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The Flow Properties of Polyvinylpyrrolidone Solutions*1

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The viscosities of solutions of polyvinylpyrrolidone ($\overline{M}_V=9\times10^5$) are determined at 35°C in pure water, in a 0.25 M $MgCl_2$ aqueous solution, in *n*-propanol, and in a water - *n*-propanol mixture at several concentrations (0.5—1.5 g/100 m*l*). Measurements are 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 viscosities of the solution show a non-Newtonian flow behavior and a capillary bore-size dependence. The viscosity decreases with the decrease in the capillary bore size within the range of shear stress studied. The results were represented by Ree-Eyring's generalized flow formula for a flow system containing one Newtonian flow unit and one non-Newtonian one. The contribution of the Newtonian term of the formula to the solution viscosity lowers in viscosity with the decrease in the capillary bore size, whereas the non-Newtonian term makes a contrary contribution. The change in the viscosity of the polymer solution with the size of the capillary tube may be attributed to the changes in the relaxation time of the solvent molecules and in the shear volume of the polymer molecules in the neighborhood of the capillary wall.

Polyvinylpyrrolidone is one of the important products[1,2] resulting from the Reppe technique; it has many interesting properties from both physical and biological aspects.

Many papers have been published concerning its characteristics, especially its physico-chemical properties.[3-11] However, the flow properties of this water-soluble polymer solution have received little attention despite of its importance in pharmacy, in food-stuffs, and in cosmetic products.

The present investigation deals with viscometric studies of this polymer solution and with the influence of the capillary bore size of the viscometer upon the flow behavior of polyvinylpyrrolidone solutions.

Experimental

Measurement. A Maron-Belner[12]-type capillary viscometer suitable for the study of the flow behavior of non-Newtonian fluids at low shear stresses of 0.2—20 dyn/cm^2 was used. Figure 1 is a sketch of the viscometer, which is made of glass and is composed of two main parts. One is the capillary part, consisting of precision-bore capillary tube, C, with an inner radius of R_c, precision-bore upper and lower bulbs, B, and a side-arm by-pass tube, E. The other is a manometer part, 30—35 cm in length and with an inner radius of R_m, consisting of a precision-bore glass tube, M, with a scale in mm. In the present work, $(R_c/R_m)^4$ was kept below 0.004 in all the viscometers in order to make the resistance to flow in the manometer part negligible in comparison to that in the capillary.

To operate the viscometer, a sample liquid is introduced through A, with the stopcock, S, open, until the meniscus reaches approximately 1—2 cm into the upper bulb, B. The height of the liquid in the manometer must be lower than the top of the manometer tube. Then the apparatus is immersed in a constant-temperature water bath and allowed to come to thermal equilibrium. Thereafter, the stopcock is closed and slight pressure is applied to the manometer in order to depress the liquid height slowly. When the level of the meniscus in the manometer part has been lowered about 30—33 cm, a short period is allowed for complete drainage, after which the applied pressure is removed and the liquid level is allowed to rise to hydrostatic balance. During this rise, readings at fixed heights are made to the nearest 0.01 cm, and the times corresponding to these are recorded to the nearest 0.1 sec. Finally, at the end of the run, the stopcock, S, is opened and the height of the meniscus in the manometer part is read. The reading gives the position of hydrostatic balance.

The relations between the instrumental dimensions and the experimentally-measurable values are as follows.

[*1] Partially presented at the 15th and 17th Symposia of the Colloid Chemistry, Okayama, Oct. 11, 1962, and Tokyo, Jan. 23, 1965, respectively.

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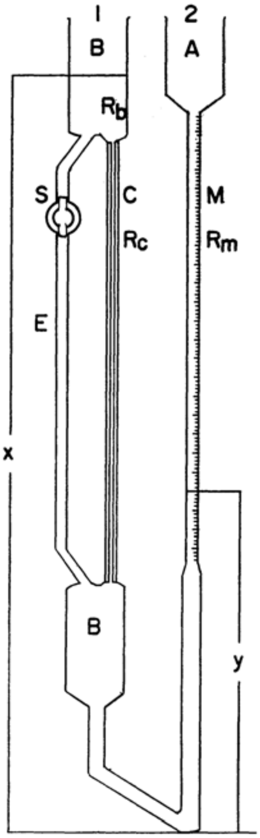

Fig. 1. Maron-Belner type low shear viscometer.

