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Study of Wall Effect on the Flow of Polyvinylpyrrolidone Solutions in Capillary[*1]

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Dependence of the viscosity of the polyvinylpyrrolidone ($\bar{M}_v=4.0\times10^4$ and 9.0×10^5) solutions on the bore-size of capillary viscometer has been studied at 35°C, in pure water, in dimethyl sulfoxide (DMSO), in water-DMSO, and in aqueous solution with various cosolutes, at various concentrations (0.5—5.0 g/100 m*l*). Viscosity measurements were carried out with a Maron-Belner type low shear capillary viscometer with various capillary radii (0.0190—0.0761 cm) within the shear stress range of 0.2—20 dyn/cm^2 at the capillary wall. The solutions showed a behavior of non-Newtonian flow and dependence on the size of the capillary. The viscosity of the polymer solutions in DMSO, and in water-DMSO decreased with the decrease in the capillary bore-size within the range of shear stress studied, and that in pure water, although similar phenomena as above were observed in higher shear stress, increased with the decrease in the capillary bore-size at the range of the lower shear stress, and this capillary bore-size dependence could not be observed with the aqueous solutions with cosolutes. The difference in the characteristics of the capillary bore-size dependence of the viscosity may be attributed to the difference in the behavior of the polymer molecules existing near the wall at which the thermal motion of the polymer molecules will be hindered by the existence of the capillary wall. The results were represented by the modified Ree-Eyring generalized flow formula for a flow system containing one Newtonian flow unit and one non-Newtonian one which included the additional terms dependent on the capillary bore-size. The viscosity equation suitable for analysing the dependence of the viscosity on the capillary bore-size at entire ranges of the rate of shear, was derived by assuming the wall layer composed of the double layers (of thickness d_o and d_i-d_o) in the flowing liquid in the capillary tube, and by combining this equation with the modified Ree-Eyring equation, the values of d_o and d_i were calculated.

Many papers[1-9] have been published concerning the phenomena that the viscosity of many suspensions, including blood, when measured with the capillary viscometer, decreases with decreasing capillary bore-size. For a similar phenomenon observed with polymer solution, experimental and theoretical treatments[10-11] were made by Oldroyd and Toms. However, as stated in the previous paper,[12] the results obtained with polyvinylpyrrolidone or PVP, solutions, could not be explained satisfactorily with their treatments. The capillary bore-size dependence of the viscosity of PVP in various solvents at the infinite high rate of shear, was treated by assuming the existence of the wall layer (of thickness d_i) in the flowing liquid.

In the present paper, the analysis of the capillary bore-size dependence of the viscosity at entire ranges of rate of shear was attempted.

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Experimental

PVP used was a commercial product, Luviskol K-90 and K-30 were obtained from Badische Anilin und Soda Fabrik A. G. Other materials were commercial chemicals.

As to the viscosity measurements, a Maron-Belner low shear capillary viscometer with continuous varying pressure head was used.[13-14] The instrumental dimensions of the viscometers are shown in Table 1. Details on viscosity measurements are the same as described in the previous paper.[15]

TABLE 1. THE DIMENSIONS OF THE VISCOMETER

Radius of capillary $R\times10^2$ (cm)	Radius of bulb R_b (cm)	Length of capillary L (cm)	Radius of manometer $R_m\times10$* (cm)
7.61	1.095	27.7	3.99
5.02	1.260	28.7	4.00
3.08	1.245	28.7	1.40
3.02	1.270	28.9	1.44
2.73	1.300	29.4	0.97
2.38	1.250	28.6	1.08
2.28	1.261	28.8	1.44
1.90	1.260	29.0	1.00

* The R_m values of the corresponding viscometer listed in Table 1 of Ref. 15 and in Table 2 of Ref. 12 should read the values listed in this table.

The measurements of extinction angle were carried out by using a Rao Flow Birefringence Viscometer Model No. B-23.

The spectrophotometric measurements were carried out with the use of a Hitachi EPS-3 Recording Spectrophotometer.

Results and Discussion

The plots of viscosity *vs.* rate of shear for K-30 aqueous solution (adjusted to pH=10.4 with KOH) and the aqueous solution with cosolute, *i. e.*, serine, aspartic acid, tryptophan, benzoic acid, and lactic acid, and K-90 aqueous solution with benzoic acid or tryptophan, in various capillaries are shown in Figs. 1(a), 1(b), 1(c), and 1(d). These substances used as cosolutes are known as the agents which induce the change in the dissolved state of the PVP molecules in various ways.[16] The viscosity of the PVP aqueous solution without cosolute shows marked dependence on the capillary bore-sizes, in the same manner as stated in the previous papers.[12,15] However, the viscosity of the aqueous solution with cosolute did not show the observable dependence on the capillary bore-size, in spite of the fact that non-Newtonian nature of the aqueous solution with cosolute, *i. e.*, serine, aspartic acid, and tryptophan, is more enhanced than that in the case without cosolute. The results show that the flow of the non-Newtonian fluids does not always

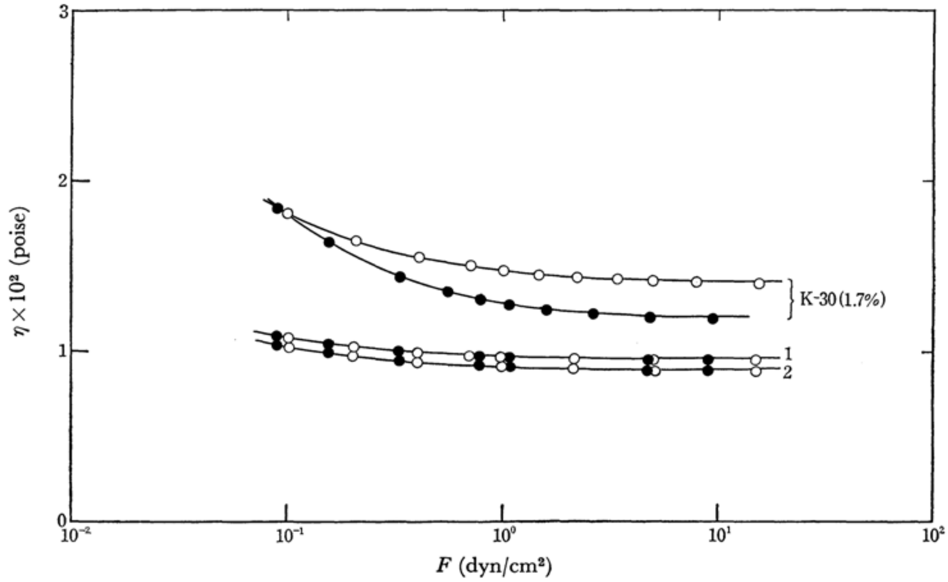

Fig. 1(a). Plots of visocsity *versus* shear stress (log scale) for K-30 (1.7%) aqueous solution with or without cosolute.
○ R=0.0308 cm, ● R=0.0190 cm
(1) cosolute, 0.05 M lactic acid; (2) cosolute, 0.025 M benzoic acid

