Consideration of adhesion to modified container walls, by use of surface energy and polarity data, and Lewis acid-Lewis base interactions

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Summary

It is acknowledged that the labelling of pharmaceutical products is essential on legal and ethical grounds. The desirability of using high speed filling operations for large bulk liquid products, has resulted in the surface coating of bottles with lubricant films, to allow smoother movement through the filling process. In this study the adhesion to bottles which have had one of two different types of lubrication treatment is considered. Simple empirical testing demonstrates that certain combinations of bottle coat and adhesive will result in adhesive failure (loss of label), whilst others are acceptable. The interaction between the adhesive and the bottles has been modelled using theories based on surface energy data. Both the polar and dispersion view of surface energy components, and the concepts of viewing the polar contribution to surface energy as comprising of non-additive Lewis acid-Lewis base components (with particular reference to monopolar surfaces) are considered. It was found that both methods of considering surface energy data gave some indication of adhesive performance, but only the acid-base approach gave a method of correlating predicted behaviour with empirical use tests. It is probable that the acid-base approach is the more appropriate for general application.

Introduction

There are many large volume products which are filled into glass bottles on high speed production lines. It is not unusual to treat glass bottles with lubricants in order to speed the passage through filling and labelling processes. It is a legal and ethical necessity that pharmaceutical

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products are not only filled correctly, but are also labelled in such a way that the essential product identification and instructions remain in place.

The aim of this publication is to consider the possible effects of surface lubrication on glass, in terms of the adhesion of labels to the product. In particular, predictions of interfacial interactions will be related to typical empirical testing procedures which are currently utilised. A further aim is to compare two approaches to considering surface energy terms, namely polar and dispersion forces, and the more recent theories of acid-base interactions (the second of which has not often

appeared in pharmaceutical literature). It is obvious, however, that the approaches used here can be applied to many other interfacial systems of pharmaceutical interest.

Theory

Considering interfacial phenomena in terms of surface energies and their polar and dispersion components

Over many years, in situations where interfacial phenomena are actually assessed, it has become usual to define surface energies of the systems, and to split the surface energy terms into two additive components, i.e., dispersion and polar forces. Numerous theories exist by which polar and dispersion components can be calculated, but one approach which is commonly utilised is that of Wu (1971), which in combination with the Young equation gives:

$$\gamma_L(1 + \cos\theta) = 4\left[\frac{\gamma_L^p \cdot \gamma_S^p}{\gamma_L^p + \gamma_S^p} + \frac{\gamma_L^d \cdot \gamma_S^d}{\gamma_L^d + \gamma_S^d}\right] \quad (1)$$

where θ is the contact angle formed by a liquid phase on the solid, and γ relates to the surface energy terms of both phases (liquid, L; and solid, S), and where the polar (p) and dispersion (d) contributions to surface energy sum to equal the total surface energy (e.g., $\gamma_L = \gamma_L^p + \gamma_L^d$). From Eqn 1, it is possible to iteratively solve for the polar and dispersion components of the surface energy of a solid, if contact angles are measured on that solid using two different liquids, each of known surface tension and polarity.

Having obtained an assessment of the surface energy terms, it is possible to consider interactions between materials by considering W_c, the work of cohesion (which is numerically equal to twice the surface energy), and the work of adhesion (W_a). The work of adhesion between any two materials (phases 1 and 2) can be calculated according to Eqn 2:

$$W_a = 4\left[\frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p} + \frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d}\right] \quad (2)$$

The spreading coefficient of phase 1 over phase 2 (S) can be calculated from the work of adhesion between the two phases, minus the work of cohesion of phase 1 (and similarly for phase 2 over phase 1, by substituting the work of cohesion of phase 2).

Considering interfacial phenomena in terms of surface energies and Lifshitz-van der Waals, and acid-base components

Based upon the failure of simple polar and dispersion contributions of surface energy to model certain liquid-liquid interfacial phenomena, many workers have now abandoned the original theories, and attempted explanations of interfacial phenomena in terms of a non-polar contribution, which is composed of Lifshitz-van der Waals (LW) forces, and a polar term, which is divided into non-additive Lewis acid-Lewis base (AB) contributions. Thus, the total surface energy (γ^{TOT}) is the sum of γ^{LW} and γ^{AB}, but γ^{AB} is not equal to the sum of the electron donor and electron receptor contributions (see below).