As is shown in Fig. 1, when the sample liquid flows through the capillary and the meniscus is at a position such as y in the manometer, the pressure drop, P, across the capillary is:

$$P = A\rho h = A\rho(y_0 - y) \tag{1}$$

where ρ is the density of the liquid, $A = \boldsymbol{g}\{(R_m^2/R_b^2)+1\}$, y_0 is the liquid level at hydrostatic balance, and $\boldsymbol{g}$ is the gravity constant. The volume rate of flow, Q, and the shear stress at the capillary wall, F, are:

$$Q = -\boldsymbol{\pi} R_m^2(\mathrm{d}h/\mathrm{d}t) \tag{2}$$

$$F = R_c P/2L \tag{3}$$

where L is the length of the capillary tube. Now, if h can be given as the function of t, and if ρ and the dimensions of the apparatus are known, P, Q, and F can be calculated from Eqs. (1), (2), and (3). The values of R_m, R_b, R_c, and L, necessary for the calculations, are shown in Table 1.

TABLE 1. THE DIMENSIONS OF THE VISCOMETERS

No.	Radius of capillary $R_c\times10^2$ cm	Radius of bulb R_b cm	Length of capillary L cm	Radius of manometer $R_m\times10$ cm
1	7.61	1.095	27.7	3.79
2	3.08	1.245	28.7	1.42
3	3.02	1.270	28.9	1.44
4	2.38	1.250	28.6	1.06
5	2.28	1.261	28.8	1.44
6	1.90	1.260	29.0	1.07

According to Hagen-Poiseulle's equation, the viscosity of a Newtonian fluid, η, is given by:

$$\eta = \boldsymbol{\pi} R_c^4 P/8LQ \tag{4}$$

When the expressions P and Q from Eqs. (1) and (2), are substituted, Eq. (4) becomes:

$$\eta = -R_c^4 A\rho h/8LR_m^2(\mathrm{d}h/\mathrm{d}t) \tag{5}$$

or

$$\mathrm{d}\log h/\mathrm{d}t = m = -\{R_c^4 A/8(2.303)LR_m^2\}\,\rho/\eta = -B(\rho/\eta) \tag{6}$$

where $$B = R_c^4 A/8(2.303)LR_m^2 \tag{7}$$

From Eq. (6), $\log h$ *vs.* t plots must be linear for a Newtonian fluid. Moreover, the viscosity can be obtained from a combination of the slope of the line, the density of the solution, and the dimensions of the instrument. The B values, the instrumental constants, can be obtained from the experimental values using Eq. (6) (B_{exp}) and by calculation with Eq. (7) (B_{calc}). Table 2 shows the calculated and experimental B values of the instruments with different capillary-bore sizes.

TABLE 2. THE B VALUES OF THE VISCOMETERS

No.	$R_c\times10^2$ cm	$B_{exp}\times10^5$ cm²/sec²	$B_{calc}\times10^5$ cm²/sec²	%-Deviation
1	7.61	45.28	45.58	−0.66
2	3.08	8.78	8.76	+0.23
3	3.02	7.49	7.46	+0.40
4	2.38	5.22	5.18	+0.77
5	2.28	2.45	2.44	+0.41
6	1.90	2.44	2.43	+0.41

The difference between the values of B_{exp} and B_{calc} is less than 1%. The B_{exp} values were used in the following calculation of the results.

