Dependence of ζ-Potential upon Particle Size and Capillary Radius at Streaming Potential Study in Nonaqueous Media[1]

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The effect of particle size and capillary radius on electrokinetic potential(ζ-potential) was studied in order to check the influence of overlapping of the electrical double layer and radius effect on the measured ζ-potential by the streaming potential method. The streaming potential was measured with varying particle size and capillary radius of glass in the benzene solution of $(C_4H_9)_4NI$. The measurement was carried out over the range where the laminar flow and the Quincke's law hold. The surface conductance was corrected experimentally. ζ-Potential increased with increase of the particle size in the glass column. It was unsuccessful to obtain the ζ-potential independent of the reduced radius of the capillary pore with the Oldham's treatment. ζ-Potential increased with increase of the capillary radius. The increase was elucidated by the Wood's method using the appropriate constants, and the constant ζ-potential which was not affected by the capillary radius was obtained. The value was still different from that obtained by the electrophoretic method, but the difference was considerably small as compared with the previous data.

Electrokinetic potential (ζ-potential) is important as the quantity used in place of surface potential which is necessary to discuss the stability of dispersion or the properties of the electrical double layer, but it is difficult to measure or estimate the ζ-potential on the insulator or the semiconductor. ζ-Potential is usually measured by the electrophoretic method or the streaming potential method. However, the retardation effect and the relaxation effect must be corrected for the former method.[2] The surface conductance and the overlapping of the double layer must be taken into consideration for the latter in order to obtain the proper value. Both values should agree with each other, provided that all proper corrections have been made.

The same system has to be investigated by both methods for comparison, but such study is rare except a few,[3] although the comparison between the streaming potential and the electro-osmosis was done and the coincidence was recognized[4] because of their similar packing column system.

The necessary corrections have to be done for each method to obtain the reliable value of ζ-potential. The correction for the surface conductance was studied for aqueous systems both theoretically and experimentally by Ghosh *et al.*[5] Oldham *et al.* proposed the theory of correcting capillary radius and the surface conductance which was applied successfully to the aqueous and nonaqueous data obtained by other authors.[6] The effect of pore orientation on the cell constant in the pore system of fiber was studied by Mason *et al.* for the streaming potential.[7]

In our laboratory, ζ-potential of the same sample system (barium sulfate powder dispersed in cyclohexane solutions of Aerosol OT) was measured with both the electrophoresis and the streaming potential methods. Both values were widely different.[8] Effects of the surface conductance and the overlapping of the double layer for the streaming potential, which were not corrected, would cause the difference. Fortunately, the thick double layer present in the nonaqueous system makes it easy to study the overlapping.

In this paper, the effect of the overlapping of the double layer was studied experimentally for the nonaqueous system of the particle column and the capillary of glass and data obtained were checked by the present theories. The surface conductance was also corrected experimentally.

Experimental

Samples. A series of spherical glass particles were purchased from the Sugito Seimitsu Glass Co. and further classified with the standard sieves. The diameter range of the samples was tabulated in the 2nd column of Table 1. Glass capillaries of different radii shown in Table 2 were used.

Glass particles were cleaned with mixture of nitric and sulfuric acids and digested on a water bath for 10 hr. After cooling, they were washed repeatedly with de-ionized water until the specific conductivity of the washings was nearly equal to that of the de-ionized water. The particles were dried in an oven at 120°C and extracted with acetone and benzene in turn for 3 hr. They were reheated for 2 hr at 200°C under 10^{-2} mmHg immediately before use. Capillaries were cleaned, washed and dried similarly to the case of particles. After cooling in a desiccator, they were immersed in purified benzene for a while before use.

