CAPILLARY RETENTION OF LIQUIDS IN ASSEMBLAGES OF HOMOGENEOUS SPHERES

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Abstract

The pore space in an assemblage of uniform spheres was initially filled with liquid. After very slow drainage the amount of liquid retained by the spheres was experimentally measured. The liquid is retained in the form of rings at the contacts of adjacent spheres. The radii of curvature of the ring surfaces are computed in terms of surface tension, grain radius and pressure drop across the liquid-vapor interface, permitting calculation of the volume retained per sphere contact. The number of contacts per unit volume of spheres is obtained from porosity measurements using the theory developed earlier. Computed and observed data on total volume of retained liquid are in agreement.

If THE pore spaces in an assemblage of spheres be completely filled by a liquid which is then allowed to drain, a portion of the liquid is retained. The retention occurs during the passage of the liquid-gas interface through the grain assemblage. It is current opinion, as expressed in the semi-technical literature, that such liquid remains in the form of a fairly uniform layer which envelops the separate grains. In order to account for the observed retention, the thickness of the layer would have to be several thousand molecular diameters. Molecular forces, however, decrease extremely rapidly with distance, and unless chemical reactions, such as those involving gel formation, take place, layers exceeding three molecular diameters are improbable. Much of the work on retention has been done with comparatively fine sands and the actual mechanism of the phenomenon has escaped notice. Under the microscope, however, one may readily observe that a small ring of liquid is retained at the point of contact of two spheres. This type of retention is easily demonstrated by dipping two small balls or shot in a liquid and observing the retained liquid when the spheres, in contact, are withdrawn. It also follows from thermodynamical considerations that the major retention occurs in this manner. Equilibrium requires a minimum of free energy, and when the spheres are sufficiently small that gravitational effects are negligible, a given amount of retained fluid must be so distributed that the surface energy is a minimum. This occurs when the liquid is collected about the points of contact of the spheres.

The ring volume can be calculated approximately. Consider a capillary ring of liquid as shown in Fig. 1 with the two principal radii of curvature y and R taken as positive numbers. Complete wetting or zero contact angle with the spheres is assumed. Let Δp be the difference in pressure just outside and inside the liquid surface, and let σ be the surface tension. Then

$$\Delta p = \sigma\left(\frac{1}{R} - \frac{1}{y}\right) \tag{1}$$

From geometry it follows, if r is the radius of the spheres, that

$$\frac{1}{R} = \frac{2(r - y)}{y^2} \tag{2}$$

and accordingly,

$$y = \frac{-3 + (9 + 8r\Delta p/\sigma)^{1/2}}{2\Delta p/\sigma}\,. \tag{3}$$

Putting $y/r = k$ and $R/r = \alpha$, the volume v of the ring of liquid is readily found to be

$$v = 2\pi r^3 \frac{\alpha}{1 + \alpha} f(k, \alpha) \tag{4}$$

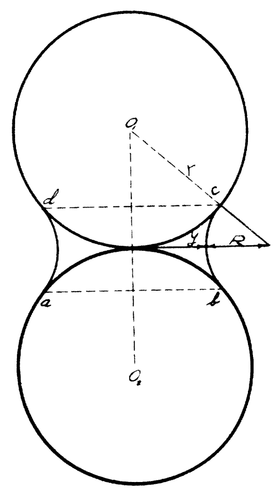

Fig. 1. Capillary ring of liquid between two spheres.

where

$$f(k, \alpha) = (k + \alpha)^2 - \alpha(k + \alpha)\left\{1 - \frac{1}{(1 + \alpha)^2}\right\}^{1/2} - \alpha(k + \alpha)(1 + \alpha)\sin^{-1}\frac{1}{1 + \alpha} + \alpha^2 - \frac{\alpha}{1 + \alpha}\,.$$

This gives the volume of a single ring formed at a contact of two spheres in terms of parameters involving the quantity Δp which will be given consideration later.

In an earlier paper[1] the writers showed that in the natural piling of uniform spheres to a porosity P, the average number n of contacts per sphere is given by the approximate relation

[1] Smith, Foote and Busang, Phys. Rev. **34,** 1271–1274 (1929).

$$n = 6\frac{1 + 1.828x}{1 + 0.414x} \tag{5}$$

where

$$x = (0.476 - P)/0.217$$

The number N of spheres per unit volume is

$$N = \frac{1 - P}{4\pi r^{3/3}} \cdot \tag{6}$$

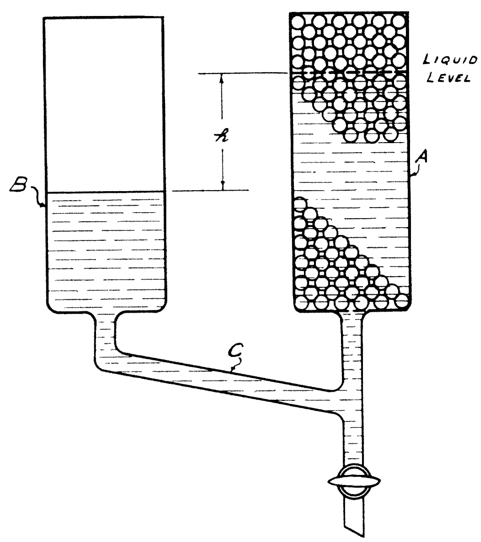

Fig. 2. Schematic diagram of drainage experiments in which the meniscus surface is above the free surface by the distance h equal to the capillary rise.

