Influence of Surface Free Energies and Cohesion Parameters on Pharmaceutical Material Interaction Parameters–Theoretical Simulations

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Purpose. The aim of this study was to perform simulations of the influence of surface free energies and cohesion parameters on various interaction parameters within binary systems.

Methods. Using predictive equations derived from surface free energies and cohesion parameters originally proposed by Wu (2, 3) and by Rowe (4), values of interfacial tension, spreading and reduced spreading coefficients, interaction parameter and strength of interaction were simulated by means of a data processor. The influence of polar and disperse fractions of the two interacting materials was also examined.

Results. From the simulations, boundary conditions could be drawn: minimum interfacial tension, positive spreading coefficient, reduced spreading coefficient superior to unity, maximum value of the interaction parameter or of the strength of interaction.

Conclusions. Simulations of the various parameters will help the formulator to select proper materials, eg. an agent that will efficiently bind some powdered substrate, a film-forming agent that will properly coat given cores or a material that will enhibit high interaction with a substrate.

KEY WORDS: surface free energy; cohesion parameter; modeling; interfacial tension; spreading coefficient; interaction parameter; strength of interaction.

INTRODUCTION

Many, if not all, of pharmaceutical processes depend on the cohesive and adhesive interactions between the materials used during the preparation of the final product. Providing a simple method of correlating and predicting the cohesive and adhesive properties of materials from a knowledge of the properties of the individual components only would be of great interest for pharmaceutical technology. This is the aim of the different theories on surface free energies and cohesion parameters.

Despite the controversy on the various components of surface tension and cohesion parameters, we used only the polar and non-polar (disperse) fractions. The hydrogen fraction was not considered as an independent fraction but was assumed to be included in the polar fraction. This choice was made for both theoretical and experimental reasons. Theoretically, surface tension and cohesion parameter can be divided into more than two fractions, depending on the interactions considered: hydrogen bonding, acid-base, Keesom (or orientation), and Debye (or induction) interactions. Unfortunately, there is still some controversy regarding the fractions that should be used. Experimentally, the determination of more than two fractions involves the addition of the experimental errors on each fractions and the benefit for the accuracy of the resulting total surface tension or cohesion parameter is not clear. Furthermore, an easy technique using contact angle measurements developed by Zografi (1) offers a convenient means to estimate the surface free energy and the contributions of non-polar and polar forces of organic pharmaceutical solid surfaces. This technique will soon be used in our laboratory to confirm the theoretical conclusions presented here.

Various parameters are derived from the different theories on surface free energy and cohesion parameter (2–4). These derived parameters include interfacial tension (${}^{AB}\gamma$), spreading (${}^{B/A}\lambda$) and reduced spreading coefficients (${}^{B/A}\lambda_r$), interaction parameter (${}^{AB}\phi$), and strength of interaction (${}^{AB}\sigma$), between two materials A and B. These parameters have been successfully applied to the pharmaceutical field (5–10) but the influence of the polar and disperse fractions on the surface free energy and the cohesion parameter has never been determined. The aim of this paper is to establish graphically the influence of surface free energy and cohesion parameter as well as of the polar and disperse fractions on the derived parameters. Such simulations, never performed to our knowledge, will help the formulator to select the best binder, disintegrant or coating agent for his formulation. Experimental work is now being performed to confirm the predicted values of the simulations.

THE PREDICTIVE EQUATIONS DERIVED FROM SURFACE FREE ENERGY AND COHESION PARAMETER

Interfacial Tension

The interfacial free energy or interfacial tension is the excess free energy due to the existence of an interface arising from the unbalanced molecular forces (11). The SI unit of interfacial and surface free energies is $\mathrm{J.m^{-2}}$ or $\mathrm{N.m^{-1}}$. The basic equation that applies to wetting is the Young equation, which is based on the change in free energy caused by an increase in the area of a solid that is wetted by a liquid (5).

Using an energy additivity concept in a semi-continuum model (all materials are separated by a plane of thickness corresponding to the equilibrium distance at zero potential energy and each site of one surface interacts with a continuum of sites on another), Wu (2) developed three equations to describe polar and non-polar interactions across an interface. Interfacial and surface tensions of molten polymers were measured directly and used to test these equations. The harmonic mean equation of the interfacial energy was preferred for low energy systems, which are the most common systems in pharmaceutics. The interfacial tension ${}^{AB}\gamma$ is defined as:

$$ {}^{AB}\gamma = {}^{A}\gamma + {}^{B}\gamma - \frac{4 \cdot {}^{A}\gamma_d \cdot {}^{B}\gamma_d}{{}^{A}\gamma_d + {}^{B}\gamma_d} - \frac{4 \cdot {}^{A}\gamma_p \cdot {}^{B}\gamma_p}{{}^{A}\gamma_p + {}^{B}\gamma_p} \quad (1) $$

where ${}^{A}\gamma$ and ${}^{B}\gamma$ are the surface tensions of two materials A and B, and d, p refer to disperse and polar respectively.