The LW contribution to surface energies can be calculated from a contact angle measurement on the solid, using an apolar liquid (for which the surface tension $= \gamma^{LW}$):

$$1 + \cos\theta = 2\left(\gamma_L^{LW}/\gamma_S^{LW}\right)^{0.5} \quad (3)$$

The contribution of acid-base components can be determined from contact angles on the solid with two liquids which have known LW and AB values (NB: LW and AB values for certain liquids have been determined and published, e.g., Van Oss et al., 1992), using the following theory.

Acid-base contributions to surface energy are divided into electron donor and electron receptor components:

$$\gamma^{AB} = (\gamma^+ \cdot \gamma^-)^{0.5} \quad (4)$$

Using

$$\gamma_L^{TOT}(1 + \cos\theta) = 2\left(\left(\gamma_S^{LW} \cdot \gamma_L^{LW}\right)^{0.5}\right.$$
$$+ \left(\gamma_S^+ \cdot \gamma_L^-\right)^{0.5}$$
$$\left. + \left(\gamma_S^- \cdot \gamma_L^+\right)^{0.5}\right) \quad (5)$$

It is now possible to calculate the unknown values for the solid. It should be stated that all values of γ^+ and γ^- are defined relative to an arbitrary assessment for the contributions for water, which is taken to be that $\gamma^+ = \gamma^- = 25.5$. Details of the derivation of equations (Eqns 3–5), and calculation methods can be obtained elsewhere (e.g., Van Oss et al., 1987, 1988a,b, 1989).

Non-additive AB contributions, and monopolar surfaces

Van Oss et al. (e.g., 1987, 1989) have reported that there is no reason why a surface should have an equal γ^+ and γ^- contribution. In fact, many surfaces will be monopolar (i.e., have only γ^+ or γ^-, but not both). From Eqn 5 it is clear that the electron donor and electron receptor contributions to the overall acid base term (and hence the total surface energy) are not additive.

Monopolar surfaces are a common occurrence, and if it is accepted that the monopole will only interact with an opposite charge, then it can be seen that a monopolar region will make no contribution to its own surface energy (as for example, a surface which contains only electron donor regions will have no electron receptor regions with which to form cohesive interactions). Thus, monopolar surfaces will have $\gamma^{AB} = 0$, and $\gamma^{TOT} = \gamma^{LW}$, however, if the monopolar surface (e.g., an electron donor) comes into contact with another phase which has either a finite γ^{AB}, or is monopolar in the opposite sense (i.e., an electron receptor), then polar interaction will occur. This model has been used to demonstrate why certain interfacial interactions occur, despite apparent lack of polarity of one component. From this reasoning, the acid-base interactions are potentially far more discriminating than the consideration of 'polar' interactions.

Materials and Methods

Probe liquids

Contact angles were measured using double distilled water, ethanediol (Sigma) and methylene iodide (Aldrich).

Bottles

Glass bottles were investigated which had been passed through two different treatment processes. Type 1 bottles were treated with a tin based compound when hot (to give strength, and to facilitate binding of the lubricant), and then subsequently passed through vaporised oleic acid. Type 2 bottles were also tin treated, then passed through a spray of polyethylene emulsion, before being treated with the oleic acid vapour. The bottles had one flat face on which it was possible to position a small drop of liquid suitable for contact angle assessment. The bottles were positioned on a moveable platform, with the flat surface horizontal, a drop of liquid (approx. 20 μl) was allowed to form on the needle of an Agla syringe, and the platform was moved up to allow the bottle to touch the drop. Instantly, the drop was photographed, and the angle measured by construction on the print. Usual precautions were taken, including mounting apparatus on a vibration proof table, use of a non-heating light source, and extensive cleaning prior to use of the syringe. The bottle was not touched by hand after coating. At least four separate drops were photographed for each liquid on each coated surface, and each photograph was measured three times to assess contact angle.

