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## The Binding Energy between a Crystalline Solid and a Liquid: the Energy of Adhesion and Emersion. Energy of Emersion of Crystalline Powders. II\*

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### 1. Introduction

Up to the present time there has been practically no knowledge of the magnitude of the binding energy between an ordinary liquid and unit area of the surface of a crystal. It is, however, extremely simple to calculate this energy from the area of the crystalline material, and its heat of immersion in the liquid (Paper I). From the value thus found the energy of binding can be calculated for the area of the solid in contact with a molecule or mole of the material of the liquid, provided the mean area covered by a molecule of the liquid is known, or can be estimated.

In this process the surface of the solid and its accompanying energy ( $\epsilon_s$ ) are transformed into the interface between the solid and the liquid (S,L) with its smaller energy ( $\epsilon_{SL}$ ). The net energy  $\epsilon_s - \epsilon_{SL}$  is transformed into the heat  $q_L$ . With water this net energy varies from 490 erg cm.<sup>-2</sup> for crystalline barium sulfate to 850 erg cm.<sup>-2</sup> for crystalline zirconium silicate.

The solid and the liquid may be brought together in another way. Assume that a bar of solid and a cylinder of liquid are put in contact to form one sq. cm. of interface (Fig. 1). In this process the energy of the two surfaces  $\epsilon_s$  and  $\epsilon_L$  are transformed into that of the interface ( $\epsilon_{SL}$ ) and heat appears in its place. The process is that of adhesion. The thermodynamics of immersion and adhesion has been developed,<sup>1,2</sup> but the relations between the change of internal energy, the heat given off, and some other quantities were not included, so a more complete thermodynamic treatment of the subject is given here.

### 2. Thermodynamics of Immersion and Adhesion

The increase in enthalpy ( $h_L$ ) which accompanies an increase by one sq. cm. in the area of the surface of a pure liquid is  $h_L = \Delta H_L / \Delta \sigma_L$ . Also  $q_L = Q_L / \Delta \sigma_L$ , where  $Q_L$  is the heat absorbed in the isothermal expansion of the surface, and  $\Delta H_L$

and  $\Delta \sigma_L$  are the total increments in the enthalpy and in the area. Now

$$h_L = \gamma_L - T(\partial\gamma_L/\partial\sigma_L)_{p,T} = \gamma_L - T\sigma_L = \gamma_L - q_L = \gamma_L - l_L \quad (1)$$

where  $\gamma = (\partial F_L / \partial \sigma_L)_{p,T}$  is the increase in the free energy,  $s$  is the increase of entropy, and  $Ts = q_L$  is the heat added in a reversible, isothermal change to keep the temperature constant, when the increment of area is 1 sq. cm. In surface chemistry  $l$  is designated as the latent heat of the surface.

Now

$$h_L = \epsilon_L + p v_L \quad (2)$$

where  $v_L$  is the volume per unit area, so

$$dh_L = d\epsilon_L + p dv_L + v_L dp \quad (3)$$

or at

$$p = \text{const.} \quad d\epsilon_L = dh_L - p dv_L \quad (4)$$

and

$$\epsilon_L = h_L - p \Delta v_L \quad (5)$$

where  $\epsilon_L$  is the increase of internal energy associated with unit increase of area. In the past either  $\epsilon_L$  or  $h_L$  has been designated as the "total surface energy," or as the "surface energy," so it is important to consider whether there is any experimentally distinguishable difference between the two. Since  $\gamma$  is usually determined at atmospheric pressure, and since  $\Delta v$  is very small for the formation of unit area of surface, the value of  $p \Delta v$  is very small in comparison with that of  $\gamma$ ,  $h$ , or  $\epsilon$ . Actually it is in general much smaller than the error in the determination of  $\gamma$ .

It is possible to calculate the value of  $p \Delta v$  at the interface between either water or ether, and mercury, from the work of Lynde<sup>3</sup> on the effect of pressure upon the interfacial tension (375 and 379 dyne cm.<sup>-1</sup>, respectively, at 20°).<sup>4,5</sup>

The value of  $\partial\gamma/\partial p$  in the equation  $(\partial v/\partial \sigma)_{p,T} = (\partial\gamma/\partial p)_{\sigma,T}$ , is  $0.9 \times 10^{-8}$  cm. for the interface mercury-water. This shows that the increase in volume which accompanies the formation of unit

\* Original manuscript received February 14, 1940.

(1) W. D. Harkins, *Proc. Natl. Acad. Sci.*, **5**, 562 (1919).

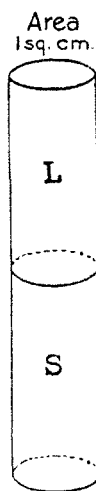
(2) W. D. Harkins and R. Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930).

(3) Lynde, *Phys. Rev.*, **22**, 181 (1906).

(4) W. D. Harkins and E. H. Grafton, *THIS JOURNAL*, **42**, 2534 (1920).

(5) W. D. Harkins and W. W. Ewing, *ibid.*, **42**, 2539 (1920).

area is  $0.9 \times 10^{-8}$  cc., and the work done at atmospheric pressure is  $0.9 \times 10^{-2}$  erg cm.<sup>-2</sup>. The corresponding value with ethyl ether is  $1.6 \times 10^{-2}$  erg cm.<sup>-2</sup>. The values of  $\partial v/\partial \sigma$  show, within the limits of accuracy of the work, that the interfacial region is 0.9 and 1.6 Å. thicker for water-mercury and ether-mercury, respectively, than if the materials had the same density as in the interior of the phases.



Since  $h_{L_1L_2}$  is considerably larger than  $\gamma_{L_1L_2}$ , the energy values thus obtained show that  $h_{L_1L_2} = \epsilon_{L_1L_2}$  is true within 0.002 and 0.004%, respectively, for these two interfaces. Thus it does not seem unwarranted to assume that in general the difference between  $h$  and  $\epsilon$  is not greater than 0.01% at pressures of one atmosphere or less, and this is very much smaller than the error in the determination of  $\gamma$ .

