Sedimentation Volume and Thixotropy.

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The present paper describes on the apparent volume of the powder precipitated in the liquid medium, i.e. sedimentation volume.

In the case of a colloidal solution, the sedimentation volume of the particles depends upon the concentration of the electrolyte which is used to coagulate the sol. The sedimentation volume of the organosol varies by the dispersion medium, which has been studied by Wo. Ostwald,(1) A. v. Buzágh,(2) and W. D. Harkins.(3)

The present author has carried out some experiments on the sedimentation volume of powders in organic liquids, and found the parallelism between the sedimentation volume and the thixotropic nature of the system, some new examples of thixotropic systems being found.

Measurement of Sedimentation Volume. The powders which had been washed with water, and then with alcohol vapour and benzene vapour

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(1) Wo. Ostwald and W. Haller, *Kolloidchem. Beihefte*, **29** (1929), 354.

(2) A. v. Buzágh, *Kolloidchem. Beihefte*, **32** (1931), 114.

(3) W. D. Harkins and D. M. Gans, *J. Phys. Chem.*, **36** (1932), 86; L. W. Ryan, W. D. Harkins, and D. M. Gans, *Ind. Eng. Chem.*, **24** (1932), 1288.

respectively, were dried in a high vacuum at 200–300°C., for four to five hours. The organic liquids were purified by the ordinary methods, the care being taken for drying.

In a graduated glass-stoppered test tube of 30 c.c. capacity, 15 c.c. of the liquid was taken, and the powder, after dried, was poured quickly into the test tube. The weight of the powder was known by the difference in weights of the test tube before and after the introduction of the powder. The tightly stoppered test tube was then shaken and allowed to stand in a large desiccator. The powders fell down to the bottom of the test tube in a few hours, however, it took usually about two or three weeks to attain the definite sedimentation volume. The reading of the sedimentation volume was taken when such an equilibrium had been attained.

Some examples are shown in Table 1 to illustrate the reproducibility of the experimental results. Table 2 shows the values obtained for various powders and liquids.

Table 1.

System	Sedimentation volume in c.c. per 1 g. of powder
Glass powder in Toluene	0.84 0.81 0.84 0.80
Zinc oxide in Ethyl alcohol	1.48 1.29
Graphite in Ethyl alcohol	1.70 1.78

Table 2. The sedimentation volume of powders settled in pure liquids.

Liquid \ Powder	Glass	ZnO	Talcum	$CaCO_3$	Graphite	Charcoal	Carbon black
Water	0.71		1.3	0.9	1.6	4.4	3.9
Ethylene glycol		1.3			1.9		3.8
Methyl alcohol		1.3			1.7		
Ethyl alcohol	0.69	1.4	1.4	0.8	1.7		
Acetone				1.1			
Toluene	0.82	2.5	1.9		1.8	4.1	3.8
Benzene				1.7			
Dioxane		1.9	1.7		1.7		3.6
Carbon tetrachloride	0.90	2.1		1.9			
Hexane				2.0			

The results show that if the powder is a polar substance, such as glass, zinc oxide, talcum and calcium carbonate, the sedimentation volume in nonpolar liquid is always larger than that in polar liquid, however, in the case of the nonpolar powder such as graphite, charcoal and carbon black, there are no disparity in the sedimentation volume according to the nature of the liquid.

W. D. Harkins and his coworkers(3) describes the fact that the monomolecular film of the fatty substance adsorbed on the pigment has a marked influence on the sedimentation volume of the pigment.

Experiments were, then, carried out for the solution instead of the pure liquid. The sedimentation volume of the glass powder in toluene containing a small quantity of oleic acid is much smaller than that in pure toluene. For example, the sedimentation volume of glass powder in toluene containing 1% oleic acid was 0.65 c.c. per 1 g. of powder. This volume corresponds to 79 percent of the volume settled in pure toluene. So small as 0.1% of oleic acid is sufficient to decrease in remarkable degree of the sedimentation volume of glass powder in toluene. The results are shown in Fig. 1 and Table 3.

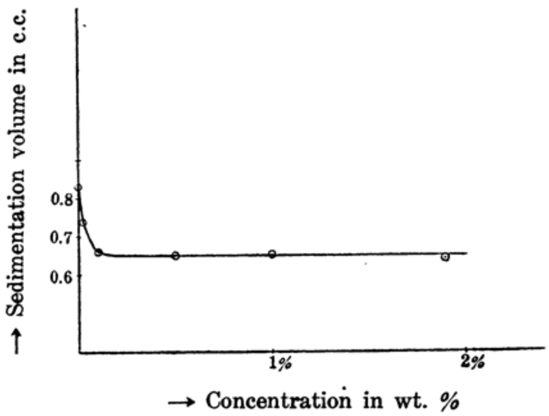

Fig. 1. Sedimentation volume of glass powder settled in Oleic acid/Toluene Solution.