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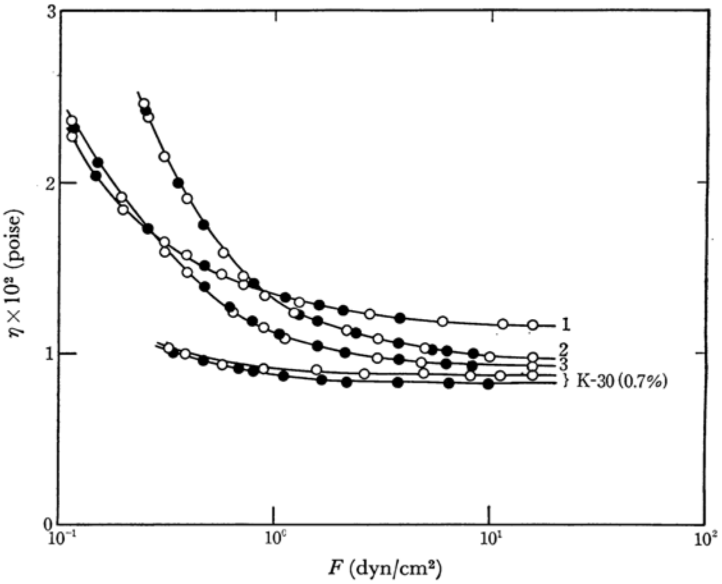

Fig. 1(b). Plots of viscosity *versus* shear stress (log scale) for K-30 (0.7%) aqueous solution with or without cosolute.
○ R=0.0308 cm, ● R=0.0190 cm
(1) cosolute, 0.1 M DL-tryptophan; (2) cosolute, 0.1 M L-aspartic acid;
(3) cosolute, 0.1 M DL-serine

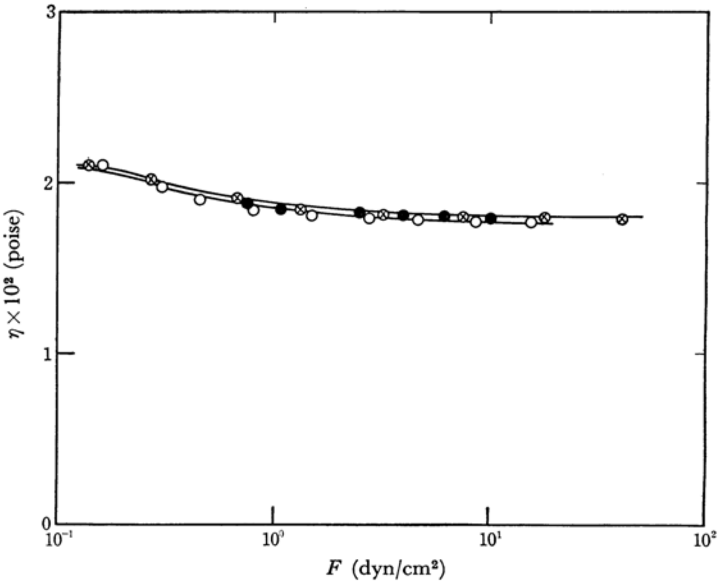

Fig. 1(c). Plots of viscosity *versus* shear stress (log scale) for K-90 (1%) aqueous solution with cosolute.
⊗ R=0.0761 cm, ○ R=0.0308 cm, ● R=0.0190 cm;
cosolute, 0.025 M benzoic acid

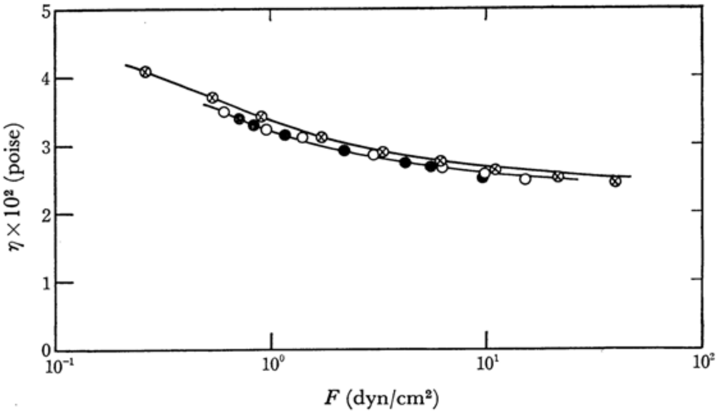

Fig. 1(d). Plots of viscosity *versus* shear stress (log scale) for K-90 (1%) aqueous solution with cosolute.
⊗ R=0.0761 cm; ○ R=0.0308 cm; ● R=0.0190 cm
cosolute, 0.1 M DL-tryptophan.

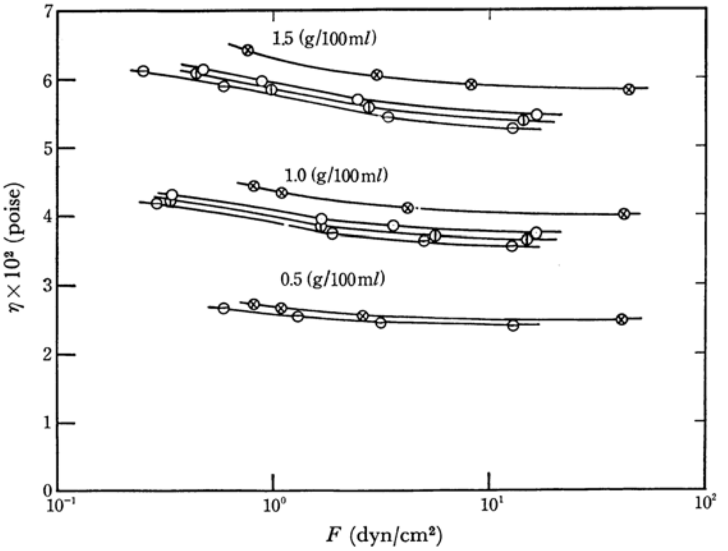

Fig. 2. Plots of viscosity *versus* shear stress (log scale) for K-90 in DMSO.
⊗ R=0.0761 cm, ○ R=0.0308 cm,
⦶ R=0.0273 cm, ⊖ R=0.0238 cm

show the capillary bore-size dependence of the viscosity. The other typical plots of viscosity *vs.* shear stress for K-90 solutions at various concentrations in DMSO in various capillaries are shown in Fig. 2.

