TABLE 2. VARIANCE OF ESTIMATE

Gas no.	Estimate	Gas no.	Estimate
1	$.8469 \times 10^{-4}$	8	$.2665 \times 10^{-3}$
2	$.4084 \times 10^{-4}$	9	$.4308 \times 10^{-4}$
3	$.1419 \times 10^{-4}$	10	$.5227 \times 10^{-4}$
4	$.2330 \times 10^{-4}$	11	$.2758 \times 10^{-3}$
5	$.1276 \times 10^{-4}$	12	$.1723 \times 10^{-4}$
6	$.4486 \times 10^{-4}$	13	$.1025 \times 10^{-4}$
7	$.2794 \times 10^{-3}$	14	$.9925 \times 10^{-4}$
		15	$.1845 \times 10^{-4}$

transfer is included in the calibration. Absorption of radiation by the gas, thermal diffusion, and the effect of pressure on cell dimensions are small and can be neglected.

Sengers specifies the accuracy of his measurements to be 1%. Since his data are used for cell calibration, this error must be added to that of the present cell. Calibration drift is estimated to be less than 1%. Random error, minimized by the smoothing process, is no more than 0.4%. Thus, the results are estimated to be accurate within 2.5%.

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NOTATION

N = number of data points
n = order of equation
k = thermal conductivity
σ = variance

Subscripts

i = experimental i^{th} value
ci = calculated i^{th} value

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Van der Waals Forces in a Three-Phase System

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An analysis is made of the Van der Waals forces of two different species when separated by a third continuous component. Results show that under certain circumstances, attractions as well as repulsions can exist between the two different species. The theory is applied to a fibrous bed coalescer to determine what type of material would best serve as a coalescence medium.

In consideration of theoretical aspects of filtration (*8*) and of coalescence in fibrous or porous media (*12*), investigators have had to account for two predominant surface effects. One of these is electrostatic in nature and arises because a zeta potential can become associated with the filtrate and the filter material. By measuring the streaming potential of the filter and the electrophoretic transfer of the filtrate, these two zeta potentials can be established. The second effect is the Van der Waals interaction between the filtrate and filter.

Most investigators consider the Van der Waals effect when the two phases are in the presence of a vacuum. Under this condition there will be an attraction between the two phases. However, if the continuous phase is a gas or liquid, this will not always be true. We shall evaluate the Van der Waals interactions in a three-phase system and consider an application to the coalescence of emulsions in fibrous beds.

THEORY

The importance of the Van der Waals interaction in a three-phase system was first realized in its effect on the contact angle of a liquid resting on a solid in the presence of a gas. The theory, however, is equally applicable to the case when two immiscible liquids are in contact with a solid. If a drop is adhering to a solid surface, as shown in Figure 1, the forces acting at the junction of the two fluid phases and the solid can be properly expressed as

$$\sigma_{31,2} = \sigma_{32,1} - \sigma_{12} \cos \theta \tag{1}$$

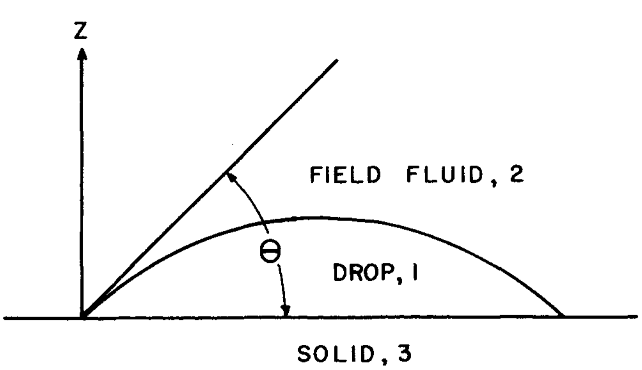

Fig. 1. Contact angle of a drop on a rigid plane surface.

where $\sigma_{31,2}$ signifies the surface-free energy of species 1 in contact with solid 3, and species 1 is saturated with species 2. According to Harkins (6), this quantity can be expressed in terms of the pure substances by Equation (2)

$$\sigma_{3i,j} = \sigma_{3i} - \pi_{i\,3,j} \tag{2}$$

where $\pi_{i3,j}$ is known as the film pressure.

