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206. **Akiko Ikekawa, Haruko Aoki, Kikuya Masukawa, and Nobuyoshi Kaneniwa**[*1]: Influence of Particle Size on Physicochemical Properties of Pharmaceutical Powders. II.[*2] On Packing of Sodium Borate and Boric Acid Powders.

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Packing problems of sodium borate and boric acid powders are investigated.

The apparent volume per gram of the samples in loosest packing is nearly constant in the region larger than the critical size, but in the region smaller than that, it increases gradually with decrease of particle diameters. The critical diameters obtained at the loosest packing in air are equal to that obtained by measurement of angles of repose and sliding angles.

The relations between porosity (ε_0, ε_c) or the apparent density (ρ_c, ρ_0) and particle diameter (D) are represented by

$$\varepsilon_0-\varepsilon_c=\mathrm{A}\exp(-\mathrm{B}D) \qquad \rho_c-\rho_0=\rho\mathrm{A}\exp(-\mathrm{B}D)$$

and the following relations have also been obtained between porosity or apparent density and C/Mg for sodium borate powders.

$$\varepsilon_0-\varepsilon_c=0.43\,C/Mg \qquad \rho_c-\rho_0=0.72\,C/Mg$$

($\varepsilon_0-\varepsilon_c$) or ($\rho_c-\rho_0$) might be adopted as the degree of cohesion.

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In the previous paper, the presence of a critical particle diameter, by which powders may be differentiated from granules, has been found.[1] The presence of critical diameter has also been found in several investigations of the packing of powders. For example, in studies of the closest packing of gypsum, Portland cement, chrome-yellow and other powders, Roller[2] found the critical diameter of 15～30 μ between the void volume per gram at the closest packing (V_v) and the specific surface diameter (d_s) and proposed the following equation,

$$V_v=\mathrm{k}(1/d_s)^n \quad d_s\leq d_c, \quad V_v=\mathrm{C} \quad d_s\geq d_c, \tag{1}$$

where d_c is critical particle diameter and C, k and n are constants. Shapiro, *et al.*[3] also showed that the above equations applied to other powders, and Hayakawa[4] discussed the theoretical treatment. In addition, Leva, *et al.*[5] reported the presence of a critical diameter of 200～400 μ from the relationship between porosity at loosest packing and particle diameter of crushed quartz, sands and several other powders.

The purpose of present study is to investigate the influence of the particle diameter on the packing of sodium borate and boric acid powders.

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[2] P.S. Roller: Ind. Eng. Chem., 22, 1206 (1930).
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Experimental

The samples used are the same as referred to in the previous paper.[1] G. p. solvents were dried and distilled.

The volume per gram of samples at loosest packing was measured in air by the double cylinder method[6] and by the JIS standard funnel method.[7] The data were reproducible when a measuring cylinder containing a certain weight of powder was inclined gradually from a horizontal position. (inclination method)

The sedimentation volume of a sample, which is equal to the volume per gram of sample at the loosest packing in a solvent, was measured in carbon tetrachloride, carbon disulfide, cyclohexane, *n*-heptane, toluene and anisole.

In order to minimize a wall effect, the following condition was chosen. A stainless cylinder (6 cm. in diameter and 6 cm. high) was used for the JIS standard funnel method and a measuring cylinder (1 cm. in diameter, 25 ml. in volume) was used for the other methods. Ten g. samples were used for the double cylinder method and inclination method, and 3 g. samples and 15 ml. of solvent for the sedimentation volume determination.

The volume per gram of closest packing was obtained after tapping the samples until the volume decreased no longer.

Results and Discussion

The experimental results are shown in Figs. 1, 2, 3 and 4.

It is found in air, as well as in solvents, that the volume per gram at loosest packing (V_s) is constant in the region larger than the critical diameter (D_c), but gradually increases in the region smaller than the critical diameter.

In the case of sodium borate in air, this effect is found by any method, but in the case of boric acid in air it is only found by the JIS standard funnel method and V_s shows only a small decrease in the region of small diameters. For boric acid powders, affinity for glass is shown in the region of small diameters, where tapping effects are observed during the inclination and double cylinder methods.