The increase of internal energy  $\epsilon$  in the formation of the surface of a liquid is brought about, by the motion of the molecules from inside the liquid into the surface, against the forces of molecular attraction. Thus  $\epsilon$ , and therefore  $h$ , may be considered as a measure of the increase in the molecular potential energy in the formation of the surface.

It is customary in the treatment of the energy changes in the surface of a liquid to consider a process in which the surface area, and therefore the surface energy ( $\sigma \partial F/\partial \sigma_L$ ,  $\sigma \partial H/\sigma \partial_L$ , or  $\sigma \partial E/\partial \sigma_L$ ) increases. It therefore seems consistent, in the treatment of the processes of *immersion* of a solid powder (or droplets of a foreign liquid) in a liquid, or of the adhesion between a solid and a liquid (or two liquids), to choose the *process* considered in such a direction as to give an increase in  $\Sigma \gamma$ ,  $\Sigma h$ , and  $\Sigma \epsilon$  where, for example,  $\Sigma h$  for adhesion represents  $h_S + h_L - h_{SL}$ . In the case

of a solid and a liquid this necessitates that the process shall take place in such a direction as to separate the solid from the liquid. Thus the interface is destroyed, and in this process, which may be designated as emersion, the surface of the solid is formed, while in that related to adhesion there is the additional formation of the surface of the liquid.

The energy changes related to the emersion (E) of a finely divided solid from a liquid are on this basis expressed by

$$\epsilon_E = \epsilon_S - \epsilon_{SL} \quad (6)$$

$$h_E = h_S - h_{SL} \quad (7)$$

Here no appreciable error is introduced if it is assumed that  $\epsilon_E = h_E$  since although  $(p \Delta v)_E$  may be somewhat larger than  $(p \Delta v)_L$ , *i. e.*, ( $\Delta v_E > \Delta v_L$ ), it is also true that  $\epsilon_E$  and  $h_E$  are in general much larger than  $\epsilon_L$  and  $h_L$  for the surface of the liquid.

The energy relations for adhesion may be written

$$\epsilon_A = \epsilon_E + \epsilon_L \quad (8)$$

$$h_A = h_E + h_L \quad (9)$$

Here again  $\epsilon_A = h_A$  is true within the limits of experimental error.

Now, since

$$h_E = \Delta H_E/\sigma \quad (10)$$

where  $\sigma$  is the area of the powder, and  $H_E$  is the increase of enthalpy on emersion, it is extremely easy to calculate the value of the increase in the heat function for adhesion, which is, within the limits of error, the increase in the internal energy ( $\epsilon_A$ ), from the values of the heat of immersion given in Paper I and the (usually known) values for the surface energy of the liquid. It is obvious that the molecular potential energy of the interfacial region increases if the solid and the liquid are pulled apart, and it is apparent from what is given above that this increment is given by the value of  $\epsilon_E$  or  $\epsilon_A$  (Table I).

The energies of adhesion for graphite vary from 255 erg cm.<sup>-2</sup> with carbon tetrachloride to 385 for water. The other solids exhibit their minimum values in the case of barium sulfate (610 with water and 155 with octane), and their maximum values in the case of zirconium silicate (970 and 240, respectively).

Table IC shows the remarkable effect of a minute concentration of a polar-non-polar substance on the energy of emersion from a non-polar solvent. The energy of emersion of ti-

TABLE I

ENERGY OF SEPARATION OF A LIQUID FROM THE SURFACE OF A CRYSTALLINE SOLID. (ERG-CM.<sup>-2</sup>) AT 25° (VALUES FOR LIQUID MERCURY FOR COMPARISON)

Liquid	Solid . . . . BaSO <sub>4</sub>	TiO <sub>2</sub>	Si	SiO <sub>2</sub>	ZrO <sub>2</sub>	SnO <sub>2</sub>	ZrSiO <sub>4</sub>	Graphite	Hg
	A. Energy of Emersion ( $h_E$ or $\epsilon_E$ )								
Water	490	520	580	600	600	680	850	265	
Ethyl alcohol		500		520				250	
Ethyl acetate	370	360		460		530			
Butyl alcohol	360	350		420		500			
Nitrobenzene		280			310		430		
Carbon tetrachloride	220	240			270	320	410	195	
Benzene	140	150		150	190	220	260	225	123
Isoöctane		105			110	120	190		
	B. Energy of Adhesion ( $h_A$ or $\epsilon_A$ )								
Water	610	640	700	720	720	800	970	385	
Ethyl alcohol		550		570				300	
Ethyl acetate	430	420		520		590			
Butyl alcohol	410	400		470		550			(195)
Nitrobenzene		360			390		510		
Carbon tetrachloride	280	300			340	380	470	255	
Benzene	210	220		220	260	290	330	295	193
Isoöctane		155			160	170	240		160

C. Energy of Emersion of TiO<sub>2</sub> from Pure Butyric Acid and its Dilute Solution in Dry Benzene (Calculated from energy values of Harkins and Dahlstrom)

	$E_E$	Molecular area of acid, sq. Å.
Benzene (very dry)	150	
Butyric acid (pure and dry)	400	
Butyric acid (0.0080 moles per kg.)	380	25.6
(Stearic acid, complete monolayer in C <sub>6</sub> H <sub>6</sub> on TiO <sub>2</sub> )		(27.1)

