Non-Newtonian Viscosity of Dilute High Polymer Solutions. I. Apparatus for Determining Shear Dependence of Viscosity over a Wide Range of Shear Rates and Measurements on Polystyrene Solution in Toluene

By Toshiaki KUROIWA

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Introduction

It appears to be a conclusion reached from a number of recent investigations on the non-Newtonian viscosities of high polymer solutions[1-16] that the viscosity of a dilute solution may persistently increase with decreasing rates of shear in a linear or an exponential fashion. This dependence is, however, in marked disagreement with the theory according to which the viscosity of a dilute high polymer solution should be given by an even function of shear rate q as follows[17,18]:

$$[\eta]_q=[\eta]_0(1-aq^2+bq^4-cq^6+\ldots\ldots), \qquad (1)$$

where $[\eta]_q$ is the limiting viscosity number at a shear rate q, $[\eta]_0$ is the one at $q=0$, and a, b, c, etc. are constants which depend on certain molecular parameters. According to Eq. (1), the reduction of the viscosity should be a function of q^2, and the tangent of $[\eta]_q$ vs. q curve must be zero at $q=0$.

Unfortunately, it is rather difficult to determine from the data of these investigations whether the viscosities have as a function of q a finite slope or a horizontal tangent at $q=0$, since either the lower limits of the shear rates dealt with are very high or the experimental uncertainties are very large in the region of low rates of shear, and experimental verification of the theory has called much attention[19].

Recently, E. Wada[20] has extended the measurements of the viscosities of polymethylmethacrylate solutions in chloroform over a wide range of shear rates down to the very small shear rates and has shown that the change in $[\eta]_q$ of these solutions with q fits quite well to the theoretical equation (1).

The chief purpose of the present study is to check the above-mentioned theoretical prediction by measuring the non-Newtonian viscosity of dilute polymer solutions over a wide range of shear rates. The lowest limit of shear rate dealt with in this study is about 30 sec^{-1} and the highest is 2000–3000 sec^{-1}. In the succeeding paragraphs, the method and apparatus used for the experiments are briefly described and the results of the preliminary measurements on dilute solutions of polystyrene in toluene are presented.

Experimental

Method.—According to the fundamental equation for laminar flow in a capillary, the maximum shear rate at the wall of the capillary is given by the following expression[21], provided that the so-called kinetic energy contribution and the end effect are ignored:

$$q=4Q/\pi R^3t\times(1-1/4t\times d(Pt)/dP), \qquad (2)$$

and the corresponding relative viscosity number η_r of a solution is given by

$$\eta_r=t/t_0\times(1-1/4t\times d(Pt)/dP)^{-1}, \qquad (3)$$

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where R is the radius of the capillary, P is the driving pressure and t and t_0 are the efflux times for a given volume, Q, of the solution and the solvent, respectively. Using these equations, η_r can be calculated as a function of q if a Pt vs. P relation for the solution is derived experimentally.

For a Newtonian flow in a capillary, as the well-known Hagen-Poiseuille's law, i.e., $Pt=$constant, holds, the second term in the bracket of Eq. (2) vanishes and the first term can be rewritten as follows:

$$q=PR/2L\eta, \tag{4}$$

where L is the length of capillary, η is the viscosity coefficient of the liquid. From this equation it may be seen that, in order to obtain a small value of q, it is necessary to make one or more of P, R small and or to make L large for a given liquid. Difficulty arises in making R small, since a decrease in R may give erroneous efflux times due to partial plugging of the capillary by either dust or small gel particles, and also large values of L would not be desirable because of difficulty in obtaining a capillary of a uniform radius. It is inevitable, therefore, to make P small; and a high precision of pressure must be secured in order to obtain reliable results in a range of low shear rates.

In order that Eqs. (2) and (3) can be applied, it is essential that there is no change in pressure during the course of an experiment[21]. When the usual viscometer such as the Ostwald-type, whose hydrostatic head of the liquid column changes during a run, is used, these equations can be applied only when the exteranal pressure is sufficiently high as compared with the change in pressure head**.

In the present investigation, a horizontal viscometer was employed in order to minimize the pressure variation during the course of an experiment. To compensate the hydrostatic head caused by a small deviation of the viscometer from a horizontal plane, the direction of flow was alternated at a given external pressure.