Non-Newtonian flow behavior is observed, and the viscosity decreases with the decrease of capillary bore-size in all ranges of shear stress studied. Similar results are obtained with the solutions in water-DMSO mixture and also in *n*-propanol and in water - *n*-propanol mixture as reported in the previous paper.[15)]

The experimental results were represented by the modified Ree-Eyring generalized flow formula for a flow system containing one Newtonian flow unit and one non-Newtonian one which includes the additional terms dependent on the capillary bore-size (radius: R) as follows:[15)]

$$\eta=\left(\eta_1'-\frac{\sigma_1}{R}\right)+\left(\frac{1}{b_2'}+\frac{\sigma_2}{R}\right)\left(\frac{1}{a_2}\right)\left(\frac{a_2}{G}\right)\sinh^{-1}\left(\frac{G}{a_2}\right) \tag{1}$$

where,

$$\eta_1'-\frac{\sigma_1}{R}=\eta_1,\ \frac{1}{b_2'}+\frac{\sigma_2}{R}=\frac{1}{b_2},$$

$$\eta_1=\frac{x_1\beta_1}{\alpha_1},\ a_2=\frac{1}{\beta_2},\ b_2=\frac{a_2}{x_2},$$

TABLE 2(a). PARAMETERS OF EQ. (1) FOR PVP (K-30) AQUEOUS SOLUTIONS (at 35°C)

Solvent	Concentration (g/100 m*l*)	$R = 0.0308$ (cm)	$R = 0.0302$ (cm)	$R = 0.0238$ (cm)	$R = 0.0228$ (cm)	$R = 0.0190$ (cm)
Pure water without cosolute	0.73	$\eta_1 =$ 8.50	8.49	8.30	8.18	8.09
		$a_2 =$ 2.0	2.0	2.0	2.0	2.0
		$b_2 =$ 93.5	91.7	81.3	80.0	69.0
		$\eta_0 =$ 13.8	13.9	14.5	14.4	15.3
0.1 M DL-Serine	0.73	$\eta_1 =$ 8.92	8.92	8.91	8.91	8.90
		$a_2 =$ 2.0	2.0	2.0	2.0	2.0
		$b_2 =$ 22.7	22.7	22.7	22.7	22.7
		$\eta_0 =$ 31.0	31.0	31.0	31.0	31.0
0.1 M L-Aspartic acid	0.73	$\eta_1 =$ 9.20	9.20	9.20	9.19	9.19
		$a_2 =$ 2.0	2.0	2.0	2.0	2.0
		$b_2 =$ 15.0	15.0	15.0	15.0	15.0
		$\eta_0 =$ 42.5	42.5	42.5	42.5	42.5
0.1 M DL-Tryptophan	0.73	$\eta_1 =$ 11.4	11.4	11.4	11.4	11.4
		$a_2 =$ 2.0	2.0	2.0	2.0	2.0
		$b_2 =$ 29.1	29.1	29.1	29.1	29.1
		$\eta_0 =$ 28.6	28.6	28.6	28.6	28.6
Pure water without cosolute	1.70	$\eta_1 =$ 14.0	13.2	12.8	12.6	11.8
		$a_2 =$ 2.0	2.0	2.0	2.0	2.0
		$b_2 =$ 75.2	75.2	62.5	55.9	50.0
		$\eta_0 =$ 20.7	19.9	20.8	21.6	21.8
0.05 M Lactic acid	1.70	$\eta_1 =$ 9.01	9.01	9.01	9.00	9.00
		$a_2 =$ 2.0	2.0	2.0	2.0	2.0
		$b_2 =$ 200	200	200	200	200
		$\eta_0 =$ 11.5	11.5	11.5	11.5	11.5
0.025 M Benzoic acid	1.70	$\eta_1 =$ 9.50	9.50	9.49	9.48	9.48
		$a_2 =$ 2.0	2.0	2.0	2.0	2.0
		$b_2 =$ 200	200	200	200	200
		$\eta_0 =$ 12.0	12.0	12.0	12.0	12.0

η_1 and η_0: unit in m poise, $\eta_0=\eta_1+(1000/a_2b_2)$.

TABLE 2(b). PARAMETERS OF VISCOSITY EQUATION (at 35°C)

PVP(K-90) 1% aqueous solution with 0.1 M DL-tryptophan, where $a_2=5.0$			PVP(K-90) 1% aqueous solution with 0.025 M benzoic acid, where $a_2=5.0$		
$R = 0.0761$	$R = 0.0302$	$R = 0.0190$	$R = 0.0761$	$R = 0.0302$	$R = 0.0190$
$\eta_1 = 25.0$	$\eta_1 = 24.2$	$\eta_1 = 24.0$	$\eta_1 = 17.2$	$\eta_1 = 17.2$	$\eta_1 = 17.2$
$b_2 = 10$	$b_2 = 10$	$b_2 = 10$	$b_2 = 50$	$b_2 = 50$	$b_2 = 50$
$\eta_0 = 45.0$	$\eta_0 = 44.2$	$\eta_0 = 44.0$	$\eta_0 = 21.2$	$\eta_0 = 21.2$	$\eta_0 = 21.2$

R: unit in cm; η_1 and η_0: unit in m poise, $\eta_0=\eta_1+(1000/a_2b_2)$.

x=the fractional area on a shear surface occupied by the flow unit, β=the relaxation time of the flow unit, and α=ratio of shear volume to twice the average kinetic energy of the flow unit. Subscripts 1 and 2 of the parameters refer to the Newtonian and non-Newtonian flow units, respectively. $\sigma_1=-\mathrm{d}(\eta_1)/\mathrm{d}(1/R)$ and $\sigma_2=\mathrm{d}(1/b_2)/\mathrm{d}(1/R)$ are the slopes of the linear plot of η_1 *vs.* $1/R$ and $1/b_2$ *vs.* $1/R$ respectively, and η'_1 and $1/b'_2$ are the extrapolated values of η_1 and $1/b_2$ at $1/R \rightarrow 0$, respectively.

