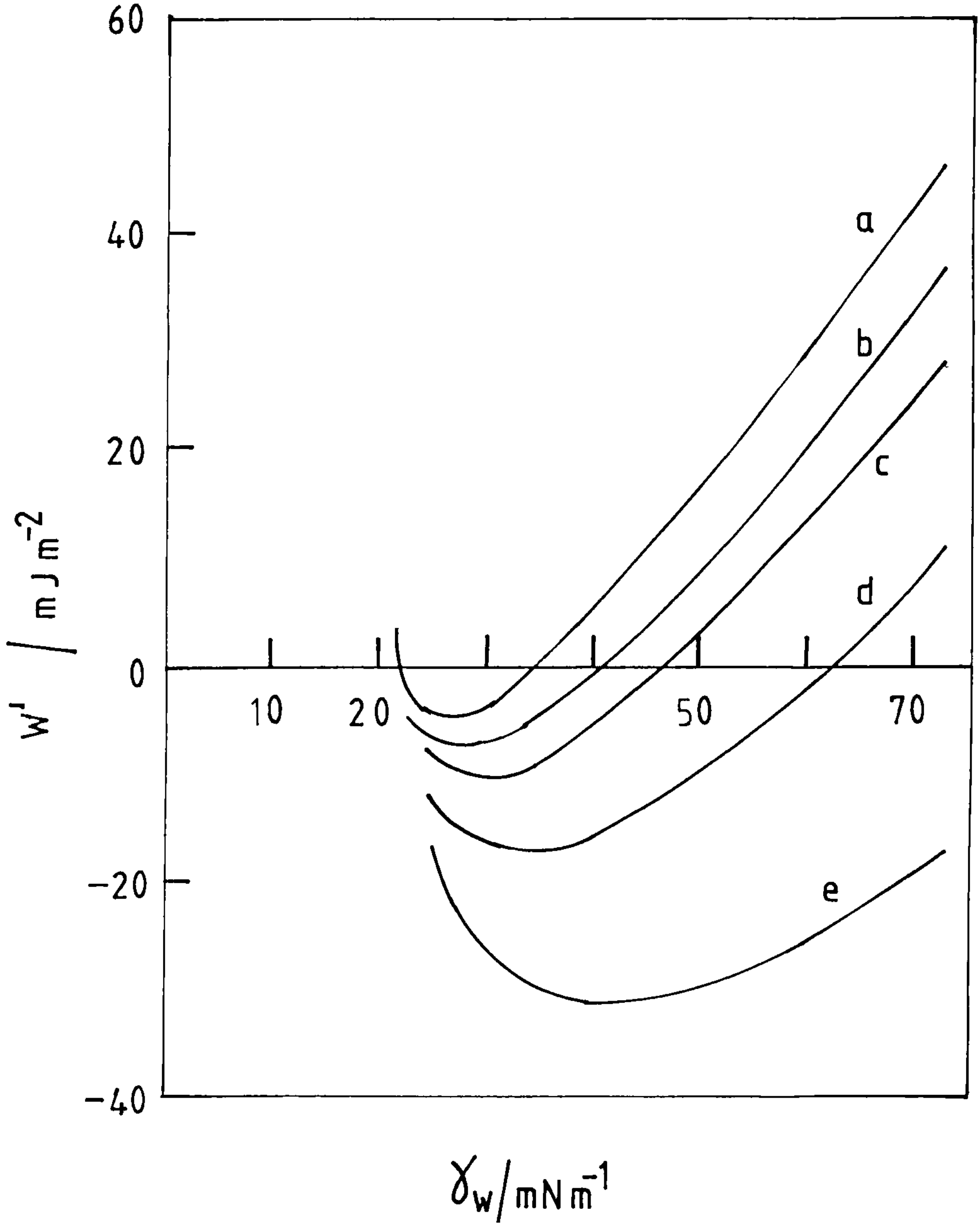

FIGURE 1 Dependence of work of adhesion upon the surface free energy of the aqueous phase for adhesive/EPS interfaces, calculated taking $\gamma_W{}^D$ as 21.8 mJ m^{-2}. Adhesives are identified as follows: a = VAVV, b = VAE1, c = VAE2, d = VABA/S and VABA/W, and e = VAE3. All the loci become slightly positive just above $\gamma_W = 20$ mJ m^{-2}, and are all very close to the locus of a. They have been omitted here for reasons of clarity.