There are currently two lines of thought in surface phenomena which would enable the evaluation of σ_{ij}. The former, promulgated by Girifalco (3) and Good (4), states that

$$\sigma_{ij} = \sigma_i + \sigma_j - 2\Phi\sqrt{\sigma_i\,\sigma_j} \tag{3}$$

where Φ is a constant less than one and a function of the molecular properties of the two phases. The latter theory was instituted by Fowkes (2). It assumes that surface tension σ_i is an energy derived from the various forces, such as metallic bonds and hydrogen bonds, and ideally can be represented by the sum of these forces. In general, Van der Waals forces constitute the major forces that cause surface tension. These interactions result from four known components, of which the London dispersion energy is the major contributor (*1*). With this basis, Fowkes assumes a dispersion interaction at an interface and expresses the interfacial tension as

$$\sigma_{ij} = \sigma_i + \sigma_j - 2\cdot\sqrt{\sigma_i^d\cdot\sigma_j^d} \tag{4}$$

where σ_i^d is the contribution of dispersion force to surface tension σ_i. For many nonpolar liquids, $\sigma_i = \sigma_i^d$ (*2*). For high energy solids, values of σ_i are not available, but those of σ_i^d are, and for this reason, the following treatment will be based on the Fowkes model.

Replacing Equation (4) and (2) into Equation (1), one can obtain (*13*)

$$\cos\theta = \frac{\sigma_2 - \sigma_1 + 2\sqrt{\sigma_3^d}\,(\sqrt{\sigma_1^d} - \sqrt{\sigma_2^d}) + (\pi_{13,2} - \pi_{23,1})}{\sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^d\,\sigma_2^d}} \tag{5}$$

Equation (5) is representative of the contact angle in a liquid-liquid-solid system. Melrose (*11*) points out that for two liquid phases in contact, both film pressures can be neglected. Therefore, Equation (5) becomes

$$\cos\theta = \frac{\sigma_2 - \sigma_1 + 2\sqrt{\sigma_3^d}\,(\sqrt{\sigma_1^d} - \sqrt{\sigma_2^d})}{\sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^d\,\sigma_2^d}} \tag{6}$$

In this expression, σ_{12} has been replaced by the dispersive approximation as this approach is also used for σ_{13} and σ_{23}. If fluid 2 is a vapor, $\sigma_2^d = 0$ and Equation (6) will reduce to the form given by Fowkes (2) for the contact angle of a liquid on a solid in the presence of a vapor. In using Equation (6), cos θ can be either calculated if σ_1^d and σ_2^d are known or used as a means of approximating σ^d by measuring the contact angle as has been done (*2*). In this regard, Haynes et al. (7) provide contact-angle data of water dispersed in carbon tetrachloride on brass and Teflon.* Their data for the contact angle of this system on brass suggest that $\sigma_{CCl_4}{}^d = 9.9$ dynes/cm. Use of this value in Equation (6) for the same two liquids on a Teflon surface gives a contact angle of 63.2 deg. Their measured value is 65.1 deg. This technique for determining σ_i^d has been discussed because we will have further use for these values.

VAN DER WAALS INTERACTION

Only the dispersive component will be considered. Hamaker (5) defines the system as fluid 1 immersed in fluid 2 in the presence of solid 3. The total change in the energy of interaction in moving a sphere of fluid 1 from infinity to solid surface 3 through fluid 2 is given as

$$E = E_{13} + E_{22} - E_{23} - E_{12} \tag{7}$$

Following Hamaker (5), we can write

$$E_{ij} = -A'_{ij}\,P_y\,(x) \tag{8}$$

and

$$A'_{ij} = \pi^2 N_i N_j \lambda_{ij} \tag{9}$$

Replacing Equations (8) and (9) into (7) yields

$$E = P_y\,(x)\cdot\pi^2\,[N_1 N_3 \lambda_{13} + N_2^2 \lambda_{22} - N_2 N_3 \lambda_{23} - N_1 N_2 \lambda_{12}] \tag{10}$$

The coefficient defined by the second parenthesis in Equation (10) will be called *A*. The London-Van der Waals constant λ_{ij} is defined as (5)

$$\lambda_{ij} = \frac{3\,\alpha_i\,\alpha_j\,l_i\,l_j}{2\,(l_i + l_j)} \tag{11}$$