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Spreading Coefficient and Reduced Spreading Coefficient

Using the harmonic mean equation, Wu (2) determined the optimum wettability condition for adhesion. The spreading coefficient of B on A, ${}^{B/A}\lambda$, is (2, 3):

$$ {}^{B/A}\lambda = {}^{A}\gamma - {}^{B}\gamma - {}^{BA}\gamma = 4\left[\frac{{}^{B}\gamma_d \cdot {}^{A}\gamma_d}{{}^{B}\gamma_d + {}^{A}\gamma_d} + \frac{{}^{B}\gamma_p \cdot {}^{A}\gamma_p}{{}^{B}\gamma_p + {}^{A}\gamma_p} - \frac{{}^{B}\gamma}{2}\right] \tag{2} $$

The thermodynamic condition for spreading or complete wetting is given by ${}^{B/A}\lambda \geq 0$.

Rowe (4) defined a different reduced spreading coefficient (${}^{B/A}\lambda_r$) as the ratio of the work of adhesion to the work of cohesion of the binder. Thus,

$$ {}^{B/A}\lambda_r = \frac{4 \cdot \left[\frac{{}^{A}\gamma_d \cdot {}^{B}\gamma_d}{({}^{A}\gamma_d + {}^{B}\gamma_d)} + \frac{{}^{A}\gamma_p \cdot {}^{B}\gamma_p}{({}^{A}\gamma_p + {}^{B}\gamma_p)}\right]}{2 \cdot {}^{B}\gamma} = \frac{2}{{}^{B}\gamma} \cdot \left[\frac{{}^{A}\gamma_d \cdot {}^{B}\gamma_d}{({}^{A}\gamma_d + {}^{B}\gamma_d)} + \frac{{}^{A}\gamma_p \cdot {}^{B}\gamma_p}{({}^{A}\gamma_p + {}^{B}\gamma_p)}\right] \tag{3} $$

Here, complete wetting will occur when ${}^{B/A}\lambda_r \geq 1$.

Interaction Parameter and Strength of Interaction

In a binary system involving two materials A and B, there are two types of interactions: inter- (A-A and B-B) and intra- (A-B) interactions. While the first one can be regarded as cohesive, the second is adhesive by nature. Based on the Leenard-Jones pair potential function, Rowe (12) could relate the strength of interaction (σ in MPa) to the solubility parameter (δ) of the two surfaces:

$$ {}^{BB}\sigma = 0.25\,{}^{B}\delta^2 \qquad {}^{AA}\sigma = 0.25\,{}^{A}\delta^2 \qquad {}^{AB}\sigma = 0.25\,\phi\,{}^{A}\delta\,{}^{B}\delta \tag{4} $$

where ${}^{AB}\phi$, the interaction parameter, is defined from the harmonic mean equation proposed by Wu (2):

$$ {}^{AB}\phi = 2 \cdot \left[\frac{{}^{A}x_d \cdot {}^{B}x_d}{({}^{A}x_d \cdot g_1 + {}^{B}x_d \cdot g_2)} + \frac{{}^{A}x_p \cdot {}^{B}x_p}{({}^{A}x_p \cdot g_1 + {}^{B}x_p \cdot g_2)}\right] \tag{5} $$

Quantities x_d and x_p are the fractional non-polarity and polarity respectively ($x_d + x_p = 1$) for each material, defined by the expressions:

$$ x_d = \left(\frac{\delta_d}{\delta}\right)^2 = \frac{\gamma_d}{\gamma} \quad \text{and} \quad x_p = 1 - \left(\frac{\delta_d}{\delta}\right)^2 = \frac{\gamma_p}{\gamma} $$

where δ_d is the dispersion or non-polar component of the Hansen three-dimensional solubility parameters (13). The parameters g_1 and g_2 can also be defined in terms of the solubility parameters of the materials:

$$ g_1 = \frac{{}^{A}\gamma}{{}^{B}\gamma} = \frac{{}^{A}\delta^2 \,.\, {}^{A}V^{1/3}}{K} \cdot \frac{K}{{}^{B}\delta^2 \,.\, {}^{B}V^{1/3}} = \frac{{}^{A}\delta^2 \,.\, {}^{A}V^{1/3}}{{}^{B}\delta^2 \,.\, {}^{B}V^{1/3}} \text{ and} $$

$$ g_2 = \frac{1}{g_1} = \frac{{}^{B}\delta^2 \,.\, {}^{B}V^{1/3}}{{}^{A}\delta^2 \,.\, {}^{A}V^{1/3}} $$

where K is a constant and V the molar volume of the material i.e., its molecular weight divided by its density, assuming that the materials are supercooled liquids or amorphous polymers.

THEORETICAL SIMULATIONS

For all the simulations presented here, the characteristics of the substrate are indicated in a text box included in the figure. Each plot represents the influence of several materials on the studied parameter. For editing reasons, in all figures $\gamma(i - j)$ refers to ${}^{i}\gamma_j$ and $\%\gamma(A - p)$ refers to the percentage of polar surface tension of material A.