In the case of non-Newtonian fluids, the $\log h$ *vs.* t plots do not show a linear relation. The relationship between the rate of shear (G) and the shear stress (F) is obtained by the Krieger-Maron method[13] as follows:

$$1/\eta = G/F = \phi_a\{1 + (1/4)(\mathrm{d}\ln\phi_a/\mathrm{d}\ln F)\} \tag{8}$$

where

$$\phi_a = 1/\eta_a = (-1/B)(m/\rho) \tag{9}$$

and where ϕ_a and η_a are the apparent fluidity and the apparent viscosity respectively, and where m is the slope of $\log h$ *vs.* t plots at any given point on the curve. When Eq. (9) is substituted into Eq. (8), with the aid of Eqs. (1) and (3), G/F becomes:

$$1/\eta = G/F = (-m/\rho B)[1+\{1/[(4)(2.303)m^2]\}(\mathrm{d}m/\mathrm{d}t)] \tag{10}$$

Materials. Polyvinylpyrrolidone (PVP) was a product of the Badische Anilin und Soda Fabrik AG,

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[13] I. M. Krieger and S. H. Maron, *J. Appl. Phys.*, **23**, 147 (1952); **25**, 72 (1954).

Luviskol K-90,*2 and was used without further purification. The sample was thoroughly vacuum-dried before use. An aqueous solution of this polymer has an intrinsic viscosity of 125 cc/g at 35°C.

Formulation of the Results. The results were represented by Ree-Eyring's generalized flow formula[14] for a flow system containing one Newtonian flow unit and one non-Newtonian flow unit, as follows:

$$\eta = F/G = x_1\beta_1/\alpha_1 + [(x_2\beta_2/\alpha_2)\sinh^{-1}(\beta_2 G)]/(\beta_2 G) \tag{11}$$

where x = the fractional area on a shear surface occupied by the flow unit, β = the relaxation time of the flow unit, and α = the ratio of the shear volume to twice the average kinetic energy of the flow unit, and where the subscripts, 1 and 2, of the parameters refer to the Newtonian and non-Newtonian flow units respectively. The above equation may be simplified as follows:

$$\eta = \eta_1 + (1/b_2)(1/a_2)(a_2/G)\sinh^{-1}(G/a_2) \tag{12}$$

$$\text{where,}\quad \eta_1 = x_1\beta_1/\alpha_1,\ a_2 = 1/\beta_2,\ b_2 = \alpha_2/x_2, \tag{13}$$

The properties of the $[\sinh^{-1}(G/a_2)]/(G/a_2)$ function are as follows:

$$\lim_{(G/a_2)\to 0} [\sinh^{-1}(G/a_2)]/(G/a_2) = 1$$

$$\lim_{(G/a_2)\to \infty} [\sinh^{-1}(G/a_2)]/(G/a_2) = 0$$

Therefore, for sufficiently small values of (G/a_2), Eq. (12) approximates to:

$$\eta = \eta_1 + 1/a_2 b_2 \tag{14}$$

The viscosity becomes independent of the rate of shear, and the flow is Newtonian. For sufficiently large values of (G/a_2), Eq. (12) reduces to

$$\eta = \eta_1 \tag{15}$$

The flow is again Newtonian, and η is now equal only to the Newtonian-flow unit contribution.

Results and Discussion

The viscosity (η) was determined at 35°C as the function of the shear stress (F) at several concentrations in various solvents. In Figs. 2 (a), (b), and (c), typical results are plotted as η against the shear stress. Non-Newtonian flow behavior is observed in all ranges of shear stress; it is more remarkable in a smaller capillary bore, while the viscosity of the solution decreases with a decrease in the capillary-bore sizes. The viscosity decreases by 10—30% when the capillary bore is changed from the largest to the smallest at the same shear stress. The shear dependence of the viscosity is observed markedly at a lower shear stress than at a higher stress, while the difference in viscosity due to the size of the capillary bore is marked at a higher shear stress. A similar decrease in the viscosity of the solution in a smaller-sized capillary tube, as has been stated above, was observed with clay suspensions[15] and blood[16] by Scott Blair. He suggested that the flow of the blood in a narrower capillary tube was more ready than in a wider one because of the change in the concentration distribution due to the radial displacement of the red and white corpuscles in the capillary tube. Theoretical treatments of the phenomena based on the hypothesis of the concentration change in

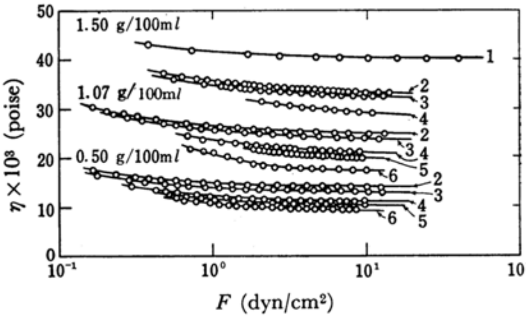

Fig. 2(a). Plots of viscosity *vs.* shear stress (log scale) of K-90 aqueous solutions at various concentrations in capillaries of various sizes.
Open circle; observed, solid line; calculated by Eq. (12).
The number designated for the curve refers to viscometer in Table 1.