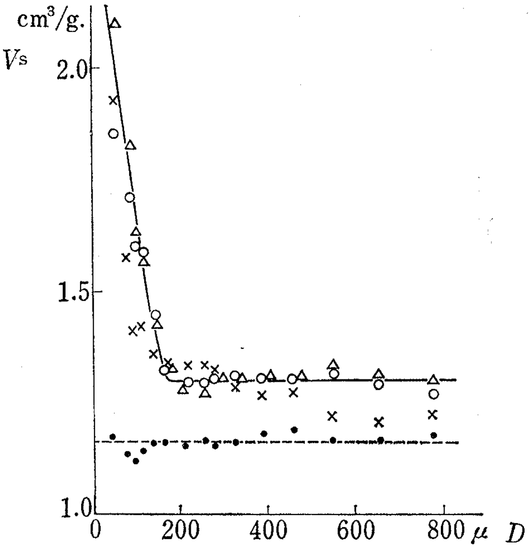

Fig. 1. Dependence of Particle Size on Packing of Sodium Borate Powders in Air

● Closest packing △ inclination method
× JIS standard funnel method
○ Double cylinder method

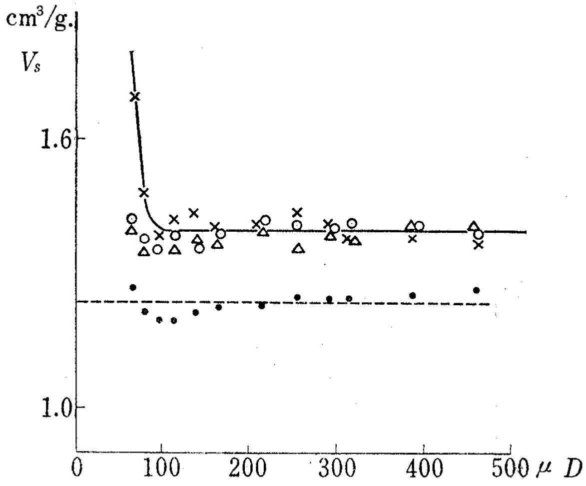

Fig. 2. Dependence of Particle Size on Packing of Boric Acid Powders in Air

● Closest packing △ Inclination method
× JIS standard funnel method ○ Double cylinder method

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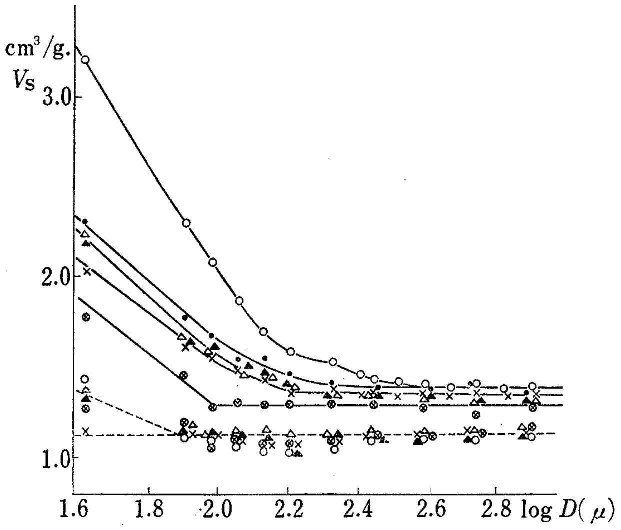

Fig. 3. Dependence of Particle Size on Packing of Sodium Borate Powders in Solvents

-------- Closest packing ———— Loosest packing
○ Carbon tetrachloride ● Carbon disulfide
△ Cyclohexane ▲ n-Heptane
× Toluene ⊗ Anisole