The areas used in the calculation of the energy values given in this table were obtained by the adsorption of nitrogen at -195.8°. The areas for TiO<sub>2</sub>, BaSO<sub>4</sub>, ZrSiO<sub>4</sub>, and graphite were determined by Professor P. H. Emmett, and excellent agreement was obtained in our own determinations by the same method, which were made later. The areas of the other powders were obtained by the use of this method, and the application of the theory of Brunauer, Emmett and Teller. The area assumed for the nitrogen molecule is 16.2 sq. Å., in accord with the usage of these authors for liquid nitrogen. In the work of H. K. Livingston and the writers it was found that if the nitrogen area were assumed as 15.4 sq. Å., and those of H<sub>2</sub>O and propyl alcohol at 24° as 10.6 and 20.0 sq. Å., respectively, a sample of TiO<sub>2</sub> gave the areas 8.27, 8.28, and 8.25 sq. meters per gram as determined by the adsorption of the vapors of these three substances at the temperatures given. It is obvious that all of the energy values given in this table would be increased if the nitrogen molecule were assumed to have a smaller area on the surface on which it is adsorbed. It seems probable that, while the area seems to be somewhat dependent on the surface lattice of the crystal on which it is adsorbed, a somewhat smaller value than 16.2 sq. Å. is more probable. However, it has been considered that further work to establish a standard area should be done before an attempt is made to change to a lower value. Brunauer and Emmett give 13.8 sq. Å. as the value obtained from solid nitrogen. This would give 9.5 sq. Å. for water, and 17.9 sq. Å. for propyl alcohol at 24°, which may be too low.

tanium dioxide from benzene is only 150 erg cm.<sup>-2</sup>, but when the surface is in equilibrium with 0.0080 molal butyric acid in benzene, the value of  $\epsilon_E$  is increased to 380, while in pure dry butyric acid it is only a very little higher (400).

The care which must be taken to exclude water from non-polar liquids is shown by the heat of emersion,  $h_E$  in erg cm.<sup>-2</sup>, as a function of the initial concentration ( $c$ ) of water in moles per kilogram of benzene. In this work one g. of titanium dioxide of area  $9.24 \times 10^4$  sq. cm. g.<sup>-1</sup> was immersed per 8.74 g. of benzene which contained  $a$  moles of water.

TABLE II

EFFECT OF A TRACE OF WATER ON THE ENERGY OF EMERSION OF TiO<sub>2</sub> (ANATASE) FROM BENZENE

Initial concn. of H <sub>2</sub> O, C × 10 <sup>3</sup> , mole kg. <sup>-1</sup>	Initial amount of H <sub>2</sub> O, a × 10 <sup>3</sup> , moles	$h_E$ , erg cm. <sup>-2</sup>
0.0	0.0	150
2.0	1.75	250
4.0	3.50	320
10.0	8.74	450
17.0	14.85	506
H <sub>2</sub> O (pure)	H <sub>2</sub> O (pure)	520

The equilibrium concentrations of the water were not determined, but they were, even at the highest concentration, below 0.00001 molal.

In acetone the energy of immersion ( $h_E$  or  $\epsilon_E$ ) of titanium dioxide is 300 erg cm.<sup>-2</sup>, which places it between butyl alcohol and nitrobenzene in Table I. The solids may be classified a (1) hydrophilic or polar, such as barium sulfate and the oxides, and (2) hydrophobic or non-polar, as graphite. Of the polar solids barium sulfate is ionic.

The energy of separation of the hydrophilic solids exhibits the two important relations: (1) If the solids are arranged in the order of increasing energy of separation from water, they are also arranged in this order for all of the other liquids. An apparent exception for butyl alcohol with barium sulfate and titanium dioxide is within the limits of experimental error. (2) If the liquids arranged in order of decreasing energy with respect to one of these solids (as titanium dioxide) they are arranged in this order for all of the other solids.

These relations are non-specific or physical, rather than specific or chemical. However, the presence of a dipole in the molecule of the liquid causes the energy of binding, as measured for immersion or adhesion, to be high.

It is obvious that the number of dipoles of the liquid, present at unit area of the surface of the solid, depends upon the area per molecule of liquid, and this is dependent upon the orientation in the first monolayer of liquid. If the molecules are polar-non-polar it is not difficult to show that the probability is extremely high that the molecules will be oriented with their dipole group toward the surface of any of the hydrophilic solids. In the case of butyl alcohol, the relative probability that the dipole will be oriented directly toward or away from the surface of the solid may be considered. For the sake of simplicity it may be assumed that the molecule is a cylinder with a circular end of 20 sq. Å. area. Let 1 sq. cm. of the liquid be pulled away from the solid. This requires an energy of 400 ergs. Assume that this corresponds to pulling away the polar end of the cylinder from contact with the solid.

In the surface of the alcohol thus formed almost all of the molecules are oriented with their non-polar groups toward the vapor, so the 400 erg cm.<sup>-2</sup> includes the energy of orientation. The liquid is now put in contact with the solid while keeping the orientation fixed. The energy thus gained may be assumed to be equal to the adhesion energy for a hydrocarbon (155 erg cm.<sup>-2</sup>

for iso-octane). Thus the potential energy ( $E$ )<sub>2</sub> with this last orientation is 400 - 155 = 245 erg cm.<sup>-2</sup> greater than for the initial contact with the solid, if the only energy considered is that at the ends of the cylinders. This corresponds in erg molecule<sup>-1</sup> to 49 × 10<sup>-14</sup>, while at 298° the value of  $kT$  is 4.09 × 10<sup>-14</sup>. The Boltzmann probability relation may be written

$$N_1/N_2 = p_1/p_2 e^{(E_2 - E_1)/kT} = e^{(E_2 - E_1)/kT} \quad (11)$$

since the ratio  $p_1/p_2$  of the *a priori* probabilities is unity. This gives

$$N_1/N_2 = e^{12} = 1.6 \times 10^5 \quad (12)$$

Thus, on the basis given there is only one molecule with the polar group directly away, to 160 thousand with the group turned toward, the solid, while with stannic oxide there is only one to 116 million. With titanium dioxide the value of  $N_1/N_2$  is reduced to 4.9 × 10<sup>4</sup> if the area per alcohol molecule is supposed to be 18 sq. Å.