Replacing Equation (11) into the coefficient in Equation (10) yields

$$A = \pi^2\left[\frac{3}{2}\frac{N_1 N_3 \alpha_1 \alpha_3 l_1 l_3}{(l_1 + l_3)} + \frac{3}{4}N_2^2\,\alpha_2^2\,l_2 - \frac{3}{2}\frac{N_2 N_3 \alpha_2 \alpha_3 l_2 l_3}{(l_2 + l_3)} - \frac{3}{2}\frac{N_1 N_2 \alpha_1 \alpha_2 l_1 l_2}{(l_1 + l_2)}\right] \tag{12}$$

As stated by Fowkes (*2*), the London dispersive force is given by

$$\sigma_i^d = \frac{\pi\,N_i^2\,\alpha_i^2\,l_i}{8\,r_{ii}^2} \tag{13}$$

Even if the ionization potentials shown in Equation (12) are widely different, small error results if it is assumed they are equal. Also express

$$k_{12} = \frac{r_{11}}{r_{22}},\quad k_{32} = \frac{r_{33}}{r_{22}} \tag{14}$$

Therefore, assuming that $l_1 = l_2 = l_3$, replacing Equations (13) and (14) into (12) yields

$$A = 6\pi\,r_{22}^2\,[k_{12}\,k_{32}\sqrt{\sigma_1^d\,\sigma_3^d} + \sigma_2^d - k_{32}\sqrt{\sigma_2^d\,\sigma_3^d} - k_{12}\sqrt{\sigma_1^d\,\sigma_2^d}] \tag{15}$$

This equation will factor into

$$A = 6\pi\,r_{22}^2\,[k_{12}\sqrt{\sigma_1^d} - \sqrt{\sigma_2^d}]\,[k_{32}\sqrt{\sigma_3^d} - \sqrt{\sigma_2^d}] \tag{16}$$

TABLE 1. DISPERSION FORCE COMPONENTS*

Solid	σ_i^d†	Liquid	σ_i^d
Teflon	19.5	Water	21.8
Polyethylene	35.0	Benzene	28.5
Silica (glass)	78.0	Carbon tetrachloride	26.9
Iron	108.0	Chloroform	27.1
Polystyrene	44.0	Isobutanol	20.7
Copper	60.0	Nitrobenzene	43.9

* Obtained from Fowkes (2).
† These values used to construct Table 3.

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* Trademark of E. I. du Pont de Nemours & Co., Inc.

TABLE 2. EXPECTED LONDON-VAN DER WAALS INTERACTIONS BETWEEN A SOLID ADSORBENT AND THE DISPERSED PHASE

Continuous phase	Dispersed phase	Interaction between the dispersed phase and solid adsorbent
Liquid	Gas	Usually repulsion
Liquid	Liquid	Attraction or repulsion
Liquid	Solid	Usually attraction; slight possibility of repulsion
Gas	Gas	Attraction or repulsion
Gas	Liquid	Attraction
Gas	Solid	Attraction

When two immiscible liquids and a solid form the system, assume that $k_{12} = k_{32} = 1$ or that the intermolecular radii of the three phases are equal. Therefore

$$A = 6\pi\, r_{22}^2\, (\sqrt{\sigma_1{}^d} - \sqrt{\sigma_2{}^d})\, (\sqrt{\sigma_3{}^d} - \sqrt{\sigma_2{}^d}) \quad (16a)$$

If σ_1 and σ_3 are one and the same component, then Equation (16) reduces to Equation (16*b*). This is the equation given by Fowkes (*2*) for the attraction of like particles of species 1 in the presence of species 2.

$$A = 6\pi\, r_{11}^2\, (\sqrt{\sigma_i{}^d} - \sqrt{\sigma_2{}^d})^2 \quad (16b)$$

The force between two particles in the presence of a third is

$$F_d = \frac{\partial E_d}{\partial d} = - \frac{A}{D_o} \frac{\partial\, P_y\, (x)}{\partial\, x} \quad (17)$$

For a flat plate and a sphere

$$\frac{\partial\, P_y\, (x)}{\partial\, x} = - \frac{1}{12} \left[\frac{1}{x^2\, (x+1)^2} \right] \quad (18)$$

and therefore

$$F_d = \frac{A}{12\, D_o} \left[\frac{1}{x^2\, (x+1)^2} \right] \quad (19)$$

If A is positive in Equation (19), there is an attraction between the solid and dispersed drop.