Benzene used as a solvent was purified and dried from GR grade reagent as usual and finally treated with Molecular Sieves 4A to remove a trace of water, Tetra-*n*-butyl amonium iodide $(C_4H_9)_4NI$ used as an electrolyte in benzene

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TABLE 1. PARTICLE SIZE OF SPHERICAL GLASS PARTICLES AND REDUCED CAPILLARY RADIUS OF GLASS-PACKED PLUG

Sample No.	Diameter (μ)	Reduced radius (μ)
P-1	297—350	20.2
P-2	125—147	13.7
P-3	88—105	12.3
P-4	44—62	7.9
P-5	26—44	5.8

TABLE 2. RADIUS OF GLASS CAPILLARY

Sample No.	Radius (mm)
C-1	1.45, 1.46, 1.55
C-2	0.95, 1.00, 1.05
C-3	0.44, 0.45
C-4	0.18

was GR grade reagent. The content of water in the benzene solution was below 100 ppm throughout this study.

Apparatus. The streaming potential was measured with an essentially similar apparatus to that used by Dodd *et al.*[9] The cell of the particle system was made of Teflon or glass coated by silicone to prevent surface leakage. Electrodes in the system were perforated stainless steel plates coated by silver. The particle column of 2 cm^2×0.5 cm was made by filling about 1.5 g glass particles between both electrodes. The capillary of the length of 25 cm was used as the cell of the capillary system. Platinum wires were placed very closely to both ends of the capillary as electrodes.

Methods. The occurring streaming potential was measured with a vibron voltmeter (DC amplifier of the Takeda Riken Ind. Type TR-85). The electric resistance of the column or capillary filled with the electrolyte benzene solution was measured with a high-resistance measuring apparatus (Modell II-3 of the Hitachi Manufacturing Co.) which can measure up to 10^{15} ohm.

The cell constant of the column or the capillary was determined from the measurement of the conductivity of 0.1 N KCl aq. solution. The measurement was carried out for the same column or capillary after the benzene solution had been thoroughly discharged and washed to avoid the effect of polarization of electrodes. The orientation effect proposed by Mason was not considered because of the sphere particle system.

Results and Discussion

Assurance of Laminar Flow. To ascertain the laminar flow of the solution in the column or capillary, the Darcy's law was examined with the streaming potential apparatus. The law says that

$$V = KP \tag{1}$$

where V is the volume rate of the flowing solution under a driving pressure P and K is the permeability. If the height of the solution column acting as pressure P is h,

$$P=kh (k\text{: constant}), \text{ and } V=-\mathrm{d}h/\mathrm{d}t \ (t\text{: time}) \tag{2}$$

Then Eq. (3) is reduced as follows:

$$\log h = -K't/2.3 + \log h_0, \tag{3}$$

where $K'=kK$ and h_0 is the extrapolated initial height of the solution column. Equation (3) was experimentally confirmed both for the particle column and capillary systems. The relation held over the range of the lower height for the capillary system. The measurement of the streaming potential was carried out within this range. Reynolds number was below 0.1.

Quincke's Law and Time Dependence of Streaming Potential. Next, the applicability of the lineality between the streaming potential (E) and pressure (P) was checked. The Quincke's law was applicable within the pressure range over which the laminar flow was ascertained. The slope of the potential-pressure curve varied with repeated measurements and approached an equilibrium value after 20—24 hr (about 8 measurements), although the constant K' was almost invariable over 24 hr. The time dependence of E/P may be due to cleansing of the wall of the cell and particles or capillary surface and the ion-exchange of particles or capillary. The capillary used once did not show the same streaming potential in repeated experiments. The equilibrium values of E/P were used for the calculation of ζ-potential.

Correction of Surface Conductance. The Helmholtz-Smolchouski's equation taking into consideration of the surface conductance for the capillary radius r is described as follows:

$$\zeta = \frac{4\pi\eta}{D}\frac{E}{P}\left(\kappa_b + \frac{2\kappa_s}{r}\right), \tag{4}$$

where κ_b and κ_s are the bulk and the surface specific conductivity, respectively, and η and D are the viscosity and the dielectric constant of the double layer which are usually substituted by the bulk values. $\kappa_b+\frac{2\kappa_s}{r}=\kappa_c$ for the present nonaqueous system was calculated from the conductivity ($1/R$) of the column or the capillary system filled with the benzene solution of the electrolyte and the cell constant (k_c) whose measurements were described in the experimental part, that is, $\kappa_c=k_c/R$. In the present system, κ_s was much larger than κ_b which had been measured separately in another cell.