Adhesives

Three adhesives were considered, which were a casein based formulation (Eticol 90, National Adhesives), a starch based system (Eticol 372) and a latex based system (Polyloc 42).

All adhesives were assessed for contact angle by spreading a coat onto thin glass plates (using a rod with a thin wire wrapped around it (in the manner of an electric fire element), which was found to deposit a uniform thin film of adhesive across the glass, which dried to form a smooth flat surface. After the plates were coated on both sides, they were used in a Wilhelmy plate apparatus (Cahn DCA, method as reported before, see Zajic and Buckton (1990)) to determine contact angle results. At least six replicate plates were used for each adhesive-liquid combination.

Empirical peal test

A simple peal test was performed, by using the adhesives to stick labels to the bottle surface, allowing the adhesive to dry for 24 h, and then removing the label by pulling from one side. The approximate percentage of adhering paper remaining was recorded as a crude guide to adhesion efficiency.

Results and Discussion

The contact angle data from which the surface energy parameters were calculated are presented in Table 1.

The label tear experiments are empirical, and poorly quantified, but do represent a guide to the success of the adhesion process. In these experiments casein adhesive was found to adhere well to type 1 glass (reasonably high% of paper residue after tear), but to fail with type 2 glass (often 0% fibre residue on glass). Starch adhesive provided acceptable adhesion on both types of coated glass, with very high fibre retention (over 95%) on type 1 glass, and slightly less on type 2. The latex adhesive was found to give over 95% fibre retention for both surfaces.

TABLE 1

Mean measured contact angle results (all in degrees), for different liquids on the coated glass and the adhesives

	θ for water	θ for ethane-diol	θ for methyl-ene iodide
Latex	69.4 (2.0)	68.5 (1.29)	70.0 (1.4)
Starch	97.0 (0.9)	63.3 (3.2)	58.7 (1.4)
Casein	66.1 (0.8)	61.1 (0.6)	67.7 (0.8)
Coat type 1	60.5 (6.4)	45.0 (4.5)	50.7 (4.1)
Coat type 2	71.6 (3.3)	65.2 (4.8)	53.6 (5.3)

Results being quoted as means (±standard deviation), the higher SD values for the results on the bottles reflect both a less suitable method, and a variability in regions of the glass coating system (this variability will reflect in the performance of the product, so all data were used in producing the average, outliers were never discarded).

TABLE 2

Calculated surface energies of the solid surfaces, using water and methylene iodide data (harmonic mean calculation), with works of cohesion (W_c)

	Dispersion (mJ m^{-2})	Polar (mJ m^{-2})	Total (mJ m^{-2})	W_c (mJ m^{-2})
Latex	25.4	16.5	41.9	83.8
Starch	27.8	27.1	54.9	109.8
Casein	31.9	19.2	51.1	102.2
Coat type 2	33.3	12.6	45.9	91.8
Coat type 1	34.8	17.6	52.4	104.8

Use of polar and dispersion components of surface energy

The surface energy terms, and their polar and dispersion components have been calculated (using Eqn 1), and are presented in Table 2 along with the work of cohesion of each material. The works of adhesion between the different combinations of adhesives and coating surfaces are presented in Table 3, as are the spreading coefficients of the adhesives over the coated glass surfaces.

The spreading coefficients (Table 3) indicate that the spreading of starch adhesive is not favoured on either glass surface (i.e., the work of cohesion is greater than the work of adhesion between Eticol and the coated glasses), and that the spreading would be worse on type 2 surfaces than type 1. However, the peal tests indicated that starch adhesive gives reasonable adhesion to both surfaces (especially type 1). The spreading coefficients for casein adhesive indicate that it

TABLE 3

Works of adhesion and spreading coefficients of glue over bottle, utilising polar and dispersion components of surface energy

	Spreading coefficient (mJ m^{-2})	W_a (mJ m^{-2})
Latex/coat type 2	2.2	86.0
Latex/coat type 1	9.1	92.8
Starch/coat type 2	− 14.8	95.0
Starch/coat type 1	− 5.2	104.6
Casein/coat type 2	− 4.2	98.0
Casein/coat type 1	1.0	103.2

has a favourable interaction with type 1, but a disfavoured spreading over type 2 surfaces: this is in agreement with the peal tests. Finally, the spreading of latex adhesive over both surfaces is favoured, and this is found to be an effective adhesive.