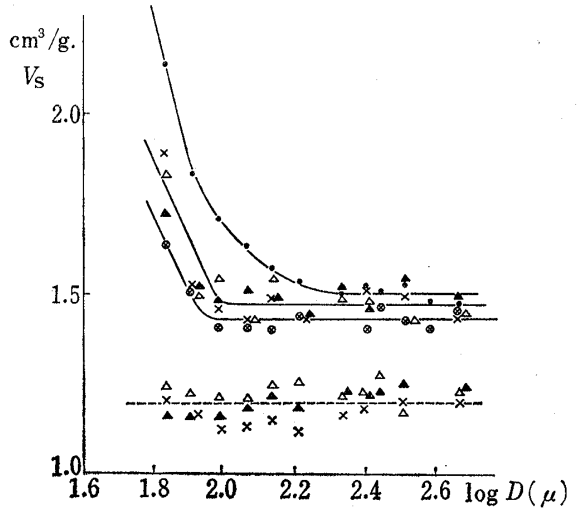

Fig. 4. Dependence of Particle Size on Packing of Boric Acid Powders in Solvents

-------- Closest packing
———— Loosest packing
● Carbon disulfide △ Cyclohexane
▲ n-Heptane × Toluene ⊗ Anisole

The volume per gram of boric acid powders at the closest packing remains almost constant in all regions investigated. At the closest paking of sodium borate powders, the apparent volume remains almost constant in air and toluene, but volume tends to increase in the regions smaller than 80~90 μ in other solvents.

In the previous paper concernig angles of repose and sliding angles, critical diameters were found to be 160 μ in sodium borate and 100 μ in boric acid. The results in Figs. 1 and 2 show that the critical diameters mentioned above are equal to those of the loosest packing in air of these powders. The results of the previous paper were interpreted in terms of cohesive force between particles of powders which was negligibly small in the region larger than the critical size, but which was larger, and influenced fluidity of powders in the region smaller than the critical size.

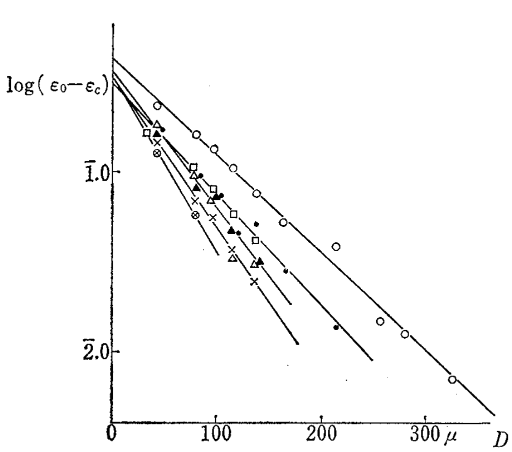

Fig. 5. Relation between Particle Size and Porosity of Sodium Borate Powders in Loosest Packing

○ Carbon tetrachloride
● Carbon disulfide
△ Cyclohexane ▲ n-Heptane
× Toluene ⊗ Anisole □ Air

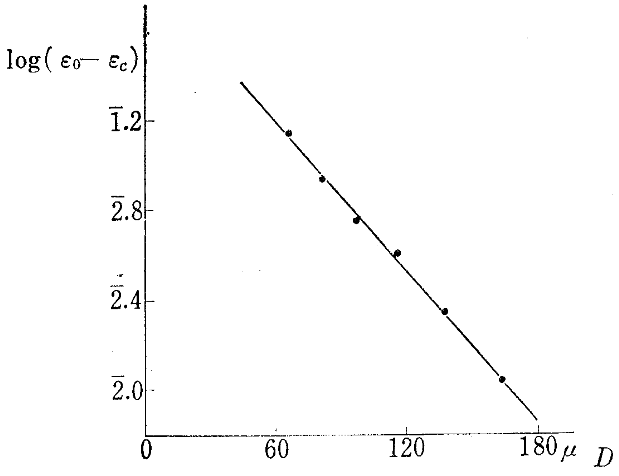

Fig. 6. Relation between Particle Size and Porosity of Boric Acid Powders in Carbon Disulfide in Loosest Packing

Porosity ε is defined as $(V_s-V)/V_s$, where V is the true volume per gram of samples. When the logarithm of the difference between the porosity smaller than the critical size ε_0 to the constant value larger than the critical size ε_c were plotted *versus* particle diameter D, straight lines were obtained as shown in Figs. 5 and 6. These data can be expressed by the following relation

$$\varepsilon_0-\varepsilon_c=\mathrm{A}\exp(-\mathrm{B}D), \tag{2}$$

where A and B are constants.