The values of η_1, a_2, b_2, σ_1, σ_2, η_1', and $1/b_2'$ are shown in Tables 2(a), (b), (c) and Tables 3(a), (b).

The flow represented by Eq. (1) becomes Newtonian under the condition of $(G/a_2)\rightarrow\infty$, and $(G/a_2)\rightarrow 0$, and the values of viscosity, η_∞(at $G/a_2 \rightarrow\infty$), and η_0 (at $G/a_2\rightarrow 0$) are respectively reduced to

$$\eta_\infty = \eta_1 = \left(\eta_1' - \frac{\sigma_1}{R}\right) \tag{2}$$

TABLE 2(c). PARAMETERS OF VISCOSITY EQUATION (at 35°C)

	Concentration (g/100 ml)								
	1.5			1.0			0.5		
$R\times10^2$ (cm)	$\eta_1\times10^3$ (poise)	b_2	$(\eta_1+(1/a_2b_2))$ $\times10^3$(poise)	$\eta_1\times10^3$ (poise)	b_2	$(\eta_1+(1/a_2b_2))$ $\times10^3$(poise)	$\eta_1\times10^3$ (poise)	b_2	$(\eta_1+(1/a_2b_2))$ $\times10^3$(poise)
PVP (K-90) in DMSO where $a_2=5.0$									
7.61	57.5	20.8	67.1	40.0	26.7	47.5	25.0	44.4	29.5
3.08	53.4	20.2	63.3	36.6	25.3	44.5	24.5	44.4	29.0
2.73	52.5	19.6	62.7	36.0	24.7	44.1	24.5	44.4	29.0
2.38	51.5	19.4	61.8	35.0	24.4	43.2	24.3	42.6	29.0
PVP (K-90) in 50% DMSO where $a_2=5.0$									
7.61	86.0	14.0	100.3	59.5	20.4	69.3	37.5	40.8	42.4
3.08	82.5	13.3	97.5	57.5	20.0	67.4	35.5	40.0	40.5
2.73	81.5	13.3	96.5	57.4	20.0	67.4	35.0	37.0	40.4
2.38	80.5	13.2	95.7	56.7	19.8	66.8	34.5	36.4	40.0
PVP (K-90) in 20% DMSO where $a_2=5.0$									
7.61	45.8	25.0	53.8	32.7	40.0	37.7	20.0	50.0	24.0
3.08	42.6	21.3	52.0	30.9	35.1	36.6	18.8	42.6	23.5
2.73	42.0	20.8	51.6	30.6	34.5	36.4	18.6	42.6	23.3
2.38	41.0	19.8	51.1	30.0	33.3	36.0	18.2	40.0	23.2

TABLE 3(a). THE VALUES OF η_1', σ_1', $1/b_2'$ AND σ_2 FOR K-30 AND K-90 IN WATER WITH VARIOUS COSOLUTES

$\overline{M}_v\times10^{-4}$	Solvent	Concn. (g/100 ml)	$\eta_1'\times10^3$ (poise)	$1/b_2'\times10^3$ (poise/sec)	$\sigma_1\times10^3$ (poise·cm)	$\sigma_2\times10^3$ (poise·cm/sec)
4	Pure water without cosolute	1.70	16.2	5.0	0.09	0.28
4	0.025 M Benzoic acid	1.70	9.5	5.0	0	0
4	0.05 M Lactic acid	1.70	9.0	5.0	0	0
4	Pure water without cosolute	0.73	8.9	5.0	0.02	0.17
4	0.1 M DL-Serine	0.73	8.9	44.1	0	0
4	0.1 M DL-Aspartic acid	0.73	9.2	66.7	0	0
4	0.1 M DL-Tryptophan	0.73	11.4	34.4	0	0
90	Pure water without cosolute	1.07	36	(−23)	0.4	(1.3)
90	0.1 M DL-Tryptophan	1.0	25.2	100	0.02	0
90	0.025 M Benzoic acid	1.0	17.2	20	0	0

TABLE 3(b). THE VALUES OF η_1', σ_1, $1/b_2'$ AND σ_2 FOR K-90 IN WATER-DMSO MIXTURES AT SEVERAL CONCENTRATIONS

Solvent	Concn. (g/100 ml)	$\eta_1'\times10^3$ (poise)	$\sigma_1\times10^3$ (poise·cm)	$1/b_2'\times10^3$ (dyn/cm^2)	$\sigma_2\times10^3$ (dyn/cm)
20% DMSO	1.5	48	0.17	35	0.4
	1.0	34	0.09	23	0.2
	0.5	21	0.06	18	0.2
50% DMSO	1.5	90	0.23	70	0.2
	1.0	61	0.11	49	0.1
	0.5	39	0.10	24	0.1
100% DMSO	1.5	60	0.20	49	0.1
	1.0	42	0.18	37	0.1
	0.5	25	0.03	22	0.1

and

$$\eta_0=\eta_1+\frac{1}{a_2b_2}=\left(\eta_1'-\frac{\sigma_1}{R}\right)+\left(\frac{1}{a_2}\right)\left(\frac{1}{b_2'}+\frac{\sigma_2}{R}\right)$$
$$=\left(\eta_1'+\frac{1}{a_2b_2'}\right)-\left(\frac{\sigma_1-\frac{\sigma_2}{a_2}}{R}\right)=\eta_0'-\left(\frac{\sigma_1-\frac{\sigma_2}{a_2}}{R}\right) \tag{3}$$