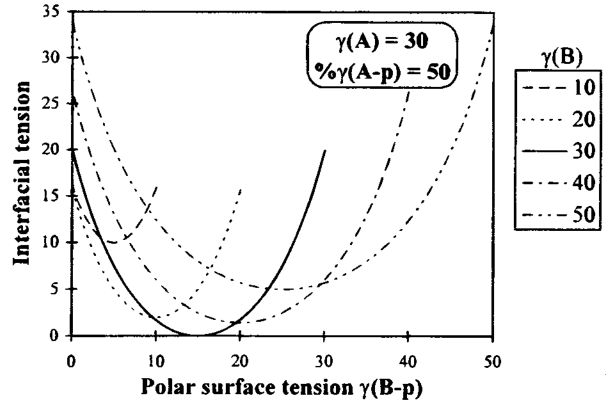
Interfacial Tension (${}^{AB}\gamma$)

Keeping the partial and total surface tensions of A constant in Equation (1), the interfacial tension varies with the polar surface tension of B as plotted in Figure 1. Figure 1 (top) indicates that the interfacial tension is null only when both materials have the same polar and disperse surface tensions. For a series of materials with the same surface tension, the interfacial tension is minimum for the material having the same polar fraction as the substrate (Figure 1, bottom). Thus,

$$ \text{if } {}^{B}\gamma = \text{cte and } {}^{A}\gamma = \text{cte}, {}^{AB}\gamma \text{ is minimum when } \frac{{}^{A}\gamma_p}{{}^{A}\gamma} = \frac{{}^{B}\gamma_p}{{}^{B}\gamma} $$

$$ {}^{AB}\gamma = 0 \text{ if } {}^{A}\gamma = {}^{B}\gamma \text{ and } {}^{A}\gamma_p = {}^{B}\gamma_p $$

Another way to consider these results is to place the materi-



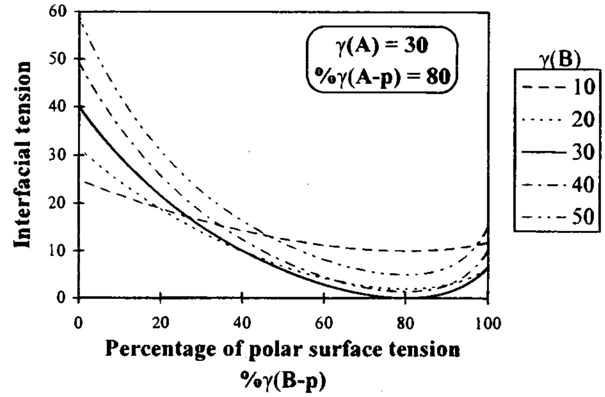


Fig. 1. Influence of total and polar surface tensions on interfacial tension (${}^{AB}\gamma$ in mN.m^{-1}). Percentage of polar surface tension for the substrate: (top) 50%, (bottom) 80%.

Another way to consider these results is to place the materials on a surface tension map (surface tension *versus* percentage of polar surface tension). The closer the two materials will be on such a map, the lower their interfacial tension will become. But the distance between two materials on a surface tension map is not the only factor in their interfacial tension. If one considers several materials *B* equidistant to a reference material *A* on a surface tension map (Figure 2), the resulting interfacial tension will not be constant.

Spreading Coefficient ($^{B/A}\lambda$) and Reduced Spreading Coefficient ($^{B/A}\lambda_r$)

As for interfacial tension, keeping the partial and total surface tensions of the substrate constant in Equations (2) and (3), it is possible to plot the spreading and the reduced spreading coefficients versus the polar surface tension of the material B (Figure 3). This figure shows the impossibility for $^{B/A}\lambda$ and $^{B/A}\lambda_r$ to be respectively strictly positive or superior to one when the surface tension of *B* is greater than the surface tension of *A*. Thus,

$$\text{if } {}^{B}\gamma > {}^{A}\gamma, \text{ then } {}^{B/A}\gamma < 0 \text{ and } {}^{B/A}\gamma_r < 1$$

These values are critical for the granule formation during wet granulating but also during coating. Rowe (7) explains that a positive value of the spreading coefficient of a binder over a substrate ($^{B/A}\lambda$) implies good film formation with a strongly adhering continuous film of binder around the substrate. A strong dense granule will be formed since there will always be a bond at all points of contact between the substrate particles. The strength of the granule will depend on the strength (i.e., the work of cohesion) of the binder.