If it is desired to take account of the sides as well as the ends of the cylinders, certain relations may be utilized to help in the calculation. Consider the relative probability that (1) *all* of the molecules should be turned with polar groups toward the solid, or (2) toward the alcohol. *Except for the effect upon the orientation of the next layer of molecules in the alcohol, which is due almost entirely to the ends*, the probability would be about unity if the orientation were determined by the sides alone. This is because polar groups would remain next to polar groups, and non-polar groups next to non-polar groups. It has been found by Harkins that the energy of attraction between such polar groups and non-polar hydrocarbon chains is practically the same (per unit area of contact) as between the hydrocarbon chains themselves. When these relations are taken into account it seems that the probabilities calculated above, in which only the energy at the ends of the molecules was considered, will not become changed very greatly if the sides are taken into account.

The area per molecule in the monolayer adjacent to the solid depends, in addition to the orientation, upon the intermolecular forces in the layer, in the liquid, and between the molecules in the monolayer and the surface of the solid. At equilibrium if one molecule enters the monolayer, another leaves it. With less than the equilibrium number the concentration in the layer increases. The factors which act to increase the concentration are the dipole and dispersion forces in the

TABLE III  
ENERGY OF SEPARATION OF A LIQUID FROM THE SURFACE OF A CRYSTALLINE SOLID (KCAL. PER MOLAR AREA OF LIQUID)  
AT 25°

Liquid	Solid . . . BaSO <sub>4</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	ZrO <sub>2</sub>	SnO <sub>2</sub>	ZrSiO <sub>4</sub>	Graphite
A. Energy of Emersion ( $H_E$ or $E_E$ )							
Water (10.6)	7.5	8.0	9.2	9.2	10.4	13.0	4.1
Ethyl alcohol (16.2)		11.7	12.2				5.9
Ethyl acetate (20)	10.7	10.4	13.3		15.4		
Butyl alcohol (20)	10.4	10.1	12.2		14.5		
Nitrobenzene (24)		9.7		10.8		15.0	
Carbon tetrachloride (29)	9.2	10.1		11.3	13.4	17.2	8.3
Benzene (24)	4.9	5.2	5.2	6.6	7.6	9.0	7.8
Isoöctane (end) (20)		3.0		3.2	3.5	5.5	
Isoöctane (side) (50)		7.5		8.0	8.8	13.7	
B. Energy of Adhesion ( $H_A$ or $E_A$ )							
Water	9.4	9.8	11.0	11.0	12.3	14.9	5.9
Ethyl alcohol		12.9	13.4				7.0
Ethyl acetate	12.5	12.2	15.1		17.1		
Butyl alcohol	11.9	11.6	13.6		15.9		
Nitrobenzene		12.5		13.6		17.7	
Carbon tetrachloride	11.7	12.6		14.3	15.9	19.7	10.7
Benzene	7.3	7.6	7.6	9.0	10.1	11.5	10.3
Isoöctane (end)		4.5		4.6	4.9	7.0	
Isoöctane (side)		10.6		11.1	11.9	16.8	

layer, the fugacity of the liquid, and the adhesive energy between the monolayer and the solid. If dipoles are present the adhesive forces are very important. Factors which limit the increase in concentration are the repulsive forces in the monolayer, and the kinetic energy as represented by  $kT$ .

If the adhesional energy were constant over the whole area, its high magnitude would give a closer packing in the monolayer than in the liquid, but since, however, its magnitude may vary greatly with the position of the molecule in the monolayer relative to the atoms or ions in the surface of the solid, this is not a necessary result. On account of this factor, which may be designated as that of fitting, the molecular areas assumed in Table III have not been made to correspond to the closest possible packing, but for polar-non-polar molecules to the closest packing in solid monolayers on water, in cases where this is known. The area for carbon tetrachloride is taken as  $v^{2/3}$  for the liquid.

The energy of separation of eight liquids from the surfaces of crystalline solids is given in Table III. The values correspond in each case to that area of solid which is covered by a mole of the liquid present in the first monolayer. It is evident that the accuracy of the values is not greater than that in the estimates of molecular area. For a single liquid the relative values are the same as

in the earlier tables. It is obvious that the relatively low values for water are due to the small area (10.6 sq. Å.) for this molecule.

#### 4. Discussion

The only values for the specific energy of immersion with which those in Table II can be compared are those of Iliin<sup>6</sup> for barium sulfate in water 1600, in ethyl alcohol 830, in carbon tetrachloride, 640. The ratio of these values is 1:0.519:0.400. The ratio in Table II, but inserting the value for butyl, instead of ethyl alcohol, is 1:0.76:0.46. Iliin's results are approximately three times those in Table II, but he used the microscopic method for the determination of area, which commonly gives too low area, that is, too high energies.

The values obtained with graphite may be com-

TABLE IV  
ENERGY OF EMERSION OF CHARCOAL AS OBTAINED FROM THE ENERGY OF ADSORPTION. (KCAL. PER MOLE, LAMB AND COOLIDGE)

The values in parentheses are those obtained by us with graphite.

CH <sub>3</sub> OH	3.6	CHCl <sub>3</sub>	6.9
C <sub>2</sub> H <sub>5</sub> OH	4.3 (5.9)	CCl <sub>4</sub>	8.1 (8.3)
CS <sub>2</sub>	5.8	C <sub>2</sub> H <sub>6</sub>	7.4 (7.8)
C <sub>2</sub> H <sub>5</sub> Cl	6.1	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	9.2
C <sub>2</sub> H <sub>5</sub> Br	7.5		
C <sub>2</sub> H <sub>5</sub> I	6.4		

(6) B. Iliin, S. Bragin and A. Leontinia, *Phil. Mag.*, [7] **33**, 298 (1927).

pared with those of Lamb and Coolidge<sup>7</sup> for active charcoal.

Although the liquids are not in general the same, it is evident that for the two non-polar liquids their magnitudes with charcoal are almost the same as ours with graphite.