Let P' be the pressure corresponding to the effective hydrostatic head*** of the horizontal viscometer during a run, and P the external pressure. It may be assumed that the efflux times of each direction t_+ and t_- correspond to the total pressure of $P+P'$ and $P-P'$, respectively. Then, for a Newtonian flow, the efflux time t at the pressure P is given by:

$$t=2t_+t_-/(t_++t_-)\fallingdotseq(t_++t_-)/2 \tag{5}$$

For a non-Newtonian flow, this relation, of course, does not hold. But fortunately, the dilute solutions of polystyrene in toluene, at least, can be regarded as the Newtonian liquids in a region of low pressures, as will be shown in the later part of this report, and so the above relation can be used without reservation. With increasing pressure, non-Newtonian behavior appears; but at the same time, the difference between t_+ and t_- decreases rapidly $(t_--t_+)/t=2P'/P)$, and Eq. (5) can be employed as a good approximation.

Apparatus.—A sketch of the manostat system is shown in Fig. 1. Water from the main flows over the rim of the tube A. The side outlet of this tube is connected through a thick-walled rubber tube to the tube B which is inserted in the large bottle C through the hole of the lower part of the bottle. As air in C is constantly escaping through the narrow opening D; water from A flows over continuously at the upper end of B, whereby the pressure in C is kept constant at the magnitude of pressure corresponding to a difference in heights of the two overflowing surfaces, which can be adjusted by the vertical position of A.

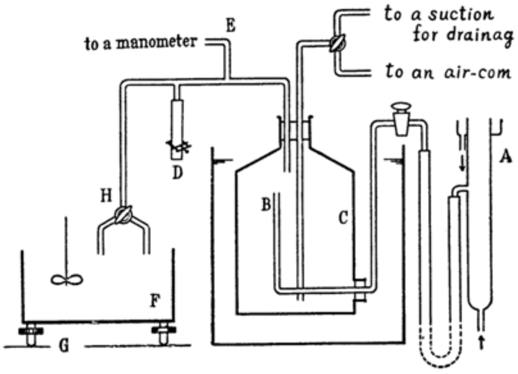

Fig. 1. Schematic diagram of the manostat system.

This apparatus is similar to that described by G. de Wind and J. J. Hermans[5]; but in their apparatus, because of the lack of an air outlet, an *increasing* pressure will not be brought under any control only leading to a lowering of the water surface in the tube B. When the water surface is once lowered below the end of B, pressure in the bottle is substantially not kept under control. In other words, it is essential that water from A is always overflowing at the upper end of B in order to secure a constant pressure-regulation****. At first sight, such a marked increase of pressure with a simultaneous lowering of water surface may be inconceivable; but before the air outlet D was provided to the present manostat, a gradual increase of pressure which followed a lowering of water surface in B was often observed. This might be due to a slow recovery of the temperature in C which had previously been cooled by water flowing into C from A during the setting of the pressure.

The pressure is read on the manometer connected to E. Water is used as manometer liquid

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** Fujita and Homma[16] have described an ingenious device by means of which the change of pressure head can be compensated and thus they have enabled the measurement at low rates of shear by means of the usual Ostwald viscometer. One drawback is that one who uses this device needs to have great patience in experimental manipulation.

*** This effective hydrostatic head reduces to the time average of the head during a run when the flow is Newtonian.

**** When the pressure is sufficiently high, this increase in pressure may be overcome by the decrease in pressure resulting from the travelling of the liquid in the viscometer.

for lower pressures (up to about 10 cm. in water) and mercury for higher pressures.

By means of this manostat, the driving pressure can be maintained constant throughout the course of measurement within ±0.005 cm. in water and this accuracy is comparable in magnitude to those of manometer reading.

Owing to the leakage of air in C, it is found unnecessary to regulate the temperature of the bath in which C is immersed.

The horizontal viscometer is shown in Fig. 2.

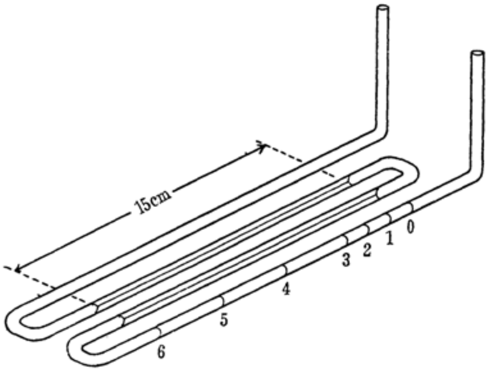

Fig. 2. The horizontal viscometer.