Table 1 gives the dispersive component for various solids and liquids. If a liquid-liquid-solid system is being considered, it is readily apparent from Equation (16*a*) that attraction or repulsion is possible between the dispersed liquid and the solid. If the continuous phase is a gas, then $\sigma_2{}^d$ would be very small and Equation (16*a*) would become

$$A = 6\pi\, r_{11}^2 \cdot \sqrt{\sigma_3{}^d\, \sigma_1{}^d} \quad (20)$$

Under these circumstances there always is an attraction between the solid and dispersed liquid, and the attraction is very high compared to those of the liquid-liquid systems. This equation also tends to favor the high energy solids, but not as strongly as in the case of two immiscible liquids.

When a granular bed is being used to remove a solid from a liquid stream, it retains the solid material and eventually becomes saturated. Heertjes and Lerk (*8*) and Mackrle (*10*) have postulated that London-Van der Waals adhesion is the most important factor in the removal of a suspended solid by a granular bed. Under these circumstances Equation (16*a*) would indicate an attraction between the dispersed phase and solid. Thus one expects good results for the removal of a solid from a liquid stream by a solid. Equation (16) can be used to determine the interaction in any three-phase systems. Table 2 shows some of the expected interactions for various systems. In the construction of this table it was assumed that σ^d for a gas was essentially zero.

APPLICATION TO FIBROUS BED COALESCENCE

The mechanisms by which coalescence occurs in fibrous beds have been previously discussed (*9, 12*). In these various mechanisms, the fibrous material can aid in coalescence in two ways. In the first method, sometimes called depth coalescence, drops of the dispersed phase cling to the fibers, grow, and are removed by the fluid stream. In the second method, the continuous phase passes through the filter whereas the dispersed phase is accumulated at the surface of the filter and is not allowed to pass through. This is referred to as surface coalescence and acts much like a hydrophobic barrier. In this study we are concerned with the former method because the high void fraction beds, usually 70 to 95% voids, would not permit the latter.

Microscopic analysis of fibrous beds in operation (*13*) shows that not all beds retain a sufficient number of dispersed drops. This dispersed material accumulates in the bed to levels of from 6% to 25% of the void volume, depending upon operating conditions. However, with certain three phase systems, there is no accumulation of material. In these systems, no coalescence is observed. The degree of coalescence is dependent upon the holdup as well as other variables of the system, such as fiber size and packing density. Further work is being carried out to determine and to correlate the degree of coalescence. Presently, we wish to explore why there is no holdup in certain systems. Consider the influence of Van der Waals forces on the attraction of the dispersed phase by the fibers. In order to estimate the influence of London-Van der Waals forces on this phenomenon, Equation (16*a*) was used to calculate values of $A/6\pi r_{22}^2$. These values were compared with quantitative observations previously reported by Sareen et al. (*12*).

Table 3 shows values of $A/6\pi r_{22}^2$ for eighteen different three-phase systems. The letter following the value of the coefficient corresponds to a test of fibrous bed. The numbers in Table 3 represent the attraction of the dispersed phase for the solid phase in the presence of the continuous phase. For all organic liquids it was assumed that $\sigma_i{}^d$ (see Table 1) was equal to σ_i.

TABLE 3. COMPARISON OF $A/\pi\, r^2{}_{22}$ TO COALESCENCE RESULTS

Fibers	Glass		Polyethylene		Teflon	
Emulsion		Coalescence		Coalescence		Coalescence
Dispersed/continuous	$A/6\pi\, r_{22}^2$	effect*	$A/6\pi\, r_{22}^2$	effect	$A/6\pi\, r_{22}^2$	effect
Benzene/water	+3.00	C	+0.92	P	−0.167	P
Water/carbon tetrachloride	−1.94	C	−0.38	P	+0.416	C
Chloroform/water	+2.27	N	+0.70	N	−0.127	N
Isobutanol/water	−0.41	N	−0.127	N	+0.02	N
Water/isobutanol	+0.436	C	+0.150	P	−0.013	P
Nitrobenzene/water	−4.20	N	+1.30	N	+4.36	P

* Effect of coalescence is complete (C or 95% efficiency), partial (P), or none (N).