In the above equations the values of η_∞, η_0, η_1, η_1', $1/b_2$, and $1/b_2'$ must be positive; however, as stated in the previous paper,[15] the values of $1/b_2'$ obtained with K-90 aqueous solution and those of $MgCl_2$ solution obtained by the extrapolation of the line representing the linear relationship between $1/b_2$ *vs.* $1/R$ at the range of relatively larger values of $1/R$ are negative. Moreover, as shown in Fig. 3 the results obtained with 2.0% K-90 aqueous solution show that the slope of the plots of $1/b_2$ *vs.* $1/R$ changes at a certain radius (R_i). This result shows that Eq. (1) holds strictly in the same manner as in the case of other systems, for the flow of K-90 solutions in water and in $MgCl_2$ solution in the capillary having the radius larger than R_i above which the values of $1/b_2'$ are positive. Therefore, with K-90 solution in water and $MgCl_2$ solution reported in the previous paper[15] the σ_2 values with the slope having a positive $1/b_2'$ will also be expected if the experiment is carried out using the viscometers having much larger capillary radius than those used in the previous study.[15]

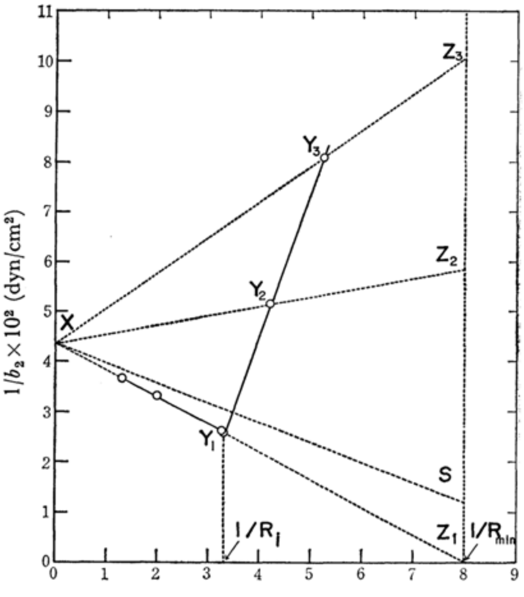

Fig. 3. Plots of $1/b_2$ *versus* $1/R$ for K-90 (2%) in water.

As shown in the previous papers,[12,15] the dependence of $\eta_\infty(=\eta_1)$ of the polymer solutions on the value of R will be explained as such a result of the decrease in the relaxation time of the solvent molecules near the wall compared with that of the bulk, because the rotational redistribution of the oriented PVP molecules in the preferred direction under the streamline of the flow may be geometrically hindered by the capillary wall and the resistance of the PVP molecules against the flow of the solvent molecules under the shear stress will become weaker near the wall than that in the bulk. From the above consideration, it may be expected that when the dissolved polymer molecules take a spherical form and have no tendency to orient under the streamline of the flow, the

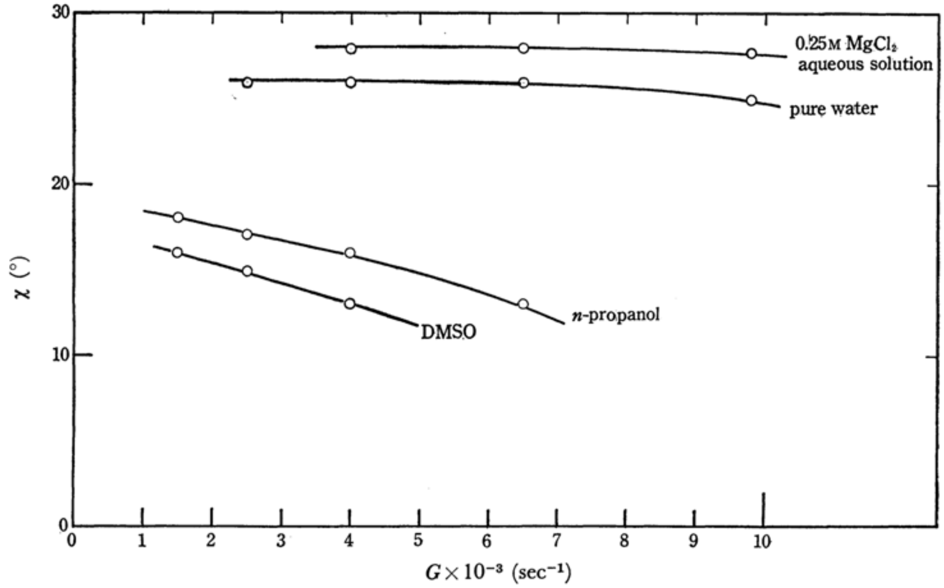

Fig. 4. Plots of extinction angle *versus* rate of shear for K-90 (1%) in various solvents.

observed viscosity would not change with the boresize of the capillary.

The dependence of the extinction angle on the rate of shear for K-90 (1%) in various solvents is shown in Fig. 4. The PVP molecules in *n*-propanol, and in DMSO, in water and in 0.25M $MgCl_2$ aqueous solution show the tendency to orient under the streamline of flow. On the other hand, in the case of the solutions with the cosolute, the position of the arms of the cross of isocline could not be detected, *i. e.* extinction angle is equal to 45° in all rates of shear, and the orientation under the streamline of flow could not be observed. From these results, the PVP molecules may be expected to interact with the cosolute and to take spherical form in solution, because the degradation of the PVP molecules with the interaction with the cosolute could not be expected. Therefore, it may be concluded that the orientation of the polymer molecules under the streamline of flow is one of the necessary conditions for the appearance of the capillary size dependence of the viscosity.

For the viscosity at a finite rate of shear, the contribution of the non-Newtonian term of Eq. (1) must be considered. The geometric hindrance of the capillary wall to the free rotation of PVP molecules described above, would control the nature of the flow pattern of the polymer solution in the capillary tube independently of the magnitude of the pressure of the streamline. When the contribution of the non-Newtonian term to the solution viscosity depends solely on a compromise between the thermal motion of the PVP molecules and the orienting effect of the streamline, the value of σ_2, will take a value satisfying the following relation

$$-\frac{\sigma_1}{\eta_1'}=\frac{\sigma_2/a_2}{1/a^2b_2'}$$

or

$$\sigma_2=-\sigma_1(1/b_2')/\eta_1' \tag{4}$$

When the observed value of σ_2 is more positive than the one expected from Eq. (4), some additional structural formation of the PVP molecules near the wall will be expected to occur and on the contrary when more negative, the slippage of PVP molecules at the wall will occur. The formation of the above structure at the wall will be facilitated by the same geometric hindrance stated above to the thermal motion of the PVP molecules near the wall, because the interaction will be promoted between the wall surface and polymer molecules, *e. g.*, the adsorption of polymers on the wall *etc.*, thus, favoring the subsequent formation of some structure in the neighborhood of the wall.