Uniformity of the capillary bore was checked by means of a thread of mercury, and the mean radius of the bore was determined by weighing the mercury and was found to be 0.0144_0 cm. Its length was about 30 cm. The volumes between the marks on the side arm of the viscometer (0–1, 0–2, etc. in Fig. 2) were determined by weighing the water between these marks before the viscometer was constructed. The volume between the mark 0 and 6 was about 1.1 cc.

The viscometer is mounted on a brass frame, which in turn, is fixed in a thermostatted water bath F. The bath is fitted with legs G whose lengths can be varied by screw mechanism. The inclination of the viscometer can be adjusted by varying the lengths of these legs, watching the level placed on the viscometer frame. The temperature in the bath F is controlled to 25±0.004°C. The direction of flow is altered by a specially designed three-way stop-cock H.

To check the reliability of the apparatus in the region of low pressures, the efflux times of benzene and water were measured in a range of 0.7–15 g./cm² of P. At each pressure, measurement was repeated 3–5 times for each direction of flow, and the pressure was read as often as possible during the period of each measurement. For example, at $P=0.715\pm0.004$ g./cm², t_+ and t_- were 1376±2 and 1409±3 sec., respectively, for flow volume of 0.0900 cc. (corresponds to the volume between the mark 0 and 1 in Fig. 2) of benzene. The lowest shear rate measured was about 30 sec⁻¹ for both liquids. The results are shown in Table I, together with the length of the capillary calculated from these results using the relation, $\eta=\pi R^4(Pt)/8LQ$ (P being converted to the unit dyn./cm²), where t is the efflux time for 0.0900 cc. Conforming to the Newtonian behavior of these liquids, Pt of each liquid is almost independent of P within the experimental error. From these results it may be assumed that no appreciable systematic errors, such as are due to the surface tension effect, are introduced into values of P.

TABLE I

PRODUCT OF APPLIED PRESSURE AND EFFLUX TIME FOR FLOW VOLUME OF 0.0900 cc. AND RELATED DATA FOR BENZENE AND H_2O

	Average of Pt (g./cm² ×sec.)	Standard deviation, $\sqrt{\overline{\delta^2}}$	Maximum deviation, $\delta_{\max}$	η* (centipoise)	L Calc'd
Benzene	989	5	11	0.603_4	30.3_4
H_2O	1460	7	13	0.894_9	30.2_5

* K. Shiba "Tables of Physical Constants", Iwanami Shoten (1944), p. 75.

Measurement on Polystyrene Solution in Toluene.—Styrene monomer was purified by washing several times successively with 2% aqueous solution of potassium hydroxide, 3% aqueous solution of sodium bisulfite and water, by drying over calcium chloride, and by freezing twice, discarding each time some unfrozen liquid. After distillation under a reduced pressure of 30 mmHg with the flow of nitrogen gas, the monomer was placed in a thick-walled test tube and sealed after replacing air in the tube with nitrogen. The polymerization of the monomer was carried out by placing the tube in a dark temperature bath regulated at 60°C for thirty-two days. The content was then dissolved in benzene and reprecipitated in a large excess of methanol and the precipitate, after being washed with methanol, was dried under high vacuum at 60°C for ten hours. The average molecular weight $\overline{M}$ of the polymer was estimated at 32×10^5 from $[\eta]$ in toluene measured at 30°C with an Ostwald viscometer by the equation[22], $[\eta]=3.70\times10^4\,\overline{M}^{0.62}$.

Commercial toluene was washed with sulfuric acid and with pure water, dried over phosphorous pentoxide and distilled. A fraction boiling at 110.4–110.7°C was used as a solvent.

Certain experiments were carried out, in order to determine if any dependence of viscosity on the heating temperature on preparing the solutions or on the period of room temperature-storage after preparing the solutions be detcted. The results showed that viscosity neither depends on the heating temperature within the range 30–100°C nor on the period of storage, at least in the case of concentration of the solutions lower than 2%.