When ρ_0 denotes the apparent density of a sample in the region smaller than the critical size, ρ_c is the constant apparent density in the region larger than the critical size and ρ is the true density of sample, then equation (3) applies

$$\rho_c-\rho_0=\rho(\varepsilon_0-\varepsilon_c). \tag{3}$$

By combining equations (2) and (3), the relation between apparent density and particle diameter of a sample becomes

$$\rho_c-\rho_0=\rho\mathrm{A}\exp(-\mathrm{B}D). \tag{4}$$

Equation (1) proposed by Roller[2] was not applicable to the present results on loosest packing even by substituting V_v for porosity (ε) or V_s.

From the data by the inclination and the double cylinder methods, the coefficients A, B and $\rho\cdot$A in the equations (2) and (4) were determined as follows for sodium borate powders.

$$\varepsilon_0-\varepsilon_c=0.35\exp(-147D) \tag{5}$$

$$\rho_c-\rho_0=0.58\exp(-147D) \tag{6}$$

The relationship which has been developed in the previous paper between (C/Mg) and particle diameter (D) is shown as equation (7) for sodium borate powders.

$$C/Mg=0.81\exp(-147D) \tag{7}$$

Therefore, by combining equations (5), (6) and (7), we obtain

$$\varepsilon_0-\varepsilon_c=0.43\ C/Mg \tag{8}$$

$$\rho_c-\rho_0=0.72\ C/Mg. \tag{9}$$

As shown in Fig. 7, the plot of $(\varepsilon_0-\varepsilon_c)$ and $(\rho_c-\rho_0)$ *versus* C/Mg results in two straight lines which meet at the origin. The slopes of the lines are 0.42 in the case of $(\varepsilon_0-\varepsilon_c)$, and 0.74 in the case of $(\rho_c-\rho_0)$, and are identical with the coefficients of equations (8) and (9), respectively. It is shown from the above findings that the parameters $(\varepsilon_0-\varepsilon_c)$ and $(\rho_c-\rho_0)$, have a direct relationship to the cohesive force between particles of powders.

On the basis of the results described above, it seems reasonable to assume that cohesive force between particles of powders is negligibly small in the regions larger than the critical size, and shows remarkable influence on angles of repose, sliding angles and the volume at the loosest packing in the region smaller than the critical size.

The above findings lead to further considerations. In the region larger than the critical size the kind of loosest packing depends on the characteristics of particles such

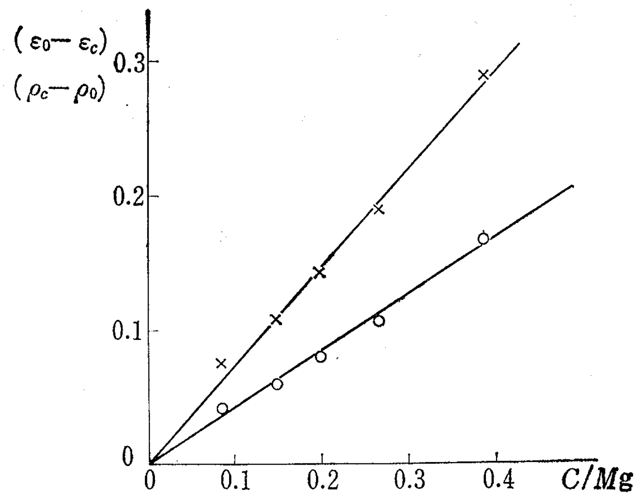

Fig. 7. Relation between C/Mg and $(\varepsilon_0-\varepsilon_c)$ or $(\rho_c-\rho_0)$ for Sodium Borate Powders

○ $(\varepsilon_0-\varepsilon_c)$ × $(\rho_c-\rho_0)$

as "shape" and "surface state" of particles, but not particle size. In addition, in the region smaller than the critical size, particles of powders agglomerate and tend to decrease the surface area and surface energy, and consequently a transformation of the packing structure occurs. Physicochemical properties of powders such as angle of repose, sliding angle and porosity at the loosest packing might be influenced by this phenomenon.