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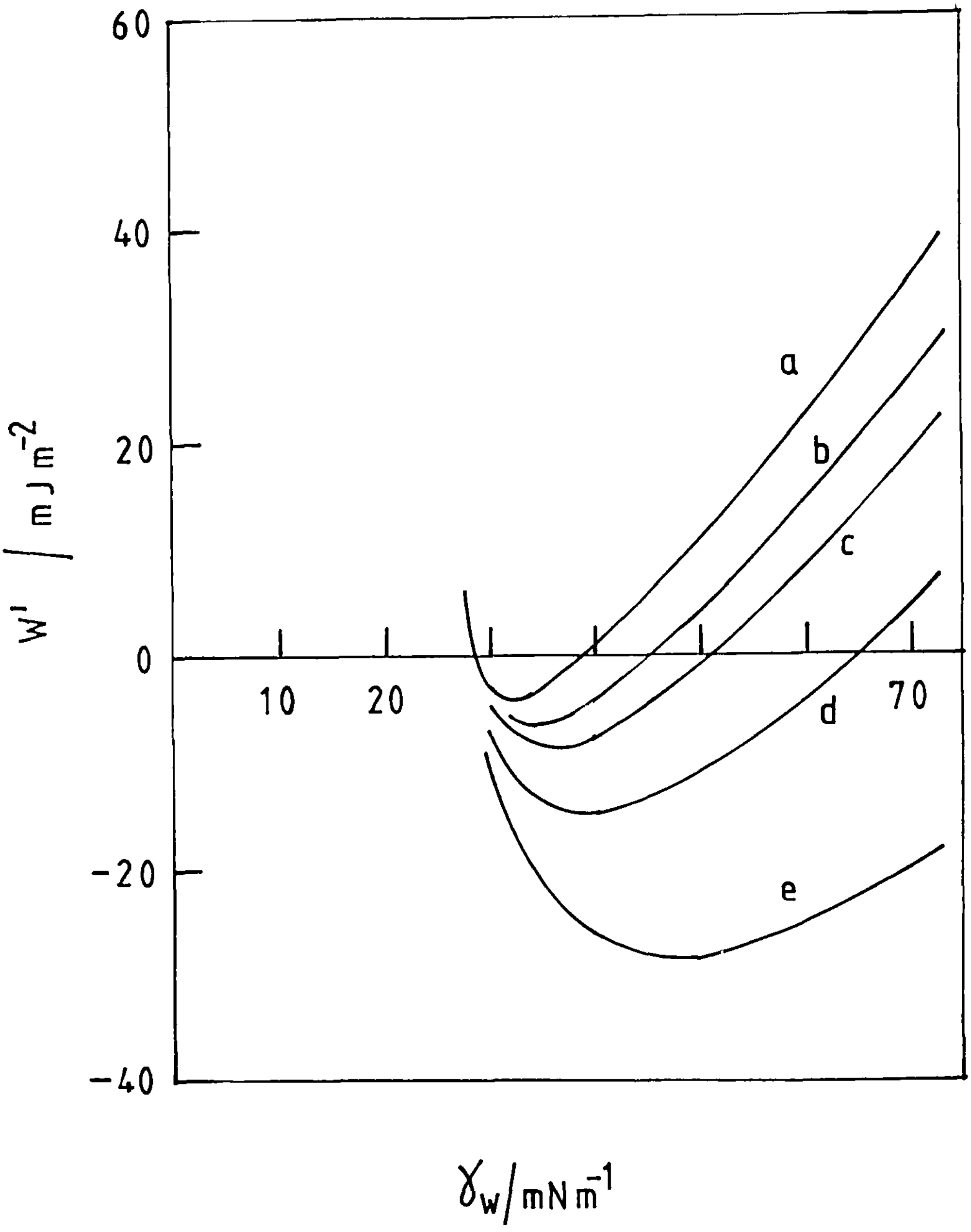

FIGURE 2 Dependence of work of adhesion upon the surface free energy of the aqueous phase for adhesive/EPS interfaces, calculated taking $\gamma_W{}^D$ as 27.7 mJ m^{-2}. Adhesives are identified as follows: a = VAVV, b = VAE1, c = VAE2, d = VABA/S, and VABA/W and e = VAE3. All the loci become slightly positive just above $\gamma_W = 20$ mJ m^{-2}, and are all very close to the locus of a. They have been omitted here for reasons of clarity.

The value of γ_W at which the work of adhesion is a minimum, denoted by ($\gamma_{W,MIN}$), can be obtained by differentiation of equation (6) with respect to γ_W, and equating the differential coefficient to zero. This gives

$$\gamma_{W,MIN} = \gamma_W^D + \frac{1}{4}[(\gamma_P^P)^{1/2} + (\gamma_A^P)^{1/2}]^2 \tag{7}$$

Values of $\gamma_{W,MIN}$ calculated from this equation are given in Table IV, together with the values of W′ at this point. The latter are obtained by substituting $\gamma_W = \gamma_{W,MIN}$ in equation (6).