TABLE 4. WATER IN CARBON TETRACHLORIDE

Solid	$A/6\pi r_{22}^2$	Removal
Glass	+8.44	Complete
Polyethylene	+4.16	Partial
Teflon	+1.91	Complete

The isobutanol-water system has an interfacial tension of 2.1 dynes/cm. at 20°C. It has long been believed that there was some minimum interfacial tension below which coalescence will not take place. Sareen et al. (*12*) reported that an oil-soluble surfactant allowed coalescence of an oil-in-water emulsion down to an interfacial tension of 3.5 dynes/cm. whereas water-soluble surfactants permitted coalescence only at high interfacial tensions (30.3 dynes/cm.). In Table 3 the calculated values of the Van der Waals coefficient agree well with the experimental results for the isobutanol-water system. The low interfacial tension for this system is also a function of the Van der Waals interactions, as previously pointed out.

Notice also that the agreement is poor for the carbon tetrachloride-water system. If, however, the dispersion interaction for carbon tetrachloride were $\sigma^d_{CCl_4} = 9.9$ dynes/cm., as was determined from the contact-angle data, the results would read as in Table 4.

As Equation (12) deals with differences, it is necessary to have accurate values of σ_i^d as in the case of contact-angle calculations.

Again referring to Table 3, the Van der Waals coefficient for glass is always higher than that of Teflon or polyethylene. This occurs because glass is a high energy solid, as classified by Zisman (*14*), and therefore has a tendency to produce stronger interactions with the dispersed drops. Table 1 lists the dispersion energies for some such solids. In general, it would be expected that the high energy solids would provide better results as coalescing media. Treating solid surfaces with coatings or the presence of surface-active materials will alter the dispersion properties of the interfaces considerably, owing to their nature.

Although the effect of electrostatic interactions have thus far been somewhat neglected, it is possible that they provide some contribution. In the filtration of colloidal matter from a solution by means of a bed of glass spheres Heertjes and Lerk (*8*) found electrical charges to be very important, and successful removal occurred when the charges between colloid and solid were opposite in sign. However, these colloidal particles were of the order of 0.04 micron in diameter whereas the secondary emulsions are closer to one micron and larger. Furthermore, secondary emulsions show a degree of stability which may be maintained by surface charges. One should consider the Van der Waals attraction in the presence of a surface charge on the drop and on the fiber.

SUMMARY

Van der Waals repulsions as well as attractions are possible and, in a system where the dispersed and continuous phases are of the same nature, both are probable. This conclusion has far-reaching implications in systems where physical forces are important, such as adsorption and catalysis. The selectivity of certain adsorbents or catalytic materials may be explained on the basis of the Van der Waals forces.

NOTATION

A = London-Van der Waals constant as defined by Equation (11)
d = distance separating two particles
D = diameter
E = energy
F_A = force of adhesion
I_i = ionization potential of species i
k_{ij} = ratio of intermolecular distances, $k_{ij} = r_{ii}/r_{jj}$
N_i = number of volume elements per cc. of species i
$P_y(x)$ = a function relating the relative size and position of two spherical particles of radii a and b
r_{ij} = intermolecular distance between species i and j
x = d/D_a
y = D_b/D_a

Greek Letters

α_i = polarizability of substance i
θ = contact angle as measured through the dispersed phase
λ_{ij} = London-Van der Waals constant for the pairs of species indicated by the subscript
$\pi_{ij,k}$ = film pressure
σ = surface free energy
Φ = constant as defined by Equation (3)

Subscripts

1 = drop fluid
2 = field fluid } as shown in Figure 1
3 = solid or fiber
f = refers to cylindrical or spherical surface
i = used to signify 1, 2, or 3
j = used to signify 1, 2, or 3
o = spherical drop in the free stream
s = drop resting on a surface

Superscript

d = indicates dispersive force contribution

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