Since in the complete assemblage, two spheres determine a single contact, the number of contacts per unit volume is $Nn/2$ and the volume V of liquid retained per unit volume of packed space is

$$V = Nnv/2. \tag{7}$$

The value of Δp depends upon the manner in which drainage occurs. In general the flow of fluid through any single pore composed of three adjacent grains is along the axis normal to the plane of the grain centers, as is the case with a meniscus falling in a simple cylindrical tube. The interface always drops in a direction parallel to the axis of the tube provided that it is not too large. Let us consider a single contact and the pores on either side. As the complex meniscus of the whole sand body falls, the portion of it in this restricted region drops through the adjacent pore spaces wrapping itself around the contact point. As the interface falls further the liquid immediately under the contact point is constricted and finally breaks, leaving that around the contact in the form of a ring and separated from the main body of liquid. The final curvatures of the ring are closely equal to those which it had just prior to breaking and these are determined by the pressure difference Δp prevailing at that instant, subject, of course, to the limitation that the spheres are not too large.

The simplest case is that in which Δp is the meniscus pressure drop prevailing at maximum capillary rise, a condition which can be produced by allowing the free liquid and meniscus to fall simultaneously and very slowly in a U-arrangement such as is shown in Fig. 2. A contains the grains and B provides the liquid receptacle and is connected to A by a small tube C. If now the liquid is allowed to drain from the system by bleeding it from the stop-cock, the meniscus will remain at a height h above the free liquid in B which will not differ greatly from normal capillary rise provided the drainage takes place sufficiently slowly. The pressure drop Δp across the meniscus formed by the liquid surface within the sphere assemblage is accordingly given by the capillary equation

$$\Delta p = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \rho g h \tag{8}$$

where r_1 and r_2 are the principal radii of curvature of an element of the meniscus, ρ the density of the liquid, g the acceleration of gravity, and h the height of capillary rise for the particular element. In a paper on "Capillary Rise of Liquids in Homogeneous Sands," to appear later, the writers show that when h is large the average value of $\rho g h$ over the entire meniscus is given by the approximate relation:

$$\overline{\rho g h} = \frac{2\sigma}{r}\left(\frac{0.651 + 0.256x}{0.349 - 0.256x}\right) \tag{9}$$

From Eqs. (3), (8), and (9), we find

$$k = \frac{y}{r} = \frac{-3 + (9 + 8A)^{1/2}}{2A} \tag{10}$$

where

$$A = 2\left(\frac{0.651 + 0.256x}{0.349 - 0.256x}\right)$$

and from Eqs. (2) and (10)

$$\alpha = k/(Ak + 1) \tag{11}$$

The Eqs. (10) and (11) determine α and k from which v can be calculated by substitution in Eq. (4).

It will be observed that retention of this type is independent of the density, surface tension and viscosity of the particular liquid used. No dependence on viscosity, of course, is to be expected because of the very slow rate of drainage. Also the retention per unit volume of packed space is independent of the radius of the spheres used, being a function of the porosity alone as can be seen by substitution of Eqs. (4) and (6) in Eq. (7) from which we obtain

$$V = \frac{3}{4}n(1 - P)\frac{\alpha}{1 + \alpha}f(k, \alpha). \tag{12}$$

Fig. 3 shows the volume V of retained liquid per unit volume of packed space as a function of the porosity and is plotted from Eq. (12). A curve of this type is to be expected. While the number of contacts increases as we decrease the porosity, the height of capillary rise increases as do also the resulting ring curvatures. Hence the volume of a single ring must decrease with decreasing porosity, offsetting the increased number of contacts.

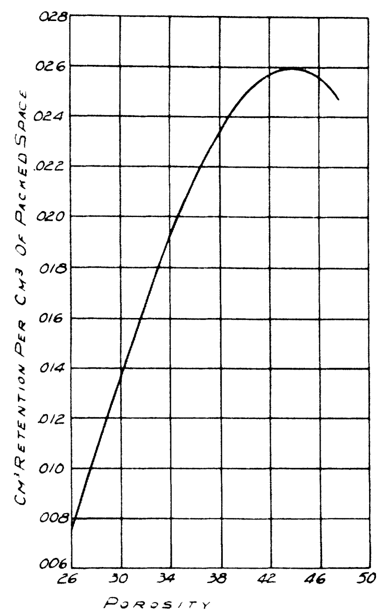

Fig. 3. Volume of retained liquid per unit volume of packed space as a function of porosity.