Coherent particles due to adsorption of water, and so on, were reported to have larger packing volumes.[8,9]

The concept of degree of cohesion (β) is often used for treatment of packing problems. Hitherto β was defined as V_r/V_∞[10] or $(V_{appi}-V_{appf})/V_{appi}$,[11] where V_r is the sedimentation volume per gram, V_∞ is the sedimentation volume per gram if the sample is dispersed completely in the same solvent as V_r, and V_{appi} and V_{appf} are the sedimentation volume per gram before and after tapping, respectively. Since $(\varepsilon_0-\varepsilon_c)$ and $(\rho_c-\rho_0)$ have a direct relationship to the cohesive force between particles of powders, they might be adopted as β.

Table I shows the critical diameter D_c and coefficients A, A′, B and B′ of equations (2) and (4′) obtained by using the data in Figs. 1, 2, 3 and 4.

$$\rho_c-\rho_0=\mathrm{A}' \exp(-\mathrm{B}'D) \qquad (4')$$

Here B is equal to B′ and A′/A is nearly equal to the true density of samples. Coefficients A and A′ are nearly constant, irrespective of the solvents. B, B′ and D_c are related to the solvents and V_c increases slightly with an increase of D_c. The larger are the values of D_c, the smaller are the coefficients B and B′. In other words, the earlier the cohesive force appears, the more slowly it increases with the decrease of the particle diameter. It is suggested that the affinity between powder and solvent is an important factor which determines the dispersal of powders in solvents. The correlation between sedimentation volume and solid-liquid adhesion tension has also been reported by Bartell and his co-workers[12] and Mack[13] has found a linear relationship between the sedimentation volume and spreading coefficients of solvents with respect to water.

Nakajima[14] and Otsubo[15] reported the correlation between angle of repose and porosity of powders. In the present study, the correlation between angle of repose, sliding angle and porosity has also been found. Namely linear relations are obtained

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15) T. Otsubo: Huntai Kogaku Kenkyu Kaishi, **2**, [1] 179 (1965); *Ibid.*, **1**, [2], 20 (1964). *Idem*: Huntai Kogaku, **1**, [3] 183; [4] 238 (1964).

by a log-log plot of tan α or tanα/tanθ *versus* $(\varepsilon_0-\varepsilon_c)$ for sodium borate powders as shown in Figs. 8 and 9. Similar relationship is obtained by a log-log plot of tanα or tanα/tanθ *versus* $(\rho_c-\rho_0)$ for sodium borate powders. By combining experimental equations obtained in the previous paper, and (2) and (4), the relations between angle and porosity or apparent density are represented by

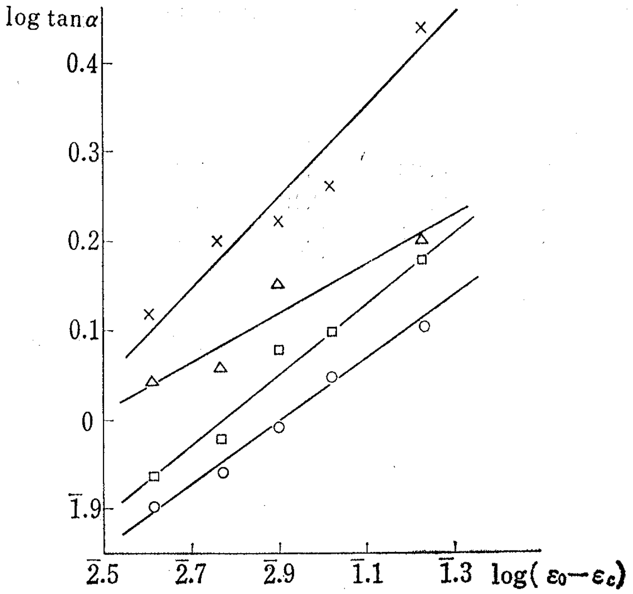

Fig. 8. Relation between tan α and $(\varepsilon_0-\varepsilon_c)$ for Sodium Borate Powders in Air