Since  $h_s = h_{SL} + h_{E}$ , and both quantities on the right-hand side of the equation are positive, the total surface energy of each of the solids listed in Table II must be higher than the highest energy of immersion for the solid, which in every case is that in water. Thus the surface energy of zirconium silicate and of titanium dioxide must be higher than 850 and 520 erg cm.<sup>-2</sup>, respectively. The energy of immersion of titanium dioxide in isoöctane is 105, while that of liquid mercury in *n*-octane at 20° is 131, in the same units. The surface energy of mercury ( $h_L$  or  $\epsilon_L$ ) is 541, and energy of the interface *n*-octane-mercury, is 410. While the energies of immersion of titanium dioxide and of mercury in octane are almost the same, the introduction of a polar group increases greatly this energy in the case of titanium dioxide, but has a relatively small effect when mercury is immersed. Thus the surface of titanium dioxide (anatase) exhibits much more the characteristic of a polar material than does that of mercury.

The molar energies of vaporization for water, carbon tetrachloride, and benzene are, at 25°, 10.5, 8.0, and 8.0 kcal. mole<sup>-1</sup>, while those for adhesion are 9.8, 12.6, and 7.6, if the solid is titanium dioxide, and 14.9, 19.7, and 11.5 if it is zirconium silicate. Thus with titanium dioxide the molar energy of adhesion is not very different from that for the vaporization of the liquids, but with zirconium silicate the energy of adhesion is much higher.

However, since in vaporization all parts of the molecule become separated from the others, and in removal by the adhesional process there is a separation on only one side of the monolayer, the latter should be much smaller (unless the molecular binding is much greater). A comparison which is more pertinent is that with the *specific* energy of adhesion between a liquid and water (Table V).<sup>8,9</sup>

This table shows that the change of the liquid from non-polar to polar-non-polar gives a much greater relative increase in the adhesional energy

(7) A. B. Lamb and A. S. Coolidge, *THIS JOURNAL*, **43**, 1146 (1920).

(8) W. D. Harkins and Y. C. Cheng, *ibid.*, **43**, 35 (1921).

(9) W. D. Harkins and W. W. Ewing, *ibid.*, **42**, 2539 (1920).

TABLE V

RELATIVE SPECIFIC ENERGY OF ADHESION ( $\epsilon_{A1}/\epsilon_{A2}$ ) BETWEEN TITANIUM DIOXIDE (ANATASE) AND LIQUIDS, AND BETWEEN WATER AND LIQUIDS (VALUE FOR OCTANE = 1.00)

	TiO <sub>2</sub>	Water	Hg
Octane	1.00	1.00	1.00
Benzene	1.42	1.24	1.00
Carbon tetrachloride	1.93	1.00	
Organic acids	2.70	1.40	
Esters	2.70	1.40	
Alcohols	2.70	1.46	1.22
Water	4.10	2.18	

with titanium dioxide than with water. Thus the increase above that with octane is 300% with titanium dioxide and about 100% with water. With the other polar solids the increases are about 460% for stannous oxide and zirconium oxide, and 350% for zirconium silicate. The ratio of the energies  $\epsilon_A(\text{TiO}_2)/\epsilon_A(\text{H}_2\text{O})$  is found to have a value of 1.47 and 1.65 for octane and benzene, respectively, but seems to be much larger and practically constant (2.8) for carbon tetrachloride, the polar-non-polar liquids, and water. That carbon tetrachloride, as determined by this ratio, is in the same class as the molecules which have dipoles, may be due to its high polarizability ( $\alpha = 10.5 \times 10^{-25}$ ). If this is correct, it seems necessary to assume that the effective polarizability for benzene is less than this. Thus it would seem that the polarizability of  $6.35 \times 10^{-25}$  perpendicular to the ring, is the one which is effective, which would indicate that most of the benzene molecules in the first layer are oriented with the plane of the ring parallel to the surface of the solid.

While the dipole moment of the molecules of the liquid is important in determining the orientation of the molecules at the interface, a comparison of the values of the energy of immersion in butyl alcohol ( $\mu = 1.65 \times 10^{-18}$ ) with those in nitrobenzene ( $\mu = 4.1 \times 10^{-18}$ ), indicates that the high magnitude of the moment of the latter does not give a significantly higher energy. While the energy per molar area of the liquid is about 14% higher for the nitro compound, this is not greater than the uncertainty in the molar areas of the liquids. On the basis of unit area of the interface the energy of immersion is 25% higher for the alcohol. There are two factors which seem to give a greater energy of the binding for the nitrobenzene, if the dispersion or London forces only are considered. These are the greater

area, and the presumably larger molecular polarizability of this substance. If this is correct it would seem that the dipole binding is somewhat higher for the alcohol, even though its dipole moment is only 40% of that of nitrobenzene. This may be accounted for by the small size of the proton, which may allow the dipole to approach closer to the surface than in the case of the nitro compound. Obviously the attraction of the dipoles is greatly affected by their orientation.

From the energies of emersion or of adhesion exhibited by graphite, it is apparent that this crystalline substance acts as a typical non-polar solid. Thus per unit area the value of  $h_E$  is only slightly smaller for benzene than for either water or ethyl alcohol. In contrast the molar value ( $H_E$ ) in either benzene or carbon tetrachloride is practically the same (*ca.* 8 kcal. mole<sup>-1</sup>), while this value is 120% higher than that in water, and 29% higher than that in ethyl alcohol. Obviously the relatively low molar energy for water is due to the small area occupied by its molecules. These relations indicate that the intermolecular energy is, with graphite, due largely to dispersion and repulsive forces.

The heat function for emersion ( $h_E$ ) is related to that for desorption ( $h_D$ ) to form vapor, by the relation

$$h_E = h_D - nH_V = h_D - Nh_v \quad (13)$$

where  $h_E$  and  $h_D$  are heat function per unit area,  $H_V$  and  $h_v$  are the molar and molecular heats of vaporization, and  $n$  and  $N$  give the number of moles and molecules, respectively, of liquid per unit area. This corresponds to the equation of Harkins and Ewing.<sup>10</sup> Lamb and Coolidge<sup>11</sup> present extensive calorimetric data on the heat of adsorption of vapors on charcoal and make the statement: "The observed heat of adsorption will then be made up of two quantities, the latent heat of vaporization of the liquid, and what may be called the *net heat of adsorption*. This is evidently nearly the same as the heat of wetting and is precisely identical with it at the saturation pressure of the liquid." If Eq. 13 is considered to refer to porous, as well as non-porous materials, then the above statement is identical with it. However, this is not strictly in agreement with the definition of  $h_E$  given in Eq. 7, since here  $h_S$  and  $h_{SL}$  refer to the enthalpy of a plane surface.