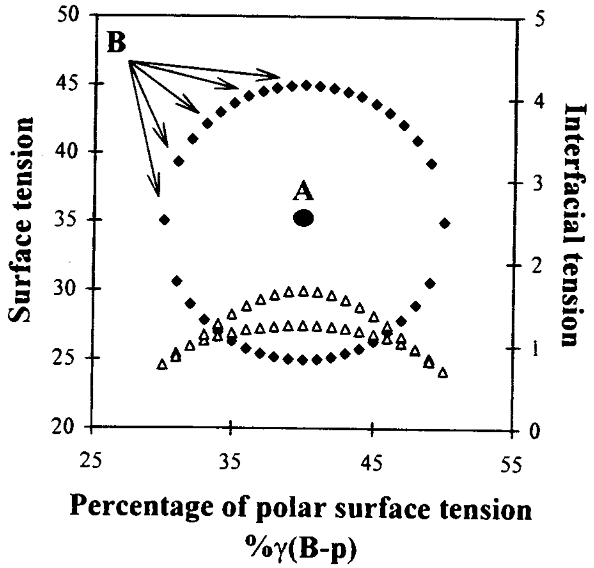


Fig. 2. Evaluation of the interfacial tensions (Δ) between a material *A* and several materials *B* of varying surface tensions (◆) as related to the percentage of the polar surface tension of *B*. Here, the surface tension of *A* and its polar component are kept constant (respectively 35 mN.m^{-1} and 40%). The characteristics of *B* (surface tension and percentage of polar surface tension) are chosen to keep *B* equidistant to *A* on a surface tension map. Surface tensions of *A* ($^{A}\gamma$) and *B* ($^{B}\gamma$) and the interfacial tensions $^{AB}\gamma$ are expressed in mN.m^{-1}.

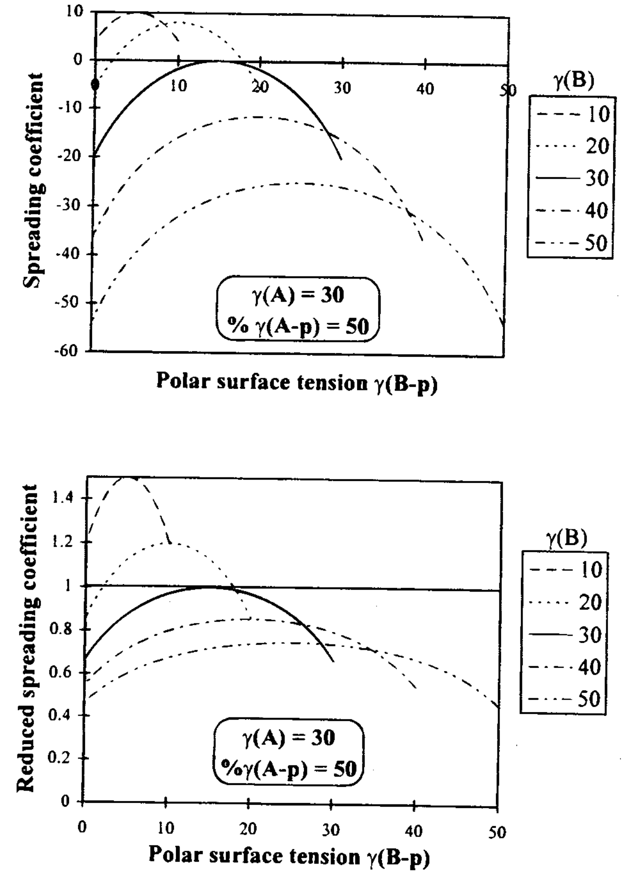


Fig. 3. Influence of total and polar surface tensions on spreading (top) and reduced spreading coefficients (bottom). Surface tensions of *A* ($^{A}\gamma$) and *B* ($^{B}\gamma$) and the spreading coefficients ($^{B/A}\lambda$ and $^{B/A}\lambda_r$) are expressed in mN.m^{-1}.

The conditions for having the maximum spreading coefficient can be estimated from the spreading coefficient equation. Thus, for a given material, the total surface tension required to have the maximum spreading coefficient at a specific polar surface tension can be determined. It is also possible to calculate the polar surface tension required to have the maximum spreading coefficient at a specific total surface tension. A development of the equations is presented in the appendix. The same calculations are possible with the reduced spreading coefficient.

Interaction Parameter ($^{AB}\phi$)

Using Equation (5), it is possible to estimate the influence of total and disperse cohesion parameters and molar volume on the interaction parameter. From Figure 4 (top), the interaction parameter is equal to unity only when both materials have the same polar and disperse cohesion parameters. As confirmed by Figure 4 (middle), the interaction parameter between two materials is maximum when the disperse fractions of both materials are equal. The influence of molar volume on the interaction parameter (Figure 4, bottom) is difficult to establish but seems minor, certainly because of the cubic root function in the formula of g_1 and g_2. Thus,