Reduced Capillary Radius of Column. The mean reduced capillary radius of the particle column (r) was determined as follows: Poiseuille's law says that

$$V = \frac{n\pi r^4 P}{8\eta l}, \tag{5}$$

where n and l are the number and the length of the capillary, respectively. Ohm's law is expressed as follows:

$$R = \frac{l}{\kappa_b n\pi r^2}. \tag{6}$$

From Eqs. (5) and (6), $r=\sqrt{\frac{8\kappa_b\eta VR}{P}}=\sqrt{8\kappa_b\eta RK}$. (7)

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The measurement of r with use of Eq. (7) was carried out with 0.1 N KCl aq. solution. The result was listed on the 3rd column in Table 1.

ζ-Potential of Column System. The change of ζ-potential of the column system with particle size was shown in Fig. 1 for 10^{-5} and 10^{-4} mol/l solutions of $(C_4H_9)_4NI$ in benzene. ζ-potential increased with increase of particle size and appears to approach the saturation value.

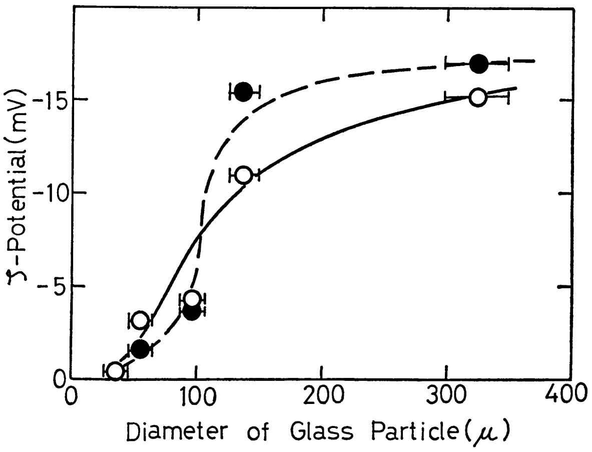

Fig. 1. Change of ζ-potential with particle size of glass in solution of $(C_4H_9)_4NI$ in benzene.
—○—: 10^{-4} mol/l, --●--: 10^{-5} mol/l

The theory proposed by Oldham *et al.*[6] was applied to obtain the ζ-potential independent of particle size. The thickness of the double layer ($1/\kappa$: Debye length) which is necessary for the study was calculated from the data of the specific conductivity.[10] The values were 3.3 μ and 10 μ for 10^{-4} and 10^{-5} mol/l solution system, respectively. The constant ζ-potential independent of the particle size could not be obtained by the Oldham's method. Insufficient reliability of the values of reduced radius for the quantitative calculation and the heterogeneity of pore radius, the contribution of which was investigated by Overbeek *et al.*[11] and by Rutgers *et al.*[12] may be considered as reasons of the failure. Therefore, the measurement for the capillary system was carried out to study the effect of the capillary radius more critically.

ζ-Potential of Capillary System. The contribution of the surface conductance to the total conductance in this system was much larger than that of the bulk conductance similarly to the case of the column system. Hence, the correction by Rutgers *et al.*[13] was improper and inaccurate to do. ζ-potential calculated from Eq. (4) was depicted against the capillary radius (a) in Fig. 2 for the 10^{-4} mol/l solution of $(C_4H_9)_4NI$ in benzene. It is seen from the figure that ζ-potential depends markedly on the radius, though the data scatter to some extent. Since the value of κa ranges over 55—450 for the capillary system used, the correction of the overlapping of the double layer by the method of Oldham[5] was virtually ineffective to obtain the value independent of the radius.