(10) W. D. Harkins and D. T. Ewing, *Proc. Natl. Acad. Sci.*, **6**, 53 (1920).

(11) Lamb and Coolidge, *THIS JOURNAL*, **42**, 1146 (1920).

While Eq. 13, when interpreted in the more general sense, is suitable for comparisons with the results of calorimetric work on adsorption, such as that of Lamb and Coolidge, the last term in the equation needs amplification if it is to be used for comparison with the adsorption theory of Brunauer, Emmett, and Teller.<sup>12</sup>

Consider two processes, E and D, related to emersion and desorption, respectively. Both begin with the powder immersed in the same amount of liquid, and both end with the vapor of the liquid and the powder from which all the liquid has been removed. In order to simplify the equations the whole system will be assumed to contain just that amount of powder which has an area of 1 sq. cm.

Process E with two steps,  $A_E$  and  $B_E$ :  $A_E$ , remove (emerge) from the liquid all of the powder (with unit area)

$$(\Delta H_E)_A = h_E \quad (14a)$$

This process is to be carried out in such a way as to make entirely negligible any change of interfacial energy other than that specified.  $B_E$ , evaporate all of the liquid

$$(\Delta H_E)_B = nH_V = Nh_v \quad (14)$$

where  $n$  and  $N$  give the number of moles and molecules of the liquid, and  $H_V$  and  $h_v$  are the molar and molecular heats of vaporization.

Process D: This process, which is one of desorption, may also be considered in two steps. The value of  $n$  or  $N$  is kept the same as for emersion.  $A_D$ , evaporate the liquid, which covers 1 sq. cm. of solid, except that material in the first monolayer which is represented by the subscript 1 (while 2, 3, 4, etc., represent the second, third, fourth, etc., molecular layers)

$$(\Delta H_D)_A = (n - n_1)H_V + H_X = (N - N_1)h_v + h_X \quad (15a)$$

Here  $H_X$  or  $h_X$  is a correction term, the significance of which is described later.  $B_D$ , desorb the first monolayer.

$$(\Delta H_D)_B = h_1 \quad (15b)$$

Since  $dH$  is an exact differential

$$(\Delta H_E)_A + (\Delta H_E)_B = (\Delta H_D)_A + (\Delta H_D)_B \quad (16)$$

or

$$h_E = h_1 - n_1H_V + n_X = h_1 - N_1h_v + h_X \quad (17)$$

For an area of solid covered by one mole in the first monolayer this may be written

$$H_E = H_1 - H_V + H_X \quad (18)$$

(12) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 316 (1938).

TABLE VI

VALUES OF  $E_1 - E_L$  IN THE EQUATION OF BRUNAUER, EMMETT AND TELLER. (VALUES OF  $E_E$  FOR COMPARISON) (KCAL. PER MOLAR AREA) $(t = 25^\circ$  except for  $N_2 = -195.5^\circ)$ 

	1 $E_1 - E_L$	$H_2O^1$ 2 $E_E$	2/1 Ratio	3 $E_1 - E_L$	$C_3H_7OH^1$ 4 $E_E$	4/3 Ratio	5 $E_1 - E_L$	$C_6H_6^2$ 6 $E_E$	6/5 Ratio	$n-C_7H_{16}^1$ 7 $E_1 - E_L$	$N_2^2$ 8 $E_1 - E_L$
TiO <sub>2</sub> (anatase)	2.4	8.0	3.3	2.1	(10.1)	4.8	2.6	5.2	2.0		0.88
	2.4			2.1			2.5				.85
	2.6			2.5						2.1	
SiO <sub>2</sub> (quartz)	2.3			1.6	(12.2)	7.6	2.3	5.2	2.3		.55
	2.5	9.2	3.7	2.8						2.0	
ZnO	2.5			1.8							
SnO <sub>2</sub>		10.4		1.9	(14.5)	7.6					.91
BaSO <sub>4</sub>	3.2	7.5	2.3	2.9	(10.4)	3.6				2.2	
ZrSiO <sub>4</sub> II		13.0									.85
Graphite										2.5	
ZnS											.57

\* The values of  $E_E$  listed are for butyl alcohol. According to the data of A. Clark and B. D. Thomas [*J. Phys. Chem.*, **43**, 585 (1939)] these values should be multiplied by 1.2 if they are to represent propyl alcohol ( $C_3H_7OH$ ). On this basis the values of the ratio should be 20% higher than the very high values given in column 4/3.

The equation is not supposed to be valid for polar molecules. However, it seems to give good values for the area of a powder when polar molecules are used. The  $E_1 - E_L$  values were calculated from the data of (1) H. K. Livingston, (2) U. S. Brooks, and (3) G. E. Boyd.

In Eqs. 14 to 18 either  $h_X$  or  $H_X$  is a (often small) composite correction. Let  $H_X = H_Y + H_Z$  (1) Suppose that  $H_2 > H_3 > H_4 \approx H_V$ : then  $H_Y = H_2 + H_3 - 2H_V$ . (2)  $H_Z$  makes allowance for any tighter packing in the first monolayer of a multilayer over that in the monolayer when alone, due to the fact that the multilayer is in equilibrium with a higher vapor pressure than the monolayer.

The value of  $h_X$  or  $H_X$  may become large with polar substances in the multilayer. With polar-non-polar molecules it is possible that  $H_Y$  may be alternately higher and lower for layers of odd and even number, although this alternation will usually not persist for a large number of layers.