Table 3.

Powder	Solvent	Solute	Sedimentation volume in c.c. per 1 g. of powder	Ratio
Glass	Toluene	—	0.82	1.00
,,	,,	Oleic acid 1%	0.65	0.79
,,	,,	Palmitic acid 2%	0.67	0.82
,,	,,	Tripalmitin 1%	0.68	0.82
,,	,,	Benzoic acid 1%	0.72	0.88
,,	,,	Acetic acid 5%	0.77	0.94
,,	Carbon tetrachloride	—	0.90	1.00
,,	,,	Palmitic acid 0.5%	0.64	0.71

Table 3.—(*Concluded*)

Powder	Solvent	Solute	Sedimentation volume in c.c. per 1 g. of powder	Ratio
Zinc oxide	Toluene	—	2.5	1.00
,,	,,	Hexyl alcohol 1%	1.5	0.60
,,	,,	Lecithin 1%	0.90	0.36
Talcum	Toluene	—	1.9	1.00
,,	,,	Palmitic acid 1%	1.6	0.84
Glass	Ethyl alcohol	—	0.69	
,,	,,	Palmitic acid 2%	0.68	
Zinc oxide	Ethyl alcohol	—	1.5	
,,	,,	Lecithin 1%	1.5	
Charcoal	Toluene	—	4.1	
,,	,,	Palmitic acid 1%	4.1	
,,	,,	,, 4%	4.2	
Graphite	Water	—	1.6	
,,	,,	Hexyl alcohol 0.3%	1.6	
,,	,,	Benzoic acid 0.2%	1.7	
,,	Ethyl alcohol	—	1.7	
,,	,,	Palmitic acid 2%	1.7	

In the fifth column of Table 3, the ratio of the sedimentation volume of a powder settled in the solution to that in the pure liquid is shown.

These results are classified in two groups, the one is the case in which the small quantity of the polar substance has marked influence to decrease the sedimentation volume, and the other is the case in which the addition of the polar substance shows no effect on the sedimentation volume. The first case has been observed when the system are made from the powder of polar substance and the solvent of nonpolar one. In those examples, it must be noticed, that the fatty substance, so-called, are especially effective to decrease the sedimentation volume, for example, oleic acid, palmitic acid or lecithin is more effective than acetic acid, benzoic acid or hexyl alcohol. The second case has been observed when the system consists of both the powder and the solvent of polar substances, or the powder of nonpolar one.

All of these results suggest that the selective adsorption and the molecular orientation take place on the surface of the powder. When the powder is polar, the polar molecules of solute are strongly adsorbed from the nonpolar solvent taking good orientation. On the other hand, when the powder is nonpolar, the molecular orientation on the solid surface will not establish.

According to Ehrenberg's[4] theory, which seems most plausible to explain the large sedimentation volume, the particles must be loosely packed when they adhere each other by their contact point (the shape of the particles are not generally sphere), and they do not slip each other. On the other hand, if the adhesion force between the particles is weak, they will slip each other and finally they will take the close packing, so the sedimentation volume will become small.

When the suspension medium is water, the chief factor for weakening the adhesion force between the particles is the electrical charge presenting on the particles by adsorbing ions. So the sedimentation volume of aqueous suspension depends upon the concentration of the electrolyte in the solution. When the suspension medium is organic liquid, we

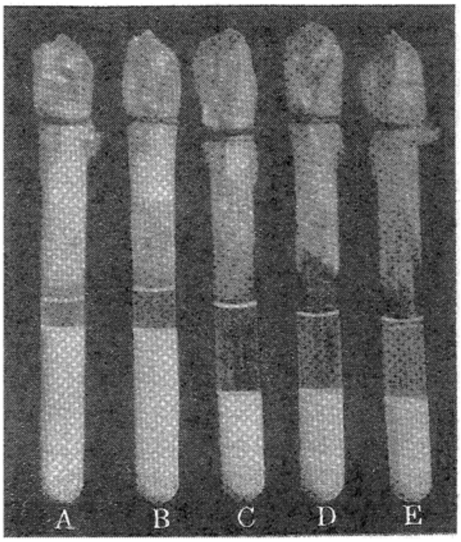

Fig. 2. Zinc oxide powder (about 7 g.) settled in

(A) Carbon tetrachloride
(B) Dioxane
(C) Ethylene glycol
(D) Ethyl alcohol
(E) *Methyl alcohol*