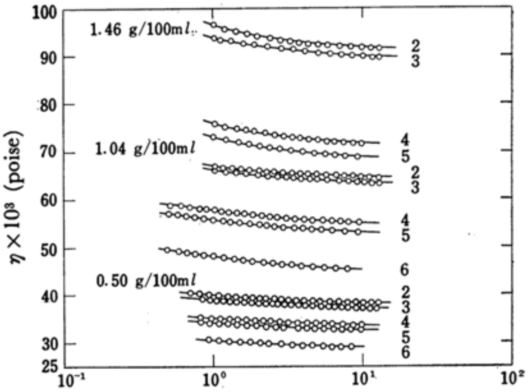

Fig. 2(b). Plots of viscosity *vs.* shear stress (log scale) of K-90 in *n*-propanol at various concentrations in capillaries of various sizes.
Open circle; observed, solid line; calculated by Eq. (12).
The number designated for the curve refers to viscometer in Table 1.

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*2 The sign, K-90, means that the Fikentscher K-value [*Cellulosechemie*, **13**, 58 (1932)] is 90, corresponding to the molecular weight of 7×10^5; however, the molecular weight determined with the aqueous solution using the equation $[\eta]=6.76\times10^{-2}M^{0.55}$ (G. B. Levy and H. P. Frank, *J. Polymer Sci.*, **17**, 247 (1955)) was 9×10^5.

14) T. Ree and H. Eyring, "Rheology," Volume II, F. R. Eirich, ed., Academic Press, N. Y. (1958), p. 83.

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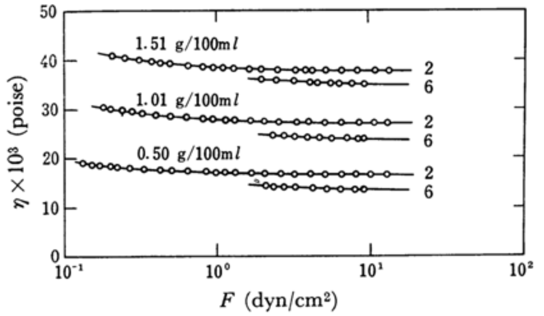

Fig. 2(c). Plots of viscosity *vs.* shear stress (log scale) of K-90 in 0.25 M $MgCl_2$ solution at various concentrations in capillaries of various sizes.
Open circle; observed, solid line; calculated by Eq. (12).
The number designated for the curve refers viscometer in Table 1.

the tube have also been made by Whitmore[17] and by Yamamoto[18].

As for the PVP solutions, however, such a radial displacement of the individual polymer molecule as a whole in the capillary tube could not be expected because of the flexible chain structure of the PVP molecule. In the case of a polymer solution, theoretical and experimental treatments have been made with a monochlorobenzene solution of polymethyl methacrylate by Oldroyd[19] and by Toms[20]. According to these authors' treatment, complete information on the increase in apparent fluidity with the decrease in capillary size can not be obtained except at an infinitely high shear stress.

In the present experiment, the formulation of the results by Ree-Eyring's generalized flow formula[14] has been made, and the phenomena of the decrease in viscosity with the decrease in capillary-bore size will be treated over the entire range of shear stress studied. The values of η_1, a_2, and b_2 obtained with Eq. (12) are shown in Table 3. The values of a_2 obtained by a trial-and-error solution take a fixed value with a given solvent. The values of η_1 and b_2 change with the bore size of the capillary and with the concentration of PVP. Therefore, the dependence of the viscosity of a given solution on the capillary-bore size may be expressed by the η_1 and b_2 parameters.