Brunauer, Emmett and Teller assume that with non-polar gases  $H_X$  is negligible, so, if this is assumed here also, then

$$H_E = H_1 - H_V \quad (19)$$

Now if their theory gives the correct value of  $H_1$ , which they designate by  $E_1$ , then Eq. 19 may be written in the form

$$H_E = H_1 - H_V = E_1 - E_L \quad (19')$$

However, they consider that the theory does not give the average heat of adsorption of the whole first layer, since they say (p. 315): "Hence  $E_1$  as obtained from the linear plot, must be regarded as the average heat of adsorption for the less active part of the adsorbing surface."

Table VI gives a comparison of the values of

$H_E$  of Table III with those obtained in this Laboratory for  $E_1 - E_L$ . In every instance the molar energy of *emersion* is from 2 to 7.6 times greater than  $E_1 - E_L$ . However, nearly all of the liquids involved are polar, so the simplifying assumption ( $E_2 = E_3 = E_4 \dots = E_L$ ) of Brunauer, Emmett, and Teller should not hold. The discrepancy between  $H_E$  and  $E_1 - E_L$  is found to exist even if the liquid is non-polar, as with benzene, but it is not so large.

Unfortunately only two ratios (2.0 and 2.3) have been determined with this liquid. The ratios have not been obtained for *n*-heptane. These depend upon the orientation assumed for the molecules in the first layer. From the work of H. K. Livingston and ourselves it may be assumed that molecules of *n*-heptane lie flat on the surface. From values of  $H_E$  for isoöctane, calculated on the basis of this assumption, it seems that the ratio  $H_E/(E_1 - E_L)$  is somewhat larger than with benzene.

Since the relation between  $H_1 - H_V$ , and the  $E_1 - E_L$  of the adsorption theory is under investigation in this Laboratory by George Jura, the ratio of the two will not be considered further here.

Brunauer, Emmett and Teller obtain a nearly constant value ( $850 \pm 50$  cal.) of  $E_1 - E_L$  for nitrogen, while (Table III) the energy of emersion ( $H_E$ ) varies much more widely. It seems that the simple method proposed for the calculation of the area by the use of a single adsorption point,



as proposed by Brunauer, Emmett and Teller, is, with certain solids, much less reliable than they suppose it to be. Nevertheless if many, properly spaced, adsorption points are taken the theory seems to give practically the same *area* if the adsorbed molecules are polar as when they are non-polar.

While the orientation of polar molecules on the surface of solids of the type of silicon dioxide, titanium dioxide, etc., is determined by the dipole moments of the molecules, the energy of interaction is dependent upon the bond moments, though in attempts to calculate the magnitude of the energy of interaction between the solid and the liquid it may be better to consider that there is a system of point charges in both. The question of the existence of hydrogen bonds is not discussed in this paper, since more evidence of their existence and magnitude should be obtained before this is done.

### Summary

1. The increase of enthalpy ( $h_E$ ) or of internal energy ( $\epsilon_E$ ) which accompanies the emersion (opposite of immersion) of various polar solids from water, is in erg cm.<sup>-2</sup>: barium sulfate, 490; titanium dioxide, 520; silicon dioxide, 600; stannous oxide, 680 and zirconium dioxide, 600; zirconium silicate, 850. With graphite, a non-polar solid, the value is much lower (265).

2. The values become lower as the liquid, from which the solid is emersed, becomes less polar. Thus with titanium dioxide (anatase) as the solid, the values for nine liquids are: water, 520; butyric acid, 400; ethyl acetate, 360; butyl alcohol, 350; acetone, 300; nitrobenzene, 280; carbon tetrachloride, 240; benzene, 150; and isoöctane, 105. With the other polar solids the energies are different, but their ratios for the different liquids are almost the same. With graphite, a non-polar solid, there is very much less difference between the values of  $h_E$  or  $\epsilon_E$  from polar and non-polar liquids. The values are: water, 265; ethyl alcohol, 250; carbon tetrachloride, 195; and benzene, 225.

3. The relative values of the molar energies of emersion ( $H_E$ ) of the various solids are, for any one liquid, the same as for unit area, but the relative molar values for different liquids are not at all the same, since they depend upon the molecular area of the liquid. With titanium dioxide the values are, in kcal. mole<sup>-1</sup>: water, 7.5; ethyl acetate, 10.4; butyl alcohol, 10.1; nitrobenzene,

9.7; carbon tetrachloride, 10.1; benzene, 5.2; while the value calculated for isoöctane is highly dependent upon the orientation assumed for the molecules of isoöctane in the interface. Actually they lie flat.

4. The energies of adhesion ( $H_A$  or  $E_A$ ) for the separation of the solid from the liquid, are given in Tables II and III.

5. The energy of immersion of titanium dioxide in butyric acid at 25°, calculated from the data of Harkins and Dahlstrom, is 400 erg cm.<sup>-2</sup>. If this acid has a concentration of 0.0080 mole in 1 kg. of dry benzene the molecular area of the adsorbed acid is 25.6 sq. Å., and the heat of emersion is 380 erg cm.<sup>-1</sup>, or only 5% lower than with the pure acid. If 1 g. of titanium dioxide, of area  $9.24 \times 10^4$  cm. g.<sup>-1</sup>, is immersed in 8.74 g. of benzene which contains initially 17 millimoles of water per kg. of benzene, the energy of immersion is 506 erg cm., which is only 2.7% less than in water.

6. The probability is very high that the polar group of a polar-non-polar molecule of a liquid, at the interface with a polar solid, is turned toward the solid. Thus the energy relations show that with butyl alcohol only one in 160 thousand molecules is oriented with its polar group directly away from the surface of titanium dioxide, and only one in 116 million with stannic oxide.

7. For the emersion of graphite  $H_E$  is found to be nearly the same as that found for charcoal by Lamb and Coolidge in carbon tetrachloride and benzene, but in ethyl alcohol the value for graphite is 37% higher.