The solutions were filtered successively through sintered glass filter No. 2 and No. 3 immediately before measurement. In order to minimize the errors due to moisture and solvent evaporation, measurements of efflux times for each solution were carried out in a random manner with respect to pressures, and each set of measurements was repeated two or three times by recharging the

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[22] A. I. Goldberg, W. P. Hohenstein and H. Mark, *J. Polymer Sci.*, 2, 503 (1947).

viscometer, covering the same range of pressures by each set. At high pressures, in order to avoid too small values of t, measurements were taken for a large volume of flow: (0–2), (0–3), etc. in Fig. 2, and Pt's corresponding to (0–2), (0–3), etc. were converted to those for (0–1) by the volume ratios.

The kinetic energy contribution and the end effect estimated from the tangent of Pt vs. P curve for toluene (shown in Fig. 3) were found to be negligible even in the most unfavorable case. The drainage effect was assumed to be negligible.

Results and Discussion

Pt vs. P relations for solutions of several concentrations and for toluene are shown in Fig. 3. It is evident that each curve for solutions has a horizontal part in a region of low pressures, indicating that the shear dependences of these solutions vanish at a low pressure region.

The evaluation of the differencial quotient, $d(Pt)/dp$, was made graphically with a smoothed curve drawn to give the best fit to

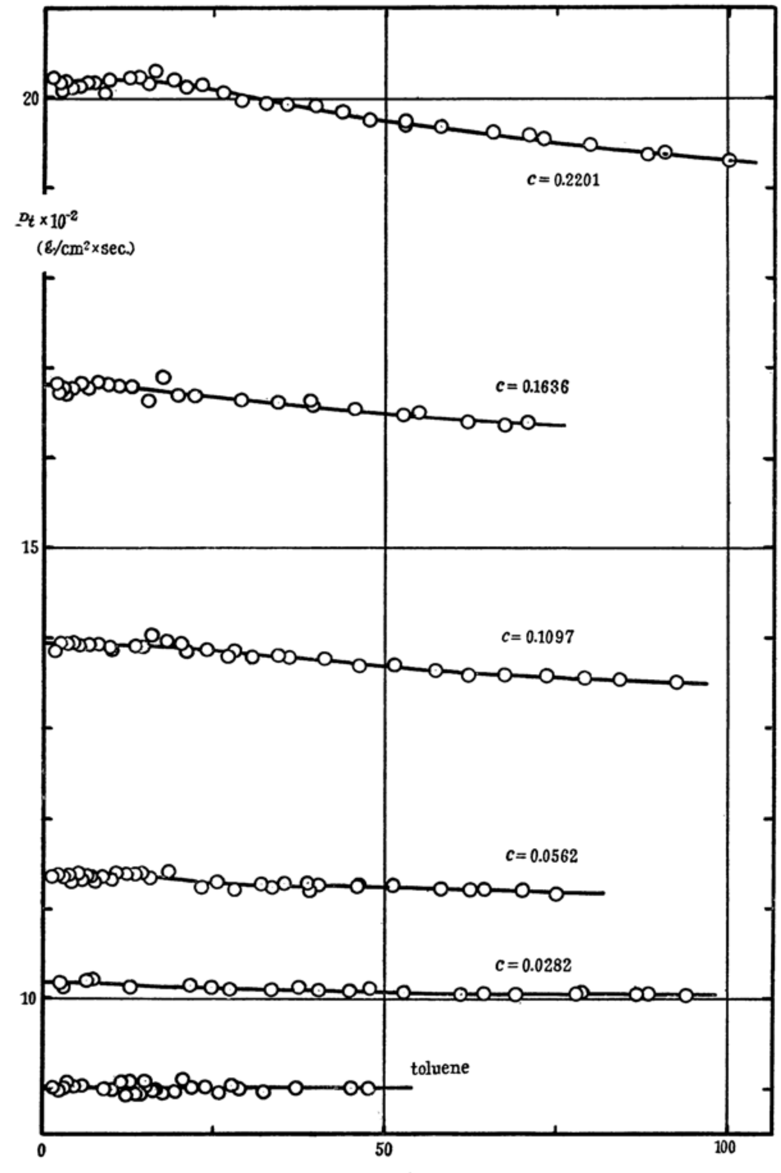

Fig. 3. Product of applied pressure and efflux time vs. applied pressure for solutions and solvent. c denotes polymer concentration in g. per 100 cc.