The adsorption and the subsequent formation of some structure at the wall will be studied by the measurement of the change in concentration of the solution before and after the filtration through the fine sintered glass filter under gravity. The concentration of the PVP was determined by the spectroscopic measurement in the range of the wavelength between 220 and 240 mμ.[*2] The first 1 m*l* of the filtrate of the 0.02 g/*l* solutions of PVP in water, in 0.25M $MgCl_2$ aqueous solution and in *n*-propanol showed the decrease in concentration of the magnitude of 5−10% compared with that of the original solution. But in the case of 0.01 g/*l* aqueous solution of PVP with 2.5×10^{-4}M tryptophan or 1.25×10^{-4}M benzoic acid, no appreciable change in the concentration was observed. Therefore, the occurrence of the adsorption of the PVP molecules on the glass wall will be one of the factors which determine the behavior of the flow of the polymer solution in capillary tube.

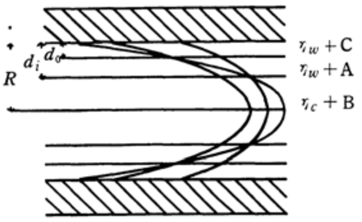

Fig. 5. Schematic model of the flow in the presence of wall layer.

Considering the above stated wall effect of the viscosity of the solutions, the flow model was proposed as shown in Fig. 5. The flowing liquid was assumed to be composed of a liquid layer near the wall (wall layer thickness d_i) and the bulk liquid. The former is divided into two layers at the distance of d_o ($d_o<d_i$) from the wall, one of which is situated on the near side of the wall, having the viscosity of η_w+C, and the other on the far-side, having the viscosity of η_w+A. The latter has the viscosity of η_c+B, to which the influence of the existence of the wall could not reach. The flow of these liquid layers may be represented by Poiseuille's law. Then the flow volume V of the liquid flowing through the tube in the interval of time t (sec) is

$$V=\frac{\pi Pt}{2L}\Big[\frac{1}{\eta_w+C}\int_{R-d_o}^{R}(R^2-r^2)r\cdot\mathrm{d}r+\frac{1}{\eta_w+A}\int_{R-d_i}^{R-d_o}(R^2-r^2)r\cdot\mathrm{d}r+\frac{1}{\eta_c+B}\int_{0}^{R-d_i}(R^2-r^2)r\cdot\mathrm{d}r$$

[*2] The PVP has the broad absorption peak with high intensity below 210 mμ, however, this range of wavelength could not be used for the concentration determination, because the $MgCl_2$ aqueous solution and *n*-propanol have also the intense absorption peaks in the same range of wavelength.

$$+ (R-d_o)^2\left\{\frac{1}{2(\eta_w+C)}[R^2-(R-d_o)^2] - \frac{1}{2(\eta_w+A)}[R^2-(R-d_o)^2]\right\} + (R-d_i)^2\left\{\frac{1}{2(\eta_w+A)}[R^2-(R-d_i)^2] - \frac{1}{2(\eta_c+B)}[R^2-(R-d_i)^2]\right\}\Bigg] \tag{5}$$

where, P: driving pressure and r: distance from the center of tube.
The experimental value of the volume of flow is expressed as follows:

$$V = \pi PtR^4/8L\eta_{exp} \tag{6}$$

where η_{exp} is the viscosity determined experimentally. The values of V of both Eqs. (5) and (6) should be equal. Hence,

$$\eta_{exp} = \frac{(\eta_w+C)(\eta_w+A)(\eta_c+B)}{(\eta_w+C)(\eta_w+A) + (A-C)(\eta_c+B)D_0 + (\eta_c-\eta_w)(\eta_w+C)D_i + (B-A)(\eta_w+C)D_i} \tag{7}$$

where,

$$D_i = 4(d_i/R) - 6(d_i/R)^2 + 4(d_i/R)^3 - (d_i/R)^4$$

$$D_0 = 4(d_o/R) - 6(d_o/R)^2 + 4(d_o/R)^3 - (d_o/R)^4$$

Comparing Eq. (7) with Eq. (3)

$$\frac{\sigma_1 - \dfrac{\sigma_2}{a_2}}{R} = \frac{(\eta_c+B)\{(A-C)(\eta_c+B)D_0 + (\eta_c-\eta_w)(\eta_w+C)D_i + (B-A)(\eta_w+C)D_i\}}{(\eta_w+C)(\eta_w+A) + (A-C)(\eta_c+B)D_0 + (\eta_c-\eta_w)(\eta_w+C)D_i + (B-A)(\eta_w+C)D_i}$$

when $$G \to 0,\quad \eta_{exp} = \eta_1 + \frac{1}{a_2 b_2} = \eta_0, \quad \text{and} \quad \eta_c + B = \eta_1' + \frac{1}{a_2 b_2'} = \eta_0' \tag{8}$$

When $(G/a_2)\to\infty$, the values of A, B, C, in above flow model are zero, *i. e.*, $A, B, C=0$, therefore, the flow model will be reduced to simpler one composed of the wall layer (thickness: d_i) having the viscosity of η_w and the bulk liquid of viscosity η_c as follows.[12]

$$\eta_{exp} = \eta_c[1-\{(\eta_c-\eta_w)D_i\}/\{\eta_w+(\eta_c-\eta_w)D_i\}] \tag{9}$$

where $\eta_c \geq \eta_{exp} \geq \eta_w$, since the values of $\eta_\infty(\eta_1)$ decrease with the decrease of capillary radii. Comparing the Newtonian term of Eq. (1) or Eq. (2) with Eq. (9),

$$\sigma_1 = \eta_c(\eta_c-\eta_w)D_iR/\{\eta_w+(\eta_c-\eta_w)D_i\},$$
$$\eta_{exp} = \eta_\infty = \eta_1 \quad \text{and} \quad \eta_c = \eta_1' \tag{10}$$

Comparing Eq. (10) with Eq. (8)

$$B = 1/a_2 b_2' \tag{11}$$

Under the conditions of $(G/a_2)\to 0$ and $\eta_0 \geq \eta_\infty$, the relations of A, B, $C > 0$ and $d_o \leq d_i$ must be satisfied.