The spreading coefficients for latex and casein adhesive are in good agreement with observed behaviour, however, the relationship is not ideal with starch adhesive.

It is possible to reflect upon the plane of failure for each system. Failure can occur in any plan of adhesion or cohesion, which could include the adhesion of the coat to the glass, the cohesion of the coat (assuming that the type 2 coat behaves as one surface, which is not necessarily true), the adhesion of the adhesive to the coat, in cohesion in the adhesive film, in adhesion at the adhesive paper join, or in cohesion in the label. In practice, an adhesive is said to be effective when the system fails in cohesion within the label, all other scenarios are deemed 'adhesive failure' (whilst clearly they could be cohesive failure). By considering the magnitude of the works of adhesion and cohesion, it is possible to consider which would be the weakest out of (1) the cohesion of the coat, (2) the coat/adhesive join, (3) the cohesion of the adhesive. A value is not available for the adhesion of the coat to the tin treated glass, equally the adhesive paper interface has not been considered.

For the starch adhesive system, the magnitude of the works of adhesion and cohesion would indicate that failure would be at the adhesive joint between the glue and the coat for type 1 surfaces, but in cohesion in the coat for type 2 surfaces (Tables 2 and 3). For casein adhesive, the magnitude of the work of adhesion (glue to surface), and the two works of cohesion are very similar for type 1 surfaces (103.2 (Table 3), 102.2 and 104.8 (Table 2)), consequently, it is likely that failure could occur in any region. On type 2 surfaces, however, failure would be predicted in the cohesive plane of the bottle coat. For latex adhesive the works of adhesion are lower than for either of the Eticol products, as is the work of cohesion of the adhesive. It would be predicted that the failure would be in cohesion within the

TABLE 4

'Acid-base' interfacial parameters (all in mJ m^{-2})

	γ^{LW}	γ^{AB}	γ^+	γ^-	γ^{TOT}
Starch	29.3	0.875	0.4	0.5	30.2
Casein	24.2	3.37	0.1	28.5	27.6
Latex	22.8	0	0	28.3	22.8
Coat type 2	32.2	0	0	17.9	32.2
Coat type 1	33.9	3.1	0.1	24.7	37.0

adhesive, when used on either surface 1 or 2. As latex adhesive is found to be a successful adhesive, it can be concluded that the cohesive failure within the paper is the preferred line of failure, demonstrating that all the cohesive and adhesive energies for the Eticol products and coating materials are also of greater strength than the cohesive energy of the paper. It follows that the failure of the Eticol products on (especially) type 2 surfaces, must be linked to an inability to spread over the coated glass.

The correlations obtained using this method of data interpretation are not perfect, they are probably not a reasonable method by which to assess adhesion. They do, however, indicate that improved adhesion can be achieved by lowering the cohesive energy of the glue to promote spreading.

Use of the acid-base approach

The calculated values for γ^{LW}, γ^{AB}, γ^+, γ^- and γ^{TOT} are presented in Table 4. It can be seen that the overall acid-base term (γ^{AB}) is rather small in all cases, and makes only a slight contribution to the total surface energy, because the surfaces are predominantly, or in some cases entirely, monopolar. It has been reported (Van Oss et al., 1987) that many surfaces are monopolar in nature, and the majority of these are γ^- monopoles. The fact that the adhesives and the coated surfaces are both predominantly monopolar, but both γ^-, will tend to limit polar interaction.