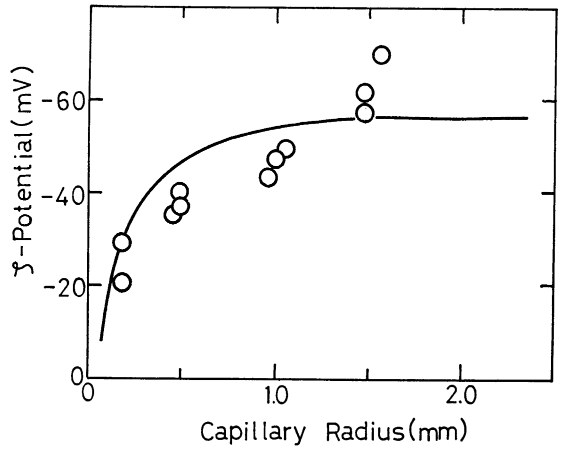

Fig. 2. Change of ζ-potential with capillary radius.
○: Observed values
——: Line by Eq. (9) as $\zeta=-62$ mV, $A=-8.8$ mm

Wood discussed the radius effect over the wide range considering the distribution of charge.[14] The following equation can be obtained from the combination of Eqs. (15), (16), and (22) in the original paper of Wood:

$$\zeta_0 - \frac{2\pi}{Da}\sum_i d_i \Delta M_i = \zeta_{\mathrm{obs}}, \tag{8}$$

where ζ_0 and ζ_{obs} are the corrected and observed ζ-potential, respectively, d_i is the distance of the element i from the wall and ΔM_i is the moment of the element. Over the range in which the overlapping of the double layer that should be corrected by the Oldham's method is absent, d_i and ΔM_i have their finite values and they are constant for a fixed concentration of the electrolyte. Then Eq. (8) reduces to Eq. (9):

$$\zeta_0 = \zeta_{\mathrm{obs}} + \frac{A}{a}, \tag{9}$$

where A is a constant. This equation was checked with the experimental values in Fig. 3. The linearity between ζ_{obs} and $1/a$ can be approximately recognized. $\zeta_0=-62$ mV as the corrected ζ-potential and $A=-8.8$ mm were obtained from the least saquares method by the computor. The allowance range of ζ_0 was -62 ± 10 mV from the figure.

Alternatively, the microelectrophoresis of fine glass powders dispersed in the 10^{-4} mol/l solution of $(C_4H_9)_4NI$ in benzene gave -120 mV as the ζ-potential.

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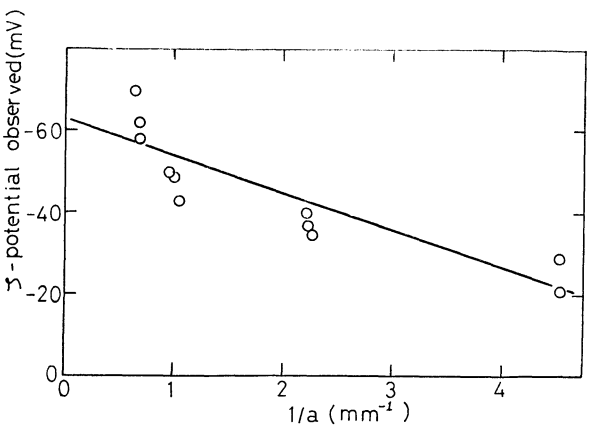

Fig. 3. The relation between ζ-potential observed (ζ_{obs}) and the reciprocal of radius ($1/a$) for the capillary system. The solid line was drawn with use of $\zeta_0 = -62$ mV and $A = -8.8$ mm.

The difference is still present between the value (−120 mV) from the electrophoresis and the one (−62 mV) from the streaming potential. However, difference has been considerably smaller as compared with the large difference of the preceding paper.[8] That is, ζ-potential from the electrophoresis and the streaming potential of barium sulfate powders dispersed in Aerosol OT solution in cyclohexane was +100 mV and +2 mV, respectively. The remaining difference may be elucidated from following reasons. (a) There is minor difference in composition of glass samples used for two methods, causing probable difference in the surface state. (b) There is difference in the washing extent of the surface, because enough washing is done in the process of the streaming potential measurement. (c) The double layer in the nonaqueous system may be distorted by the large local field strength resulting from the high applied potential (40—60 V/cm).

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