In the present case, the theoretical curves calculated from Eq. (12) using the parameters in Table 3 are in good agreement with the experimental values shown in Figs. 2 (a), (b), and (c). Therefore, it may be assumed that there exist only two types of flow unit in the systems considered, namely that of a solvent,*3 whose behavior may be taken as Newtonian, and that of the PVP molecules, whose flow may be non-Newtonian.

The x_1 and x_2 parameters in Eq. (11) are the fractional areas on a shear surface occupied by a solvent and by PVP molecules respectively; both the parameters may be determined from the concentration of PVP in a solution at a constant temperature. Therefore, the value of η_1 in Eq. (13) may be proportional to β_1/α_1 and the value of b_2, proportional to α_2 at a fixed concentration of PVP and temperature. Furthermore, the α_1 value of the solvent molecules (small molecules) could not be expected to change with the experimental conditions at a fixed temperature. Thus, the value of η_1, may be assumed to change with the change in the value of β_1 (relaxation time of the flow of the solvent molecules). Table 3 shows that the values of η_1 decrease with the decrease in capillary-bore size, provided the other experimental conditions are kept constant. Therefore, with the Newtonian term of Eq. (12), the value of β_1 must be decreased in the narrower capillary.

From Eq. (15), η_1 may be said to represent the solution viscosity at $(G/a_2)\rightarrow\infty$; as the value of a_2 is a constant, η_1 coincides with the solution viscosity at $G\rightarrow\infty(\eta_\infty)$.

Under such conditions as $(G/a_2)\rightarrow\infty$, the decrease in the relaxation time of the solvent molecules near the wall compared with that of the bulk may be expected to occur, because the rotational redistribution of the oriented PVP molecules in the preferred direction under the streamline of the

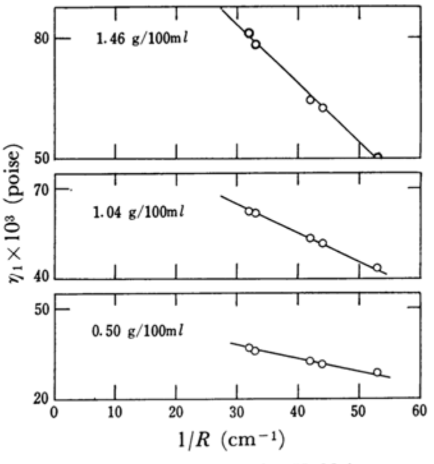

Fig. 3. Plots of η_1 *vs.* $1/R$ for K-90 in *n*-propanol at various concentrations.

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17) R. L. Whitmore, "Rheology of Disperse Systems," C. C. Mill, ed., Pergamon Press, London (1959), p. 49.
18) M. Yamamoto, "Rheology" (in Japanese), Maki Shoten, Tokyo (1964), p. 162.
19) J. G. Oldroyd, *J. Colloid Sci.*, **4**, 333 (1949).
20) B. A. Toms, *ibid.*, **4**, 511 (1949).

*3 This is the solvent under the hydrodynamic influence (at $G/a_2\rightarrow\infty$) of the dissolved polymer; therefore, in the following discussion the solvent molecules are treated as having larger values of β_1 compared to those in a pure state.

Table 3. Parameters of viscosity equation (at 35°C)