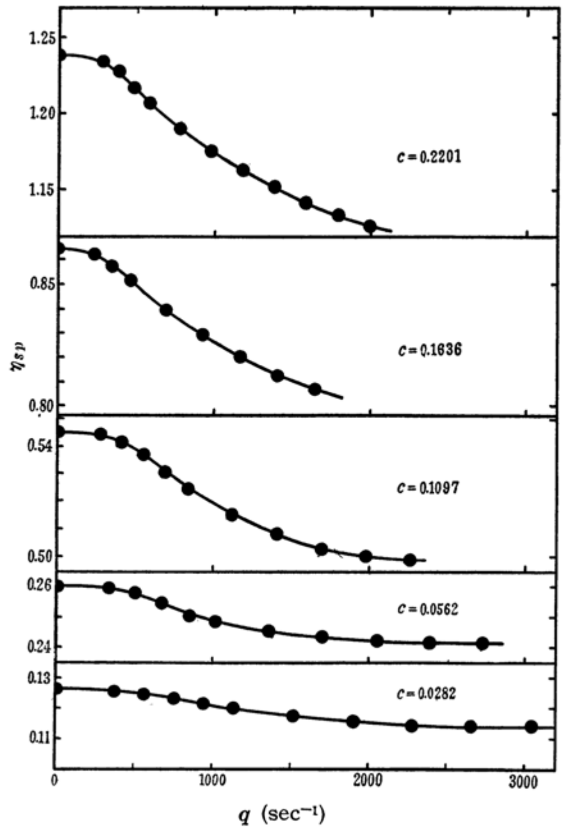

Fig. 4. Specific viscosity number vs. shear rate q.

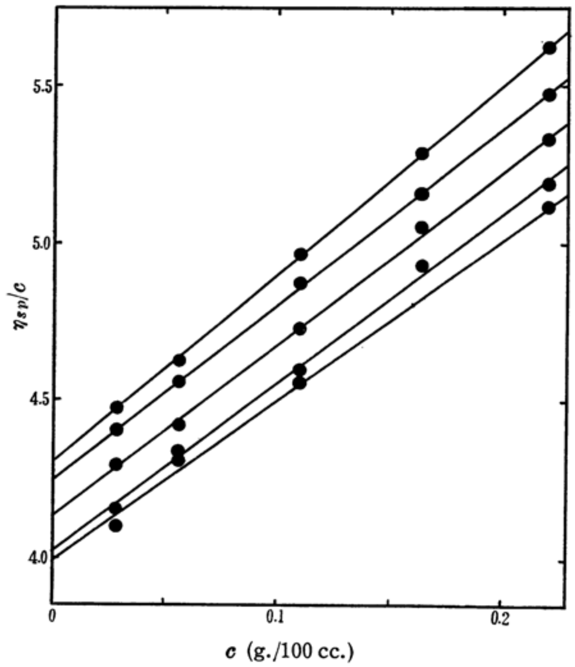

Fig. 5. η_{sp}/c vs. c curves at constant q for $q=0$, 600, 1000, 1600, 2000 sec^{-1} respectively, successively from the top.

the experimental points in a magnified graph of the data in Fig. 3. From these values at several pressures and the data for the dimensions of the viscometer, q and the corresponding η_r were calculated according to Eqs. (2) and (3). The relations of the resulted specific viscosity number, η_{sp}. vs. q are illustrated in Fig. 4 ($\eta_{sp}=\eta_r-1$). The η_{sp}/c vs. c plots at constant q for several values of q are shown in Fig. 5. These are almost linear within the range of concentrations studied, and fit the well-known Huggins' equation[23] well:

$$\eta_{sp}/c=[\eta]+k'[\eta]^2c. \qquad (6)$$

The $[\eta]_q$ obtained by extrapolating the curve at constant q to $c=0$ and Huggins' constant k' are plotted in Fig. 6 as functions of q.