By four methods.
○ Nogami-Sugiwara △ Nelson
□ Neumann × Awata-Nakajima

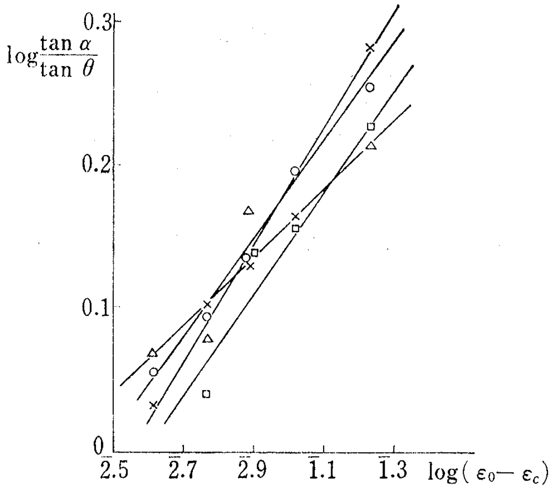

Fig. 9. Relation between tan α/tan θ and $(\varepsilon_0-\varepsilon_c)$ for Sodium Borate Powders in Air

By four methods.
○ Nogami-Sugiwara △ Nelson
□ Neumann × Awata-Nakajima

$$\tan\alpha=H(\varepsilon_0-\varepsilon_c)^m=H'(\rho_c-\rho_0)^m \qquad (10)$$
$$H=\mathrm{A}_1/\mathrm{A}^m,\ H'=H/\rho^m,\ m=\mathrm{B}_1/\mathrm{B}$$

$$\tan\alpha/\tan\theta=L(\varepsilon_0-\varepsilon_c)^n=L'(\rho_c-\rho_0)^n \qquad (11)$$
$$\mathrm{L}=\mathrm{A}_1/\mathrm{A}_1'.\mathrm{A}^n,\ L'=L/\rho^n,\ n=(\mathrm{B}_1-\mathrm{B}_1')/\mathrm{B}$$

TABLE I. Experimental Constants at the Loosest Packing

Sample	Solvent	D_c	V_c	A	B	A′	B′	A′/A
Sodium borate	Carbon tetrachloride	330	1.41	0.39	121	0.65	120	1.68
	Carbon disulfide	270	1.37	0.31	148	0.55	148	1.78
	Cyclohexane	180	1.34	0.38	181	0.63	176	1.68
	n-Heptane	180	1.34	0.38	181	0.63	176	1.68
	Toluene	160	1.35	0.32	188	0.57	191	1.78
	Anisole	95	1.28	0.32	214	0.55	213	1.72
	Air	160	1.31	0.34	147	0.58	147	1.70
Boric acid	Carbon disulfide	180	1.50	0.80	278	1.20	278	1.50
	Cyclohexane	80	1.47					
	n-Heptane	80	1.47					
	Toluene	80	1.47					
	Anisole	80	1.44					
	Air	95	1.40					

D_c: μ V_c: cm^3/g B: cm^{-1} A′: cm^3/g. B′: cm^{-1}

The coefficients of the equations (10) and (11), H, H', m, L, L' and n are tabulated in Table II. Relations similar to Figs. 8 and 9 probably apply to boric acid powders.

TABLE II. Coefficients of the Equations (10) and (11) for Sodium Borate Powders

Method	m	H	H'	n	L	L'
Nogami–Sugiwara	0.35	2.3	1.9	0.32	3.2	2.7
Nelson	0.27	2.6	2.2	0.22	2.5	2.2
Neumann	0.38	3.0	2.4	0.35	3.2	2.6
Awata–Nakajima	0.51	6.2	4.7	0.41	3.9	3.0

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