PVP in pure water where $a_2=2.0$*

Capillary radius cm	Concentration, g/100 ml								
	1.50			1.07			0.50		
	η_1 poise $\times 10^3$	b_2	η_1+1/a_2b_2 poise $\times 10^3$	η_1 poise $\times 10^3$	b_2	η_1+1/a_2b_2 poise $\times 10^3$	η_1 poise $\times 10^3$	b_2	η_1+1/a_2b_2 poise $\times 10^3$
0.0761	39.8	88.5	45.4						
0.0308	32.0	44.2	43.3	24.5	55.0	33.6	13.6	66.0	21.2
0.0302	31.5	42.0	43.4	24.0	52.5	33.5	13.1	63.5	21.0
0.0238	28.0	21.2	51.6	20.8	31.8	36.4	10.5	42.5	22.3
0.0228	27.2	15.4	59.7	20.0	25.5	39.6	9.8	36.7	23.4
0.0190	—	—	—	17.0	23.5	38.3	9.0	31.3	25.0
PVP in 0.25 M $MgCl_2$ aqueous solution where $a_2=2.0$*									
	1.51			1.01			0.50		
0.0308	37.2	99.0	42.1	26.5	113.8	30.9	16.3	135.0	20.0
0.0302	37.0	90.9	42.5	26.2	110.2	30.7	16.0	131.0	19.8
0.0238	35.7	59.3	44.1	25.0	78.0	31.4	14.7	98.0	19.8
0.0228	35.2	50.5	45.1	24.7	68.5	32.0	14.5	89.0	20.1
0.0190	34.0	22.4	56.3	23.5	40.0	36.0	13.3	60.3	21.6
PVP in 20% *n*-propanol aqueous solution where $a_2=5.0$*									
	1.52			1.08			0.57		
0.0308	72.3	75.0	75.0	48.5	99.5	50.5	27.9	160.0	29.2
0.0302	71.4	74.1	74.1	48.2	98.2	50.2	27.7	158.5	29.0
0.0238	63.5	63.2	66.7	45.3	87.5	47.6	27.4	147.6	28.8
0.0228	62.0	60.7	65.3	44.4	84.3	46.8	27.2	145.2	28.6
0.0190	54.6	50.4	58.6	41.7	75.0	44.4	26.9	134.9	28.4
PVP in 50% *n*-propanol aqueous solution where $a_2=5.0$*									
	1.41			1.08			0.45		
0.0308	92.3	67.5	95.3	70.2	90.0	72.4	37.0	112.0	38.8
0.0302	90.5	66.6	93.5	69.2	89.1	71.4	36.9	111.2	38.7
0.0238	75.2	61.3	78.5	59.5	83.0	61.9	34.4	105.0	36.3
0.0228	71.7	60.0	75.0	57.1	81.5	59.6	33.8	103.3	35.7
0.0190	52.0	54.9	55.6	47.5	75.9	50.1	31.3	97.0	33.4
PVP in *n*-propanol where $a_2=5.0$*									
	1.46			1.04			0.50		
0.0308	91.0	25.2	98.9	62.7	34.8	68.4	37.5	44.3	42.0
0.0302	87.7	24.8	95.8	61.9	34.2	67.8	36.8	44.0	41.4
0.0238	69.8	21.7	79.0	53.5	31.5	59.8	32.9	41.0	37.8
0.0228	66.8	21.0	76.3	51.7	30.5	58.2	32.0	40.0	37.0
0.0190	49.9	18.3	60.9	44.0	27.7	51.2	28.3	37.2	33.7

* The value of parameter a_2 is constant irrespective of the concentration of PVP in a fixed solvent.

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; this effect of the wall on the orientation of the PVP molecules described above will extend a certain distance from the wall into the central portion of the flowing solution in the capillary, and a liquid layer (wall layer) with a lower viscosity than the other parts of the liquids may be formed in the neighborhood of the capillary wall. Because of the existence of the wall layer, the viscosity of the solution in the narrower capillary will decrease compared with that in the wider one.

Applying the term of the capillary bore size (R) on the Newtonian term of Eq. (12), an approximately linear relationship is obtained with η_1-to-$1/R$ plots having the slope of σ_1 shown in Fig. 3.

TABLE 4. THE VALUES OF η_1' and σ_1, $1/b_2'$ AND σ_2 FOR K-90 IN VARIOUS SOLVENTS AT SEVERAL CONCENTRATIONS

Solvent	Concentration g/100 ml	η_1' $\times 10^3$ poise	σ_1 $\times 10^3$ poise·cm	$1/b_2'$ $\times 10^3$ dyn/cm^2	σ_2 $\times 10^3$ dyn/cm
Pure water	1.50	46	0.4	−80	3.2
	1.07	36	0.4	−23	1.3
	0.50	24	0.4	−10	0.8
0.25 M $MgCl_2$ soln.	1.51	42	0.2	−12	0.7
	1.01	31	0.2	−12	0.6
	0.50	21	0.2	−7	0.4
20% *n*-Propanol	1.52	98	0.9	5	0.3
	1.08	59	0.3	5	0.2
	0.57	29	0.1	4	0.1
50% *n*-Propanol	1.41	145	1.7	10	0.1
	1.08	104	1.1	8	0.1
	0.45	45	0.3	6	0.1
n-Propanol	1.46	150	2.0	18	0.7
	1.04	93	1.0	16	0.4
	0.50	50	0.5	15	0.3