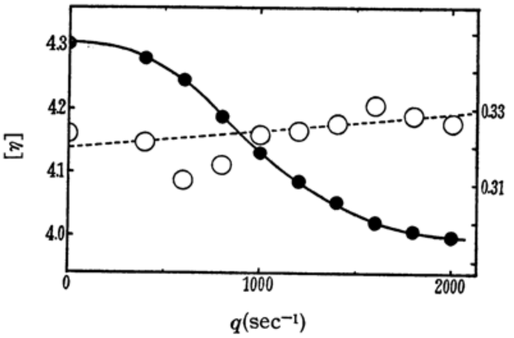

Fig. 6. Influence of rate of shear on the limiting viscosity number, (●), and Huggins' constant k', (○).

Although the values of $[\eta]_q$ at higher rates of shear are less reliable in view of the rather large scattering of points at high values of q shown in Fig. 5, it is apparent from Fig. 6 that the influence of rate of shear on the limiting viscosity number of the solution may be described adequately by an even function of q conforming, qualitatively at least, with the theoretical equation (1). A precise comparison of these data with the theory which takes into account the numerical values of a, b, etc. in Eq. (1) was not made since $\overline{M}$ of this sample was estimated roughly.

The k' vs. q relation in Fig. 6 seems to show that the dependence of k' on the magnitude of q is, if any, relatively small for the present case. This does not mean, however, that the usual viscometry such as made with an Ostwald viscometer always gives k' which is not very much different from k' at $q=0$: because, in the Ostwald viscometer,

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23) M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).

***** τ-values were calculated by the relation $\tau=PR/2L$, P being converted to the unit dyn./cm^2.

measurements are made at a constant shearing *stress* rather than at a constant q by keeping the average driving pressure constant, the smaller the polymer concentration, the greater is the mean shear rate in the capillary as may be seen from the relation, τ (shearing stress)$=\eta\times q$. Moreover, it is customary to evaluate the relative viscosity number of a solution by the ratio t/t_0, which is merely the apparent η_r rather than the true η_r because of discarding the second term in the bracket of Eq. (3). Under these circumstances, a very marked difference appears between η_{sp}/c vs. c relation at constant q and apparent η_{sp}/c vs. c relation given by the usual viscometry to the extent that the shear rate effect of solution is appreciable.

The apparent η_{sp}/c at constant τ calculated from the present data are plotted in Fig. 7 as functions of c for $\tau=4.7$, 9.4 and 14.1 dyn./cm^2*****. For comparison, true η_{sp}/c vs. c plot at constant q for $q=800$ and 1800 sec^{-1} are inserted in the same figure. The k' derived from these apparent η_{sp}/c vs. c plots are also inserted in Fig. 7. It appears that apparent k' at constant τ is strongly dependent on τ in contrast with the relatively small variation in true k' with q.

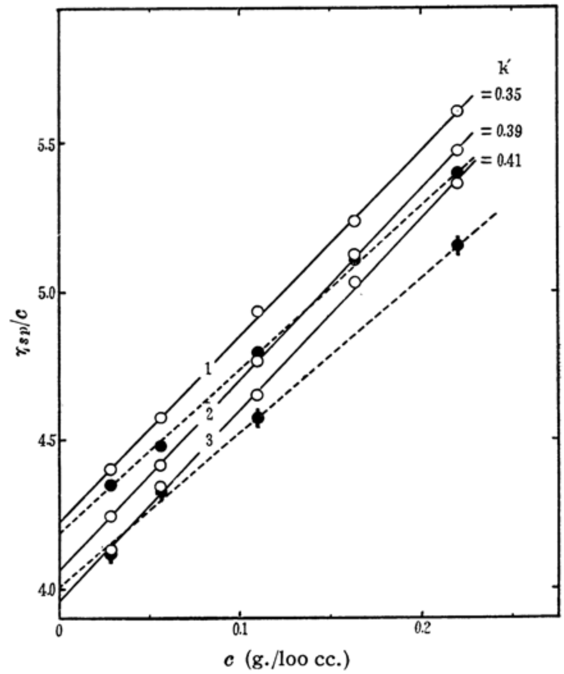

Fig. 7. Apparent η_{sp}/c v. c curves at constant τ for $\tau=4.7$ (1), 9.4 (2) and 14.1 dyn./cm^2 (3); η_{sp}/c vs. c curves at constant q for $q=800$ (●) and 1800 sec.$^{-1}$ ⧳.

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Department of Chemistry, Faculty of
Science, Osaka University, Osaka