For the calculation of the value of d_i and d_o, the value of η_w must be determined. However, there is no satisfactory way, either experimentally or theoretically, of determining the value of η_w. Whenever the polymer molecules near the wall are oriented completely by the geometric hindrance of the capillary wall under the pressure of the streamline at G/a_2 or $G\to\infty$, the expected viscosity value of flowing polymer solution near the wall, could not be lower than that of the solvent or that calculated by the Einstein equation. In the following calculation, the value of the viscosity expected from the Einstein equation was arbitrarily taken as the value of η_w.

Moreover, when the line of the plot of experimental $1/b_2$ *vs.* $1/R$, taking a more negative slope than the one expected from Eq. (4), intersects the $1/R$ axis at a point (where $1/b_2=0$) having a smaller value of $1/R$ than the one corresponding to the η_w value on η_1 *vs.* $1/R$ plots, the value of viscosity corresponding to the $1/R$ where $1/b_2=0$ on the line of η_1 *vs.* $1/R$ plots must be taken as the value of η_w in order to satisfy the condition of $\eta_0 \geq \eta_1\ (\eta_\infty) \geq \eta_w$.

Applying the value of η_w to Eq. (9) with the aid of Eq. (10), values of d_i corresponding to each R will be calculated. The value of $1/R$ corresponding to the η_w above stated, on the line of η_1 *vs.* $1/R$ relation gives the maximum value of $1/R\ (=1/R_{\min})$ where Eq. (1) could hold. Therefore the value of $R_{\min}$ is the minimum radius below which the capillary bore-size dependence of the viscosity could not be observed.

In calculating the value of d_o, the values of A and C must be determined. The value of A is given by the product of $1/a_2$ times the value of $1/b_2$ (*e. g.* point S in Fig. 3) corresponding to the $1/R_{\min}$ on the line drawn from $1/b'_2$ (point X) with a slope of σ_2 satisfied by the Eq. (4). The value of C is obtained from the value of $1/b_2$ corresponding to $1/R_{\min}$ on the slope of experimental $1/b_2$ *vs.* $1/R$ relation. Applying these values of A and C with the value of B obtained with Eq. (11) and the values of η_c, η_w and d_i already obtained, to Eq. (7), the values of d_o corresponding to each R will be calculated.

The relationships between d_o or d_i and R obtained with 2% K-90 in water and 1% K-90 in DMSO are shown in Figs. 6 and 7. In the case of 2% K-90 in water as shown in Fig. 3, where the relation $1/b_2$ *vs.* $1/R$ has been represented by two straight lines crossing at a point of a certain

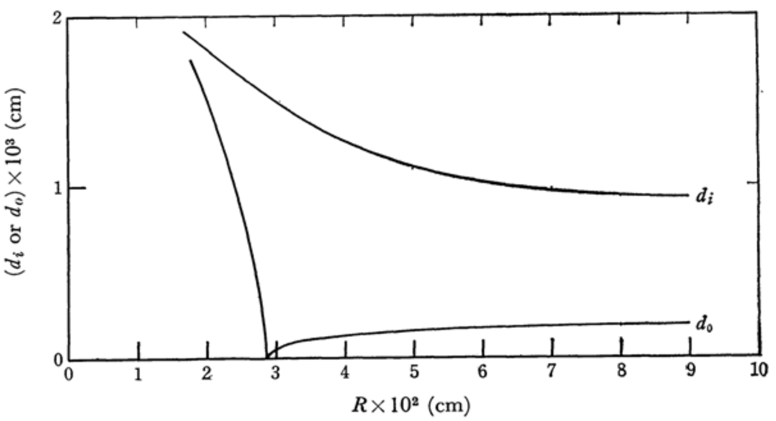

Fig. 6. Relation between d_i or d_o, and R, calculated from Eq. (7) and Eq. (9), with polymer K-90 (2%) in water, where $\eta_w=14.0\times 10^{-3}$ (poise), $\eta_c=53.0\times 10^{-3}$ (poise), $A=5.8\times 10^{-3}$ (poise), $B=22.0\times 10^{-3}$ (poise), $C=0$ (where $R > 0.0302$ (cm)) and $C=30\times 10^{-3}$ (poise) (at $R=0.0238$ (cm)) and so on.

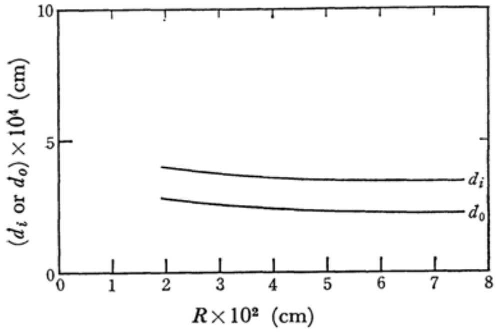

Fig. 7. Relationship between d_i or d_o and R, calculated from Eq.(7) and Eq. (9), with polymer K-90 (1%) in DMSO, where $\eta_w=1.00\times 10^{-2}$ (poise), $\eta_c=42.4\times 10^{-3}$ (poise), $A=1.63\times 10^{-3}$ (poise) $B=6.9\times 10^{-3}$ (poise), $C=11.1\times 10^{-3}$ (poise).

radius (R_i), the value of C for the range of $1/R$ smaller than the value of $1/R_i$, is given by the product of $1/a_2$ times the value of $1/b_2$ (point Z_1 in Fig. 3) obtained on the extrapolated line from the experimental $1/b_2$ *vs.* $1/R$ relationship (line XY_1) of the corresponding range of $1/R$ as stated above. In the range of $1/R$ above the $1/R_i$, the value of C is obtained from the value of $1/b_2$ (point Z_2 or Z_3) corresponding to $1/R_{\min}$ on the straight line drawn from $1/b_2'$ (point X) through the experimental $1/b_2$ (point Y_2 or Y_3); therefore, in this range not only the values of d_o changes with R but also the values of C changes with R. The results obtained with K-90 2.0% aqueous solution show that in a larger capillary bore the nature of capillary dependence of the viscosity of the solution at $G/a_2 \rightarrow 0$ may be predominantly determined by the slippage of the PVP molecules at the wall, and in a smaller capillary bore it may be determined by the existence of the some structure formed at the wall.