Therefore, η_1 must be written as:

$$\eta_1 = \eta_1' - (\sigma_1/R) \quad (16)$$

where η_1' is the extrapolated value of η_1 at zero $1/R$ and $\sigma_1 = \mathrm{d}(\eta_1)/\mathrm{d}(1/R)$. Equation (16) would express the capillary-bore-size dependence of the value of η_1, provided the value of R is larger than a certain minimum value where the value of η_1 coincides with the viscosity of the wall layer liquid described above.

For the viscosity at a finite rate of shear, the contribution of the non-Newtonian term of Eq. (12) must be considered. By applying the approximately linear relationship in $1/b_2$ *vs.* $1/R$ plots shown in Fig. 4 and the slope obtained as σ_2, the term of $1/b_2$ is found to be:

$$1/b_2 = 1/b_2' + (\sigma_2/R) \quad (17)$$

where $1/b_2'$ is the value of $1/b_2$ at zero $1/R$ and where $\sigma_2 = \mathrm{d}(1/b_2)/\mathrm{d}(1/R)$.

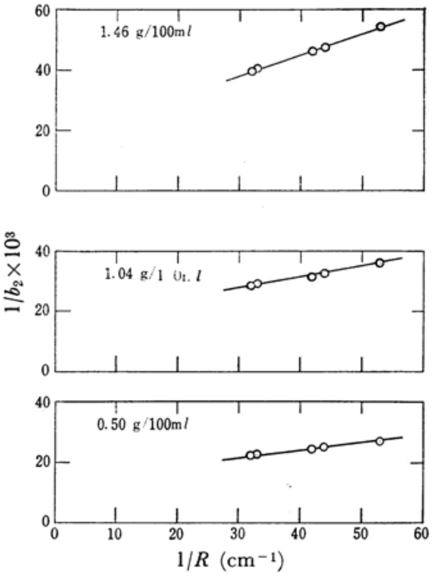

Fig. 4. Plots of $1/b_2$ *vs.* $1/R$ for K-90 in *n*-propanol at various concentrations.

The values of b_2 (or $1/b_2$) must be positive; therefore, in the cases of the PVP solution in pure water and the $MgCl_2$ solution, where the values of $1/b_2'$ take a negative value, as is shown in Table 4, Eq. (17) could not hold with a flow in the capillary with a bore size larger than a critical radius above which the calculated values of $1/b_2$ become negative.

According to Eq. (17), the value of b_2, *i. e.*, that of α_2, decreases with the decrease in the capillary-bore size. The decrease in α_2, shear volume of PVP molecules, may be expected to occur because of the same geometric hindrance of the capillary wall to the free rotation of PVP molecules described above; by this hindrance 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. Moreover, the enhanced resistance to the flow by this structure will reveal itself as the decrease in the value of α_2, *i. e.*, the decrease in the distance (λ) between two equilibrium positions for the viscous flow of PVP molecules near the wall. Therefore, on the wall layer will be superimposed a layer with a viscosity higher than that of the layer which will be superimposed on the central part; these superimpositions of the layers originated from non-Newtonian term of Eq. (12) will occur on those of Newtonian term. As is shown in Table 3 in the cases of PVP in water and a $MgCl_2$ solution at $(G/a_2)\rightarrow 0$, the solution viscosity, $\eta_0(=\eta=\eta_1+1/a_2b_2)$, increases with the decrease in the capillary-bore size. These phenomena may be brought about by the poor nature of water and the $MgCl_2$ solution as solvents; in them, compared with the case of a good solvent, the adsorption of the polymer molecules on the wall surface occurs more easily and the subsequent formation of a rather stiff structure is facilitated by the more frequent polymer-polymer contacts. Therefore, the weight of the contribution of the non-Newtonian term of Eq. (12) is much more enhanced in poor solvent than in good solvent and it will result in the increase in the solution viscosity in the narrower capillary tube.