Also of interest are the values of γ_W at which W′ is zero, denoted by $\gamma_{W,CRIT}$. These are the values of γ_W at which the adhesive interface makes the transition from thermodynamic stability to thermodynamic instability as γ_W changes. The values of $\gamma_{W,CRIT}$ are obtained by setting W′ = 0 in equation (6), and then solving the resultant equation for γ_W. The equation to be solved is

$$\begin{aligned} W + 2\{\gamma_{W,CRIT} - (\gamma_P^D\gamma_W^D)^{1/2} - (\gamma_P^P[\gamma_{W,CRIT} - \gamma_W^D])^{1/2} - \\ (\gamma_A^D\gamma_W^D)^{1/2} - (\gamma_A^P[\gamma_{W,CRIT} - \gamma_W^D])^{1/2}\} = 0 \end{aligned} \tag{8}$$

Equation (8) can be rearranged to give

$$\begin{aligned} \gamma_{W,CRIT} - [(\gamma_P^P)^{1/2} + (\gamma_A^P)^{1/2}][\gamma_{W,CRIT} - \gamma_W^D]^{1/2} = \\ (\gamma_P^D\gamma_W^D)^{1/2} + (\gamma_A^D\gamma_W^D)^{1/2} - \frac{1}{2}W \end{aligned}$$

This can be written in the form

$$\gamma_{W,CRIT} - \lambda(\gamma_{W,CRIT} - \gamma_W^D)^{1/2} = \mu$$

where λ and μ are constants such that

$$\lambda = (\gamma_P^P)^{1/2} + (\gamma_A^P)^{1/2} \tag{9}$$

and

$$\mu = (\gamma_P^D\gamma_W^D)^{1/2} + (\gamma_A^D\gamma_W^D)^{1/2} - \frac{1}{2}W \tag{10}$$

TABLE IV

Surface free energy of water, $\gamma_{W,MIN}$ at which thermodynamic work of adhesion is a minimum, together with minimum value of thermodynamic work of adhesion, W'_{MIN}

Adhesive bond	values using $\gamma_W^D = 21.8$ mJ m^{-2}		values using $\gamma_W^D = 27.7$ mJ m^{-2}	
	$\gamma_{W,MIN}$ (mJ m^{-2})	W'_{MIN} (mJ m^{-2})	$\gamma_{W,MIN}$ (mJ m^{-2})	W'_{MIN} (mJ m^{-2})
VAVV-EPS	26.1	−4.6	32.0	−3.7
VAE1-EPS	27.9	−7.3	33.8	−6.2
VAE2-EPS	29.6	−10.2	35.5	−8.5
VAE3-EPS	41.8	−31.4	47.7	−28.2
VABA/S-EPS	33.5	−17.1	39.4	−14.4
VABA/W-EPS	33.5	−17.1	39.4	−14.4

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Thus the value of $\gamma_{W,CRIT}$ must be such that

$$\lambda(\gamma_{W,CRIT} - \gamma_W{}^D)^{1/2} = \gamma_{W,CRIT} - \mu$$

i.e.,

$$\gamma_{W,CRIT}{}^2 - (2\mu + \lambda^2)\gamma_{W,CRIT} + \mu^2 + \lambda^2\gamma_W{}^D = 0$$

i.e.,

$$(\gamma_{W,CRIT})^2 + B\gamma_{W,CRIT} + C = 0 \tag{11}$$

where $B = -(2\mu + \lambda^2)$ and $C = \mu^2 + \lambda^2\gamma_W{}^D$. Equation (11) is a quadratic in $\gamma_{W,CRIT}$. Its roots are

$$\gamma_{W,CRIT} = \frac{-B \pm (B^2 - 4C)^{1/2}}{2} \tag{12}$$

Of the two solutions to equation (12), the higher value gives the value of γ_W at which the interface first becomes unstable as the surface free energy of water is lowered. The lower values of $\gamma_{W,CRIT}$ are probably not experimentally attainable. Values of $\gamma_{W,CRIT}$ calculated for the two different values of $\gamma_W{}^D$ are given in Table V. VAE3/EPS interfaces are predicted to be stable in the presence of water only if the surface energy free energy exceeds 90 mJ m^{-2}. This is, of course, not realisable in practice.

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TABLE V
Upper values of surface free energy of water, $\gamma_{W,CRIT}$ at which thermodynamic work of adhesion is zero

Adhesive bond	values using $\gamma_W{}^D = 21.8$ mJ m^{-2} (mJ m^{-2})	values using $\gamma_W{}^D = 27.7$ mJ m^{-2} (mJ m^{-2})
VAVV-EPS	35.3	40.0
VAE1-EPS	40.6	45.2
VAE2-EPS	47.3	51.3
VAE3-EPS	92.6	95.1
VABA/S-EPS	62.5	65.3
VABA/W-EPS	62.5	65.3

CONCLUSIONS

i) In contact with films from the emulsion adhesives, the surface free energy of water falls during the first 24 hours, and then remains fairly constant. The surface free energy is not sensitive to the ratio of adhesive film to water.

ii) The surface free energy of water is not lowered significantly by contact with EPS beads.

iii) The dispersive component of the surface free energy of water after contact with the various adhesive films is 27.7 ± 1.6 mJ m^{-2}.

iv) The work of adhesion of adhesive-EPS bonds is less in water which has been contaminated by contact with the adhesive film than in pure water.

v) An equation has been derived which shows that adhesive bonds become less thermodynamically stable as the surface free energy of a contiguous water phase is lowered, but eventually reaches a minimum and may then increase slightly.

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