It is possible to determine a form of spreading coefficient for the adhesive over the surfaces, by considering the difference between the work of adhesion and cohesion for each pair. The work of cohesion for any material can be regarded as twice the value of γ^{TOT}. The work of adhesion

TABLE 5

The interfacial tensions, works of adhesion and spreading coefficients for adhesive-coated glass combinations, calculated from the data in Table 4: in each case the spreading of the adhesive over the coat is considered (all values in mJ m^{-2})

	γ_{12}^{TOT}	W_a	Spreading coefficient
Latex/coat type 2	0.8	54.2	8.6
Latex/coat type 1	0.9	58.9	13.3
Starch/coat type 2	−4.4	66.8	6.4
Starch/coat type 1	−2.5	69.7	9.3
Casein/coat type 2	1.3	58.5	3.3
Casein/coat type 1	0.8	63.8	8.6

(W_a) between any two phases (1 and 2) is obtained from Eqn 6:

$$W_a = \gamma_1^{TOT} + \gamma_2^{TOT} - \gamma_{12}^{TOT} \tag{6}$$

where γ_{12}^{TOT} is the total interfacial tension (i.e., that due to AB and LW forces) between the two phases, which is determined from:

$$\gamma_{12}^{TOT} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 + 2\left(\sqrt{\gamma_1^+ \cdot \gamma_1^-}\right.$$

$$\left. + \sqrt{\gamma_2^+ \cdot \gamma_2^-} - \sqrt{\gamma_1^+ \cdot \gamma_2^-} - \sqrt{\gamma_1^- \cdot \gamma_2^+}\right) \tag{7}$$

The interfacial tensions, works of adhesion and spreading coefficients are presented in Table 5. The work of adhesion values demonstrate that in each case the adhesion to type 2 coatings are less favoured than the same adhesive to type 1 coatings. However, latex adhesive was found to be the most effective adhesive (empirical tests), and this has the lowest W_a values, thus the magnitude of the work of adhesion does not seem to be the critical factor in determining adhesive efficiency. The spreading coefficients are also lower in each case for the type 2 surface (compared to the same adhesive on type 1 surfaces). This also indicates that the adhesion to type 2 surfaces will be less favourable than to type 1, as the adhesive will be less able to spread. With the spreading coefficients, there is a correlation with perceived adhesive efficiency, in that the value is lowest for casein adhesive, then starch adhesive, then the latex adhesive. This ranking is the same for both surfaces, but presumably becomes significant only for the type 2 surface, as the spreading coefficients are lower. The fact that the spreading coefficients are all positive implies that spreading should be favourable in each situation, but from the observations that adhesion fails for the systems with lowest spreading coefficients, it is probable that these low values are close enough to zero to be problematic. It is also clear that the bottle surfaces are not homogeneous, and that the coating will vary, consequently, the spreading over the bottles with low spreading coefficients may be at risk, as the variation in bottle surface may lead to a resistance to spreading such that the spreading coefficient is negative at certain points (whilst for the systems which have higher spreading coefficients, the coating variability may only alter the magnitude of the positive number).

The results demonstrate that certain properties of adhesives are desirable (i.e., high spreading coefficient, which would relate to low surface energy). It is also interesting to postulate that the development of an adhesive with a larger γ^+ component would result in a more favourable interaction with the coating surfaces, and thus a higher work of adhesion. However, this would also contribute to the total surface energy of the system, and thus significantly increase the work of cohesion, and consequently limit spreading. A compromise for maximum interaction would be an adhesive with low surface energy, which would aid spreading, and for these coated glass surfaces, spreading would be aided further if the adhesive was a γ^+ monopole (which would not contribute to the total surface energy or the work of cohesion, but which would improve the work of adhesion).

This publication considers the situation of the binding of adhesive to a coated surface, with application to a packaging problem, but clearly the technique, and the data manipulation approach, has application to many other areas of the pharmaceutical sciences (e.g., any aspect of wetting, detergency, dispersion, coating, adhesion, etc.).

Conclusion

Unfortunately, the true effectiveness of adhesives has been assessed by a simple empirical test, to which the interfacial studies have had to be related. It is never desirable to have to relate theoretical concepts to such a crude use test.

The two methods of considering interfacial phenomena relating to adhesion seemed to fit with the observed adhesion efficiency to some extent. The application of acid-base concepts seemed to be a more useful approach to modelling of interfacial phenomena, with spreading coefficients correlating with observed performance. In situations where monopolar materials of both γ^+ and γ^- exist, it is even more likely that the acid-base approach would be most useful, as its use would predict interactions that would not be expected by simple polar and dispersion considerations.

Acknowledgements

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