An experimental investigation was undertaken to test the validity of Eq. (12). The arrangement used is shown in Fig. 4. In principle it is a duplication of that shown in Fig. 2. A, C and D are spherical reservoirs each enclosing a volume of about two liters. A wire gauze was placed at the bottom of A in which the spherical grains were packed. C and D respectively served to fill and collect the liquid whose retention was to be investigated. B, a 3 cm cylindrical glass tube was used as a free liquid container during capillary drainage. a, b and c denote stop cocks for closing off the principal reservoirs. f and g are ground glass stoppers each provided with a small capillary to prevent excessive loss of liquid by evaporation, but permitting atmospheric pressure to prevail.

The procedure was to fill the flask *C* and weigh it. It was then placed in connection with the free liquid reservoir *B* by means of a large ground glass stopper *d*. With stop-cocks *a* and *c* open and *b* closed, the liquid was allowed to slowly fill *A* to the top of the grains. Valve *a* was then closed and the surplus liquid in *C* drained into the flask *D*, connected to the system $A-B$ by a ground glass stopper *e*. The valve *b* was closed so that initially *B* was completely filled. Valve *b* was now opened a little and the liquid in the U-system $A-B$ allowed to drop sufficiently slowly to keep capillary equili-

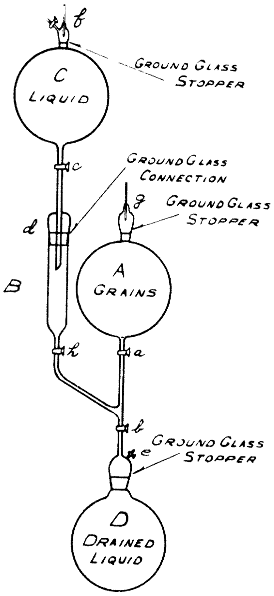

Fig. 4. Arrangement of apparatus in drainage experiments.

brium preserved. The surplus liquid was collected in *D* and weighed. That which remained in *A* was calculated from the difference in weights of liquid drained from *C* and into *D*.

With the smaller sizes the drainage time was necessarily longer, with a consequent increase in experimental losses. For this reason the retention of glass pearls and sands, was determined by taking small samples of about 100 grams each from the grain reservoir immediately after drainage. These were quickly weighed, dried in an oven at 80°C and reweighed, the difference being the weight of the retained liquid. Lead shot of radii 0.219 cm and 0.165 respectively as well as glass pearls of radii 0.0316 cm and standard Ottawa silica sand of radius 0.0443 cm were used in conjunction with a series of liquids of different surface tension and viscosity, the former varying between 25 and 72.8 dynes/cm and the latter from 0.009 to 1.38 poises. Kerosene was used in the cases of glass pearls and sands owing to the impracticability of the methods when volatile liquids such as CCl_4 are used. Its viscosity is such as to permit drainage in a reasonable time. Table I summarizes the results. The observed retentions in cm³ of liquid per cm³ of packed volume are listed in column 5 of the table. Column 6 gives the corresponding quantities computed from Eq. (12). The agreement in general is good.

TABLE I. *Experimental data on retention.*

Grain Material	Grain Radius cm	Porosity	Liquid	Retention per cm³		Density of Liquid	Surface Tension dynes/cm
				Obs.	Computed		
Lead Shot	0.219	0.404	CCl_4	0.0235	0.0250	1.587	24.9
			C_6H_6	.0261	.0250	.875	27.7
			$C_6H_5CH_3$	.0258	.0250	.861	26.7
			Turbine Oil	.0201	.0250	.918	34.3
			Zephyr Oil	.0245	.0250	.846	30.9
			Cayuga Oil	.0222	.0250	.883	32.3
			C_2H_5OH	.0246	.0250	.807	25.4
			Water	.0273	.0250	1.000	72.0
			Mean	.0243	.0250		
Lead Shot	0.165	0.396	CCl_4	.0264	.0279	1.587	25.0
			Zephyr Oil	.0285	.0279	.847	30.9
			Cayuga Oil	.0290	.0279	.847	32.3
			Pequod Oil	.0250	.0279	.893	33.7
			C_2H_5OH	.0276	.0279	.807	25.6
			Water	.0283	.0279	1.000	72.8
			Mean	.0275	.0279		
Glass Pearls	0.0316	0.373	Kerosene	.0255	.0235	.811	28.6
20–24 mesh sand	0.0443	0.359	Kerosene	.0292	.0222	.811	28.5

The results indicate that the wetting layer, a few molecules in thickness, is the only film present in assemblages of uniform spheres, and the volume of liquid so held is negligible in comparison with that found in the form of rings at the grain contacts. The quantities retained are obviously too large to be accounted for by the molecular forces involved in the formation of adsorbed films on a uniform surface. The shot and glass beads used had fairly uniform surfaces while the sand did not. Where rough surfaces are involved, small depressions filled with liquid can exist provided only that they are sufficiently deep to permit proper equilibrium curvatures. Such a type of surface film is permissible, and may account for the fact that the experimental values for sands are in excess of those calculated, although the lack of sphericity of the sand grains may be the controlling factor.