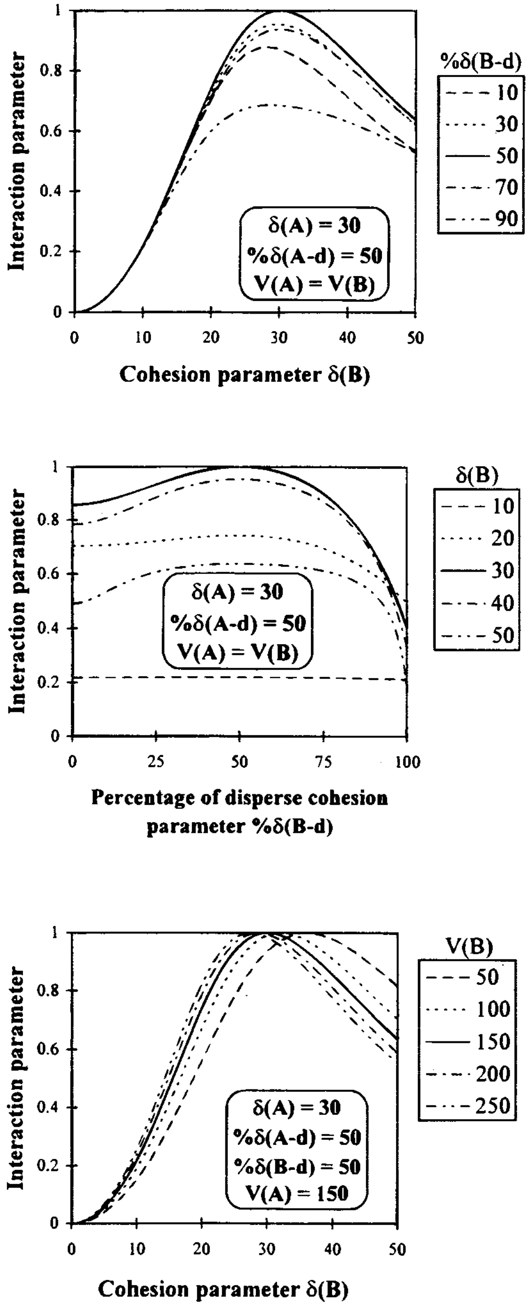


Fig. 4. Influence of total (top) and disperse (middle) interaction parameters and molar volume (bottom) on interaction parameter. Cohesion parameters of A ($^A\delta$) and B ($^B\delta$) are expressed in MPa$^{1/2}$. The units of the molar volumes of A and B, $V(A)$ and $V(B)$ respectively, are mol.cm^{-3}.

$$\text{if } {}^BV = {}^AV,\ \phi \text{ is maximum when } \frac{{}^A\delta_d}{{}^A\delta} = \frac{{}^B\delta_d}{{}^B\delta}$$

$$\phi = 1 \text{ if } {}^A\delta = {}^B\delta,\ {}^A\delta_p = {}^B\delta_p \text{ and } {}^AV = {}^BV$$

Strength of Interaction ($^{AB}\sigma$)

As expected from Equation (4), the strength of interaction is maximum when both materials have the same polar and nonpolar cohesion parameters fractions (Figure 5 top). However, the strength of interaction is not maximum when both materials are identical. In Figure 5 (middle), all the materials with a cohesion parameter between 30 and 55.2 MPa$^{1/2}$ exhibit a stronger strength of interaction with material A($^A\delta$ = 30 MPa$^{1/2}$, $^A\delta_p/^A\delta$ = 50%, identical molar volumes). Using successive iterations, the cohesion parameter needed to obtain the maximum strength of interaction ($^{AB}\sigma_{max}$) can be determined. In our example, $^{AB}\sigma_{max}$ is 256 MPa for a cohesion parameter of 39.45 MPa$^{1/2}$ (Figure 6).

Thus, for a material B with the same molar volume as a material A and with a cohesion parameter between 30 and 55.2 MPa$^{1/2}$, the adhesive interaction $^{AB}\sigma$ is greater than the cohesive