The abnormal phenomenon observed with K-90 in water, may be expected to occur under the conditions as follows. As shown in Figs. 3 and 8, the experimental results that the relation $1/b_2$ *vs.* $1/R$ or η_0 *vs.* $1/R$ must be represented by two straight lines, were obtained with K-90 aqueous solutions in the concentration range of 0.5—2.0%; however, in the case of K-30 aqueous solution, such a result was obtained only with the solution of such a high concentration as 5.6%. On the other hand, the tendency of the increase of η_0 with the decrease of capillary radius is always observed with the aqueous solution of PVP irrespective of molecular weight; therefore, this tendency may be said to be the general character of the flow of the PVP aqueous solution in a capillary and may be brought about

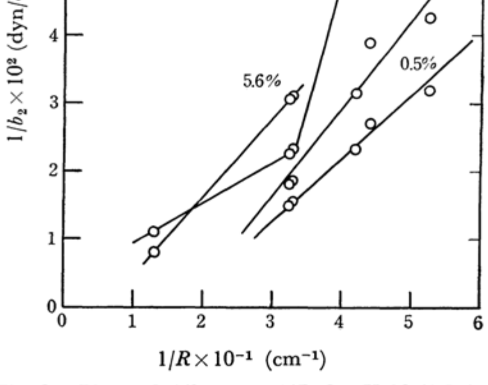

Fig. 8. Plots of $1/b_2$ *versus* $1/R$ for K-90 (1.5%, 1.0%, 0.5%) and K-30 (5.6%) in water.

by the poor nature of water as solvent. In water, compared with the case of good solvent, the adsorption of PVP molecules on the wall surface occurs more easily and subsequent formation of a rather stiff structure is facilitated by the more frequent contacts and the stronger entanglement of PVP molecules under the geometric hindrance of the wall to the thermal motion of the PVP molecules. Such a sturcture at the wall may be formed more easily in a narrower tube than in a wider one, because the geometric hindrance of the wall to the thermal motion of the PVP molecules will be more enhanced in the narrower capillary tube in which the hindrance for the rotational motion of the PVP molecules in the shear surface will occur more frequently than in the case in a wider tube. The flow behavior of the solution in the capillary tube of radius $R_{\min}$ is determined by the structure at the wall as stated above.

On the other hand, when the concentration of PVP in the solution becomes higher or the molecular weight becomes larger, the more frequent contacts and stronger entanglements of PVP molecules in the solution will assist the formation of a certain structure throughout the solution and the PVP molecules near the wall will be forced to move with the adjacent molecules existing at the far-side of the wall, that is, the slippage of the PVP molecules at the wall will occur. Such a slippage will occur in the case of the flow of the solution in the capillary tube of radius larger than R_i.

In the solution flowing through the capillary tube of radius between R_i and $R_{\min}$ the actual behavior of the PVP molecules at the wall will be determined by a compromise between the two effects stated above on the PVP molecules near the wall. A similar situation will also hold with the solution of PVP in $MgCl_2$ aqueous solution.

As shown in Fig. 9, when the value of η_0 is larger than that of η_0', the calculated value of d_o (this distance is designated as d_c) becomes larger than that of d_i and this does not satisfy the prerequisite of $d_o<d_i$. The change of d_i and d_c with R is shown in Fig. 10. This result may be brought about under circumstances where the formation of the structure near the wall extends from the wall to the central bulk liquid beyond the region of the wall layer. The result also shows the development of the very viscous layer (thickness; d_c-d_i, viscosity$=(\eta_w+A)+(\eta_w+C)+(\eta_c+B)$) on the far-side of the wall and in contact with the wall layer (thickness; d_i, viscosity$=\eta_w+C$) with the disappearance of the layer of viscosity of (η_w+A). Referring to the observation made by Segré and Silberberg[17] with the dilute suspension of macroscopic spherical particles of polymethyl methacrylate in a liquid of high viscosity that the collection of the particles occurs in a thin annular region within the flowing liquid through a tube, such a development of high viscous layer as stated above is not an unrealizable phenomenon. Furthermore by the application of the present treatment to the analysis of the capillary bore-size dependence of the viscosity of blood,[18] which shows a similar characteristics as shown in Fig. 9, a possible mechanism for the above phenomenon will be obtained.

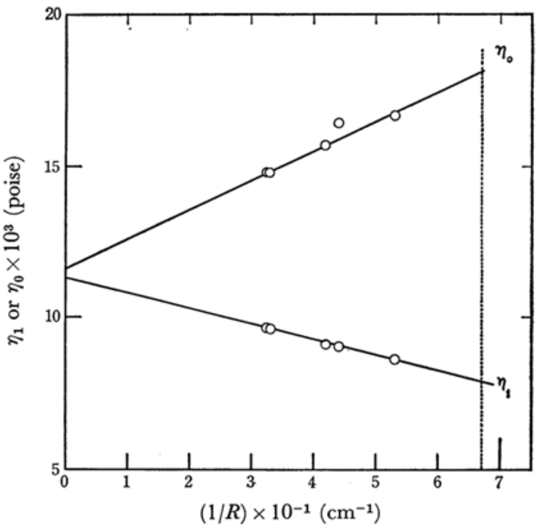

Fig. 9. Plots of η_1 *versus* $1/R$, and η_0 *versus* $1/R$, for K-30 (1%) 0.25 M $MgCl_2$ aqueous solution, where $\eta_w=7.9\times10^{-3}$ (poise), $\eta_c=11.3\times10^{-3}$ (poise), $A=0.21\times10^{-3}$ (poise), $B=0.3\times10^{-3}$ (poise), $C=10.2\times10^{-3}$ (poise).

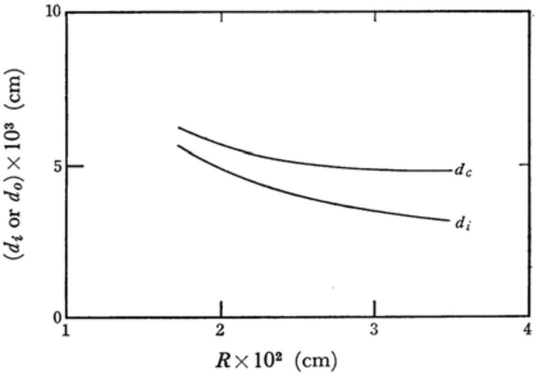

Fig. 10. Plots of d_c or d_i *versus* R for K-30 (1%) 0.25 M $MgCl_2$ aqueous solution.

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