8. Graphite exhibits no apparent increase in its interaction energy with polar as compared with non-polar groups, so the forces at the interface are attributed to attractive London dispersion energy, mostly of the  $r^{-6}$  type, together with repulsive forces. With polar solids there is in addition the dipole-dipole energy, and possibly a small coördination energy, when polar groups are present in the liquid. As shown by the case of nitrobenzene, this energy may not be at all proportional to the dipole moment, since it depends on the distance and orientation of the dipole.

9. The molar energy of demersion of a powder ( $E_E$ ) which is equal to  $H_1 - H_V$  should equal  $E_1 - E_L$  of the Brunauer, Emmett and Teller equation if certain very simple assumptions are valid. The fact that  $E_E$  is very much larger than  $E_1 - E_L$  indicates that the assumptions are too simple.

Here  $H_1$  or  $E_1$  represents the energy of desorption of the first monolayer, and  $H_V$  or  $E_L$  the

energy of vaporization of a mole of liquid.

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## The Rheology of the Blood. II. The Effect of Fibrinogen on the Fluidity of Blood Plasma\*

BY EUGENE C. BINGHAM AND RAYMOND R. ROEPKE

Treffers<sup>1</sup> has shown recently that the fluidity-concentration relation is linear for solutions of a number of different proteins over a relatively wide range of concentrations. The fluidity-concentration relation may be expressed as

$$\varphi_{\text{rel}} = \varphi/\varphi_0 = (1 - kC) \quad (1)$$

where  $\varphi_{\text{rel}}$  = the relative fluidity of the solution,  $\varphi$  = the fluidity of the solution,  $\varphi_0$  = the fluidity of the solvent,  $C$  = the concentration of the solute in grams per 100 ml. of solvent, and  $k$  = a constant which is dependent on the nature of the solute. This equation is similar to that found by Bingham<sup>2</sup> to hold for various suspensions. The constant,  $k$ , in the above equation will be referred to as the fluidity lowering constant (FLC) of the solute and is equal to the fractional lowering of the fluidity of the solvent brought about by unit concentration of the solute

$$kC = (\varphi_0 - \varphi)/\varphi_0 = 1 - \varphi/\varphi_0 \quad (2)$$

Treffers<sup>1</sup> has expressed the fluidity of a mixture of two proteins which do not interact by the relation

$$\varphi_{\text{mix}}/\varphi_0 = 1 - k_1C_1 - k_2C_2 \quad (3)$$

where  $\varphi_{\text{mix}}$  = the fluidity of the mixture,  $\varphi_0$  = the fluidity of the solvent, and  $k_1C_1$  and  $k_2C_2$  are the FLC's and the concentrations of the two proteins. If this relation holds true for all of the constituents of blood plasma, then the effect of fibrinogen on the fluidity of plasma may be expressed by the relation

$$\varphi_p/\varphi_0 = \varphi_s/\varphi_0 - k_f C_f \text{ or } k_f C_f = (\varphi_s - \varphi_p)/\varphi_0 \quad (4)$$

where  $k_f$  and  $C_f$  are the FLC and concentration, respectively, of the fibrinogen;  $\varphi_p$  is the fluidity of the plasma and  $\varphi_s$  is the fluidity of the serum (plasma less the fibrinogen).

\* The work reported in this communication was presented before the Division of Colloid Chemistry at the St. Louis meeting, April, 1941, and was supported by a grant from the John and Mary R. Markle Foundation.

(1) H. P. Treffers, *THIS JOURNAL*, **62**, 1405 (1940).

(2) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y.

The FLC was determined for blood fibrinogen in solutions of oxalated sodium chloride. An attempt was also made to determine the value of the FLC of fibrinogen in blood plasma by measuring the fluidity of heparinized plasma and of the serum obtained by coagulation of the plasma either by the addition of protamine, to "neutralize" the effect of the heparin,<sup>3</sup> or by the addition of thrombin.

### Experimental

Fibrinogen was separated from ox-blood plasma according to the procedure described by Smith, Warner and Brinkhous<sup>4</sup> and modified by Warner, Brinkhous and Smith.<sup>5</sup> The fibrinogen preparations were dissolved in a solution containing 0.855% sodium chloride and 0.092% potassium oxalate, dialyzed against oxalated saline and adjusted to approximately pH 7.5 with 0.1 *N* sodium hydroxide using phenol red as the indicator. The various concentrations were obtained by diluting the original solutions with oxalated saline.

The heparinized plasma was obtained by using a sterile heparin solution (Connaught Laboratories, Toronto) in the proportion of 0.5-0.7 ml. to 100 ml. of whole blood. The heparin solution, containing approximately 17 mg. of dry solids per ml., was evaporated to dryness on the wall of the tube before collection of the sample. Coagulation of the heparinized plasma was brought about by the addition of 0.5-1.0 mg. of a thrombin preparation (250 units of activity per mg.) or by the addition of 0.25 mg. of protamine (salmine) sulfate per ml. of plasma. We are indebted to Dr. Walter H. Seegers, State University of Iowa for the thrombin preparation and to E. R. Squibb and Sons, New Brunswick, N. J., for the protamine sulfate.

Fibrinogen was estimated by nitrogen determination on the washed clot, using the micro-Kjeldahl method of Keys.<sup>6</sup> The centrifugalized clot was washed once with 0.9% sodium chloride and twice with distilled water, allowing an hour or more for each washing. Fibrinogen was calculated from the nitrogen content by use of the factor 6.25, and the concentration of fibrinogen was expressed in grams per 100 ml. of solution.

(3) E. Chargaff and K. B. Olson, *J. Biol. Chem.*, **123**, 153 (1938).

(4) H. P. Smith, E. D. Warner and K. M. Brinkhous, *J. Exp. Med.*, **66**, 801 (1937).

(5) E. D. Warner, K. M. Brinkhous and H. P. Smith, *Am. J. Physiol.*, **125**, 296 (1939).

(6) A. Keys, *J. Biol. Chem.*, **132**, 181 (1940).