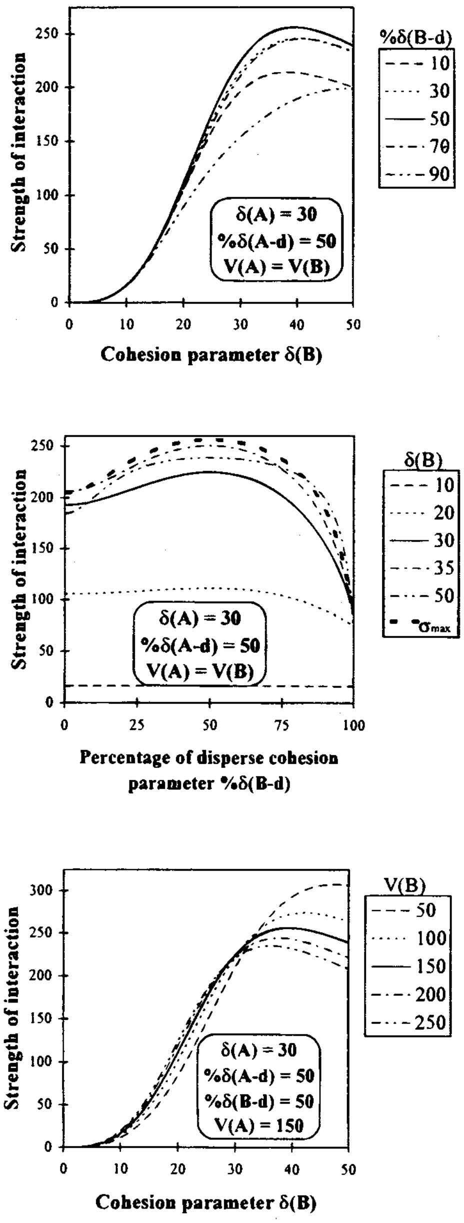


Fig. 5. Influence of total (top) and disperse (middle) interaction parameters and molar volume (bottom) on strength of interaction. Cohesion parameters of A ($^A\delta$) and B ($^B\delta$) and strength of interaction ($^{AB}\sigma$) are expressed in MPa$^{1/2}$. The units of the molar volumes of A and B, $V(A)$ and $V(B)$ respectively, are mol.cm^{-3}.

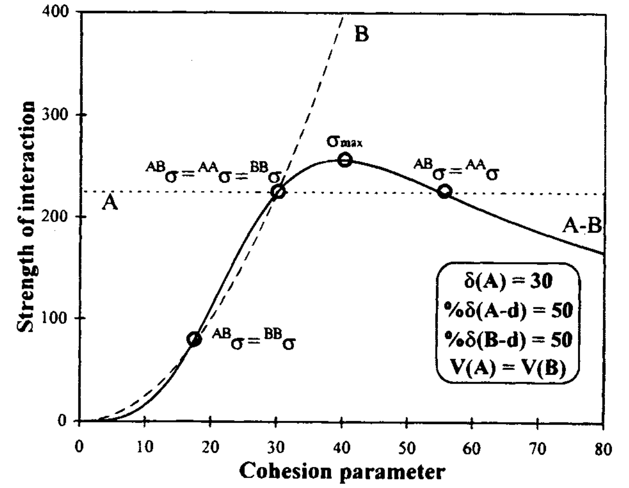


Fig. 6. Influence of cohesion parameter on strength of interaction ($^{AB}\sigma$, $^{AA}\sigma$, $^{BB}\sigma$). Cohesion parameters of A ($^{A}\delta$) and B ($^{B}\delta$) and strengths of interaction ($^{AB}\sigma$, $^{AA}\sigma$, $^{AB}\sigma$) are expressed in MPa$^{1/2}$. The units of the molar volumes of A and B, $V(A)$ and $V(B)$ respectively, are mol.cm^{-3}. —— $^{AB}\sigma$ — .. — . $^{AA}\sigma$ ...... $^{BB}\sigma$

interaction $^{AA}\sigma$. Furthermore, the adhesive interaction $^{AB}\sigma$ of a material B with a cohesion parameter between 30 and 55.2 MPa$^{1/2}$ will be lower than its cohesive interaction $^{BB}\sigma$ (Figures 6 and 7).

From the direct relation between the ideal interfacial adhesive bond strength ($^{AB}\sigma$) and the work of adhesion (W_a) showed by Gardon (14), the reduced spreading coefficient ($^{B/A}\lambda_r$) defined by Rowe (4) can be rewritten as:

$$^{B/A}\lambda_r = \frac{W_a}{W_{c(B)}} = \frac{^{AB}\sigma}{^{BB}\sigma}$$

As illustrated in Figure 7, depending on the value of the reduced spreading coefficient ($^{B/A}\lambda_r$), material B will coat or not material A. Thus, without calculation, and only from a knowledge of the properties of two materials, it is possible to:

- choose a binder that will exhibit the higher or the lower surface tension with the substrate,
- avoid the use of a coating agent that will not coat the substrate,
- select the material that will present the higher interaction parameter with the substrate.

Nevertheless, the strength of interaction cannot be directly inferred from the properties of the materials. Therefore, calculation is required to choose the binder or the dye that will present the higher strength of interaction with a specific substrate.

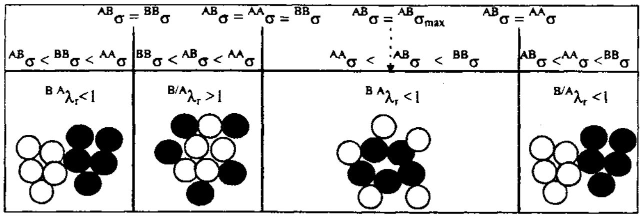


Fig. 7. Influence of cohesion parameter of two materials A(○) and B(●) on strength of interaction ($^{AB}\sigma$, $^{AA}\sigma$, $^{BB}\sigma$) and reduced spreading coefficient ($^{B/A}\lambda_r$).

The understanding of the influence of surface free energy and cohesion parameter on material interactions is a great help to the formulator because it gives the possibility to choose *a priori* the best binder, coating agent or wetting agent without any experiment. It also helps the formulator to better justify from a qualitative and quantitative point of view the various excipients present in the formulation.