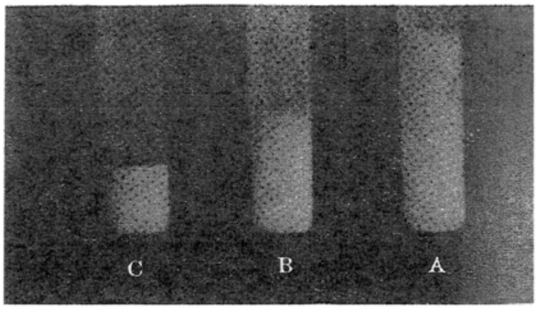

Fig. 3. Zinc oxide powder (about 4.5 g.) settled in

(A) Toluene
(B) Toluene containing 1% Hexyl alcohol
(C) Toluene containing 1% Lecithin

(4) A. v. Buzágh, "Kolloidik," 172, Dresden (1936).

may assume the dipole adsorption instead of the ion-adsorption. Present experimental results appear to suggest the close relationship to this assumption. We can not discuss, however, further since there are little data about the electro-kinetic potential of such a system consisting in solid-organic liquid interfaces.

Thixotropy. It can generally be said that there is the parallelism between the large sedimentation volume and thixotropic nature, for both of these phenomena occur by the loose packing of a system. The author has tested the thixotropic nature of the system consisting of powder and organic liquid, and found that a system which has large sedimentation volume shows always marked thixotropic nature.

For example, a thixotropic system was made by shaking in a test tube about 5 c.c. of toluene with 3.7 g. of calcium carbonate powder. This system is liquefied by shaking which is perceived by a fluid sound, while set to solid paste when shaking has stopped. However, syneresis occurred when this system left to itself for a few minutes, probably because of large particles.

Thixotropies have been tested on the combination of powders and liquids shown in Table 4.

Table 4.

Liquid \ Powder	Glass	ZnO	Talcum	$CaCO_3$	Al_2O_3	Graphite
Carbon tetrachloride	++	++	++	++	++	
Toluene	++	++	++	++	?	++
Benzene	++	+	++	++	+	
Dioxane	++	+	+	+	—	
Hexane	+	+	+	++	?	+
Ethyl alcohol	—	?	—	—	—	—

++ distinctly thixotropic, + thixotropic, — no thixotropic

We come to conclusion from these results, that almost every kinds of powder can make a thixotropic system in the nonpolar liquid.

These are the macroscopic system, the particles being comparatively large, so it may not be called "the sol-gel transformation" in its proper meaning. It may be more natural to say that there occurs the phase inversion, viz., the powders are suspended in the liquid phase by shaking, while "the liquid sets in the powder" when stopped the shaking.

We saw, from the experiments described above, that the small quantity of the polar substance (surface active substance) decreases the sedimentation volume in the nonpolar solvent. So the small quantity of the surface active substance destroy the thixotropic nature of the system. For example, a thixotropic system is obtainable from 5 c.c. of carbon tetrachloride and 6.4 g. of glass powder. If, however, the solution contained 1.6% palmitic acid beforehand, the system consisting in the same ratio as above is completely fluid on shaking and it does not set to solid paste when shaking has stopped. Furthermore, even after adding 14 g. of glass powder, the system shows no thixotropic nature. Some examples are shown in Table 5.

Table 5.

Powder	Liquid phase	Nature of the system
Glass 6.4 g.	CCl_4 5 c.c.	thixotropic
,,	CCl_4 solution 5 c.c. containing 1% Oleic acid	no thixotropic
,,	CCl_4 solution 5 c.c. containing 1.6% Palmitic acid	no thixotropic
Al_2O_3 9.5 g.	CCl_4 5 c.c.	thixotropic
,,	CCl_4 solution 5 c.c. containing 1% Oleic acid	no thixotropic
ZnO 1.6 g.	Toluene 5 c.c.	thixotropic
,,	Toluene solution 5 c.c. containing 1% Hexyl alcohol	thixotropic ?
,,	Toluene solution 5 c.c. containing 1% Lecithin	no thixotropic
$CaCO_3$ 3.7 g.	Toluene 5 c.c.	thixotropic
,,	Toluene solution 5 c.c. containing 1% Hexyl alcohol	no thixotropic

In conclusion, the author wishes to express his thanks to Professor J. Sameshima for his kind advices and encouragement.

Summary.

(1) Measurements were carried out on the sedimentation volume when a powder settled in an organic liquid or solution.

(2) A parallelism was found between the large sedimentation volume of the powder and thixotropic nature of the system.

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