APPENDIX

CONDITIONS FOR A MAXIMUM SPREADING COEFFICIENT

The equation defining the spreading coefficient is:

$$^{B/A}\lambda = 4\left[\frac{^{B}\gamma_d \cdot {}^{A}\gamma_d}{^{B}\gamma_d + {}^{A}\gamma_d} + \frac{^{B}\gamma_p \cdot {}^{A}\gamma_p}{^{B}\gamma_p + {}^{A}\gamma_p} - \frac{^{B}\gamma}{2}\right]$$

where $^{A}\gamma$ and $^{B}\gamma$ are the surface tensions of two materials A and B, and d, p refer to disperse and polar respectively. The spreading coefficient is nul when:

$$\frac{^{B}\gamma_d \cdot {}^{A}\gamma_d}{^{B}\gamma_d + {}^{A}\gamma_d} + \frac{^{B}\gamma_p \cdot {}^{A}\gamma_p}{^{B}\gamma_p + {}^{A}\gamma_p} = \frac{^{B}\gamma}{2}.$$

Since $^{A}\gamma = {}^{A}\gamma_d + {}^{A}\gamma_p$ and $^{B}\gamma = {}^{B}\gamma_d + {}^{B}\gamma_p$, then the spreading coefficient is nul when:

$$\frac{(^{B}\gamma_p \cdot {}^{A}\gamma_p) \cdot (^{B}\gamma - {}^{B}\gamma_p + {}^{A}\gamma_d) + (^{B}\gamma_p + {}^{A}\gamma_p) \cdot (^{B}\gamma - {}^{B}\gamma_p) \cdot {}^{A}\gamma_d}{(^{B}\gamma_p + {}^{A}\gamma_p) \cdot (^{B}\gamma - {}^{B}\gamma_p + {}^{A}\gamma_d)} = \frac{^{B}\gamma}{2}, \qquad \text{thus}$$

$$(^{B}\gamma_p \cdot {}^{A}\gamma_p) \cdot (^{B}\gamma - {}^{B}\gamma_p + {}^{A}\gamma_d) + (^{B}\gamma_p + {}^{A}\gamma_p) \cdot (^{B}\gamma - {}^{B}\gamma_p) \cdot {}^{A}\gamma_d = \frac{1}{2} \cdot {}^{B}\gamma \cdot (^{B}\gamma_p + {}^{A}\gamma_p) \cdot (^{B}\gamma - {}^{B}\gamma_p + {}^{A}\gamma_d)$$

By developing and rearranging, one obtains:

$$\left({}^{A}\gamma - \frac{1}{2}\,{}^{A}\gamma_d + \frac{1}{2}\,{}^{A}\gamma_p\right) \cdot {}^{B}\gamma{}^{B}\gamma_p - {}^{A}\gamma \cdot {}^{B}\gamma_p^2 + \left({}^{A}\gamma_d{}^{A}\gamma_p - \frac{1}{2}\,{}^{A}\gamma_d{}^{A}\gamma_p\right) \cdot {}^{B}\gamma - \frac{1}{2}\,{}^{B}\gamma_p{}^{B}\gamma^2 + \frac{1}{2}\,{}^{B}\gamma{}^{B}\gamma_p^2 + \frac{1}{2}\,{}^{A}\gamma_p \cdot {}^{B}\gamma^2 = 0$$

which can be simplified to:

$$^{A}\gamma_p \cdot {}^{B}\gamma^2 - 2{}^{A}\gamma \cdot {}^{B}\gamma_p^2 + {}^{B}\gamma{}^{B}\gamma_p^2 - {}^{B}\gamma_p{}^{B}\gamma^2 + (^{A}\gamma + 2{}^{A}\gamma_p) \cdot {}^{B}\gamma{}^{B}\gamma_p + {}^{A}\gamma_d{}^{A}\gamma_p \cdot {}^{B}\gamma = 0$$

Determination of the Polar Surface Tension when the Total Surface Tension Is Constant

To determine the polar surface tension ($^{B}\gamma_p$) required to get the maximum spreading coefficient at a specific total surface tension ($^{B}\gamma$ constant), we consider:

$$(^{B}\gamma - 2{}^{A}\gamma) \cdot {}^{B}\gamma_p^2 + [(^{A}\gamma + 2{}^{A}\gamma_p){}^{B}\gamma - {}^{B}\gamma^2] \cdot {}^{B}\gamma_p + [{}^{A}\gamma_p{}^{B}\gamma^2 + (^{A}\gamma_p{}^{A}\gamma_d){}^{B}\gamma] = 0$$

Since $^{B}\gamma$, $^{A}\gamma$, $^{A}\gamma_d$ and $^{A}\gamma_p$ are constant, the equation defining the spreading coefficient is a parabolic equation. The spreading coefficient will be maximum when:

$$ {}^{B}\gamma_p = -\frac{({}^{A}\gamma + 2{}^{A}\gamma_p) \cdot {}^{B}\gamma - {}^{B}\gamma^2}{2 \cdot ({}^{B}\gamma - 2{}^{A}\gamma)} $$

If the spreading coefficient is positive at ${}^{B}\gamma_p$, then it will be positive for all the polar surface tensions between:

$$ {}^{B}\gamma_p + \frac{\sqrt{[({}^{A}\gamma + 2{}^{A}\gamma_p){}^{B}\gamma - {}^{B}\gamma^2]^2 - 4 \cdot [{}^{B}\gamma - 2{}^{A}\gamma] \cdot [{}^{A}\gamma_p{}^{B}\gamma^2 + ({}^{A}\gamma_p{}^{A}\gamma_d){}^{B}\gamma]}}{2 \cdot ({}^{B}\gamma - 2{}^{A}\gamma)} < {}^{B}\gamma_p < {}^{B}\gamma_p $$

$$ - \frac{\sqrt{[({}^{A}\gamma + 2{}^{A}\gamma_p){}^{B}\gamma - {}^{B}\gamma^2]^2 - 4 \cdot [{}^{B}\gamma - 2{}^{A}\gamma] \cdot [{}^{A}\gamma_p{}^{B}\gamma^2 + ({}^{A}\gamma_p{}^{A}\gamma_d){}^{B}\gamma]}}{2 \cdot ({}^{B}\gamma - 2{}^{A}\gamma)} $$

Determination of the Total Surface Tension when the Polar Surface Tension Is Constant

To determine the total surface tension (${}^{B}\gamma$) required to obtain the maximum spreading coefficient at a specific polar surface tension (${}^{B}\gamma_p$ constant), we consider:

$$ ({}^{A}\gamma_p - {}^{B}\gamma_p) \cdot {}^{B}\gamma^2 + [{}^{B}\gamma_p^2 + ({}^{A}\gamma + 2{}^{A}\gamma_p){}^{B}\gamma_p + {}^{A}\gamma_d{}^{A}\gamma_p] \cdot {}^{B}\gamma - 2{}^{A}\gamma{}^{B}\gamma_p^2 = 0 $$

Since ${}^{B}\gamma_p$, ${}^{A}\gamma$, ${}^{A}\gamma_d$ and ${}^{A}\gamma_p$ are constant, the equation defining the spreading coefficient is a parabolic equation. The spreading coefficient will be maximum when:

$$ {}^{B}\gamma = -\frac{{}^{B}\gamma_p^2 + ({}^{A}\gamma + 2{}^{A}\gamma_p){}^{B}\gamma_p + {}^{A}\gamma_d{}^{A}\gamma_p}{2 \cdot ({}^{A}\gamma_p - {}^{B}\gamma_p)} $$

If the spreading coefficient is positive at ${}^{B}\gamma$, then it will be positive for all the surface tensions between:

$$ {}^{B}\gamma + \frac{\sqrt{[{}^{B}\gamma_p^2 + ({}^{A}\gamma + 2{}^{A}\gamma_p){}^{B}\gamma_p + {}^{A}\gamma_d{}^{A}\gamma_p]^2 + 8{}^{A}\gamma{}^{B}\gamma_p^2 \cdot ({}^{A}\gamma_p - {}^{B}\gamma_p)}}{2 \cdot ({}^{B}\gamma - 2{}^{A}\gamma)} < {}^{B}\gamma < {}^{B}\gamma $$

$$ - \frac{\sqrt{[{}^{B}\gamma_p^2 + ({}^{A}\gamma + 2{}^{A}\gamma_p){}^{B}\gamma_p + {}^{A}\gamma_d{}^{A}\gamma_p]^2 + 8{}^{A}\gamma{}^{B}\gamma_p^2 \cdot ({}^{A}\gamma_p - {}^{B}\gamma_p)}}{2 \cdot ({}^{B}\gamma - 2{}^{A}\gamma)} $$

REFERENCES

1. G. Zografi and S. S. Tam. *J. Pharm. Sci.* **65**:1145–1149, (1976).
2. S. Wu. *J. Adhesion* **5**:39–55, (1973).
3. R. C. Rowe. *Int. J. Pharm.* **52**:149–154, (1989).
4. R. C. Rowe. *Int. J. Pharm.* **56**:117–124, (1989).
5. G. Cavé. *Labo-Pharma - Probl. Tech.* **29**:167–172, (1981).
6. R. C. Rowe. *Int. J. Pharm.* **53**:47–51, (1989).
7. R. C. Rowe. *Int. J. Pharm.* **53**:75–78, (1989).
8. R. C. Rowe. *Int. J. Pharm.* **58**:209–213, (1990).
9. P. Sakellariou, A. Hassan, and R. C. Rowe. *Polymer* **34**:1240–1248, (1993).
10. P. Sakellariou, A. Hassan, and R. C. Rowe. *Eur. Polym. J.* **29**:937–943, (1993).
11. A. F. M. Barton. *Handbook of solubility parameters and other cohesion parameters*, CRC Press Inc. Boca Raton, 1991.
12. R. C. Rowe. *Acta Pharm. Technol.* **34**:144–146, (1988).
13. C. M. Hansen. *J. Paint Technol.* **39**:505–511, (1967).
14. J. L. Gardon. *Prog. Org. Coatings* **5**:1–20, (1977).