Viscometric Study on Polystyrenesulfonic Acid Solutions

By Masaaki KATO, Tsurutaro NAKAGAWA and Hideo AKAMATU

(Received August 17, 1959)

Among the physico-chemical properties of polyelectrolytes their flow property makes an important field of study from the viewpoint of polymer science and of electrolyte theory, and many theoretical and experimental investigations on viscosity behavior of various polyelectrolyte solutions have since been reported. Of these, however, comparatively few works have been done on polyelectrolytes of the sulfonic acid type.

It seems, therefore, to be interesting to compare the authors' viscosity data on the polystyrenesulfonic acid, which itself is a strong polymeric acid, with other workers' experimental and theoretical results previously reported, chiefly on sodium salts of polycarboxylic acids or polyquaternary halides.

This paper presents a viscometric study on polystyrenesulfonic acid in various solvents: water, water-dioxane mixed solvent, and aqueous solutions of sodium chloride and some other inorganic salts.

Part I. Viscosity Behavior of PSA Solution

Experimental

Samples.—For the preparation of polystyrenesulfonic acid, polystyrene pellets manufactured by the American Bakelite Company were used. Its viscosity-average molecular weight is about 180,000 from the viscosity measurement in benzene solution at 25°C.

The main feature of the sulfonation procedure is analogous to that of Neihof[1].

In a 500 cc. conical flask 10 g. of polystyrene pellets and 0.2 g. of silver sulfate as catalyst were taken. To this was added 200 cc. of concentrated sulfuric acid, and the flask was completely corked to exclude moisture and was immersed in a constant temperature bath at 100°C with frequent stirring for 20 hr. By this treatment, polystyrene is completely dissolved in concentrated sulfuric

---

[1] R. Neihof, *J. Phys. Chem.*, 58, 916 (1954).

acid and the content of the flask becomes brown in color and very viscous. The reaction product (i. e. mixture of polystyrenesulfonic acid, sulfuric acid and silver sulfate) is poured into cold distilled water. Then polystyrene sulfonic acid precipitates in the form of a white gummy mass, which is quickly washed with water several times until heat emergence is no longer felt. The precipitate of polystyrenesulfonic acid was then completely dissolved into 500 cc. of distilled water. The large excess of sulfuric acid present could be removed by prolonged dialysis of the aqueous solution using a cellophane membrane. The last trace of remaining sulfuric acid was removed by successive electrodialysis. The presence of sulfuric acid was detected by adding barium chloride solution to the dialyzed polystyrenesulfonic acid solution²⁾; a white precipitate which does not dissolve on heating indicates the presence of sulfuric acid. Barium salt of polystyrenesulfonic acid appears also as white precipitate, but it dissolves away on heating. This test was negative after the electrodialysis for three days.

Another sample of polystyrenesulfonic acid was obtained by making the above-mentioned mixture (polystyrene, silver sulfate and conc. sulfuric acid) react in the dark and at the room temperature with frequent stirring for long days, and the following procedure was the same as above-described. The authors will hereafter refer to this as PSA-R and the sample prepared at 100°C as PSA-100.

Determination of the concentration was carried out by completely evaporating the weighed solution to dryness on a steam bath and then drying in an air oven at 110°C until the constant weight was reached.

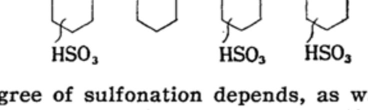
The degree of sulfonation was determined by the back titration of the PSA solution, to which excess alkali was added, with hydrochloric acid using methyl red as an indicator. The results are:

91% for PSA-100
85% for PSA-R

where 100% is assumed for PSA having one sulfonic acid group on each benzene ring.

A solid sample of the polystyrenesulfonic acid was obtained by freeze-drying of the solution as a white cotton-like material. But throughout the present measurement, PSA as the state of aqueous solution was used.

The polystyrenesulfonic acid, thus prepared, is considered to have the structure shown below.



The degree of sulfonation depends, as was mentioned above, upon the condition of sulfonation.

Viscometers.—All our viscosity measurements were carried out at 30°C by using four viscometers of Ostwald type. Their flow time for water (ca. 2 cc.) is about 147, 153, 193 and 254 sec., respectively.

Effect of Rate of Shear. — Recently many investigators³⁻⁶⁾ have pointed out the pronounced shear dependence of the observed viscosity of linear chain polyelectrolyte solutions at low ionic strength. But, according to the results of our viscosity measurement with a horizontal capillary viscometer in the range of 80∼1400/sec. of velocity gradient, our PSA sample exhibited

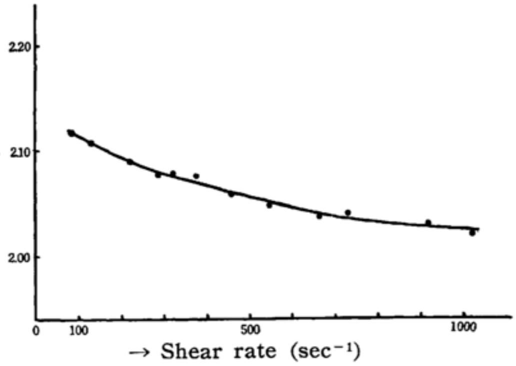


Fig. 1. Effect of rate of shear on relative viscosity. (0.0531%)

TABLE I. EFFECT OF RATE OF SHEAR ON RELATIVE VISCOSITY (0.385%)

Rate of shear q(/sec.)	Relative viscosity $\eta_r \times 10$
623	38.2
600	38.6
586	38.7
554	38.5
541	38.5
525	38.6
505	38.5
478	38.5
450	38.5
430	38.5
401	38.5
368	38.5
340	38.5
310	38.5
280	38.5
254	38.5
230	38.5
209	38.5
169	38.4
125.0	38.5
98.0	38.6
62.8	38.2
36.1	39.0

---

2) H. H. Waxman, B. R. Sundheim and H. P. Gregor, ibid., **57**, 969 (1953).

3) R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **8**, 593 (1952).

4) R. M. Fuoss and W. N. Maclay, ibid., **6**, 305 (1951).

5) A. Katchalsky and N. Sternberg, ibid., **10**, 253 (1953).

6) H. Fujita and T. Homma, ibid., **15**, 277 (1955).

only a very slight shear rate effect even in the absence of added electrolytes.

Fig. 1 shows an example* of the shear rate effect. Table I is another example** of viscosity measurement by varying the rate of shear. Here the influence of shear rate is not observed. (η_r is relative viscosity, and q is rate of shear.)

It may therefore be accepted that the following data are free from shear-rate dependence to the first approximation. The kinetic energy correction was negligible in all cases studied.

Results and Discussion

In Aqueous Solution.—The viscosity data obtained for the aqueous solutions are shown in Fig. 2, where reduced viscosity η_{sp}/c is plotted against concentration c (g./100 cc.). It is noticed that the PSA aqueous solutions have abnormally large η_{sp}/c value compared with ordinary non-polar polymer solutions in which η_{sp}/c is 2 or 3 at most. $\eta_{sp}/c-c$ plot exhibits a curve strongly concave upward, which is characteristic of polyelectrolyte solutions. In the experimental curves the tendency of decreasing in the low concentration range was not observed.

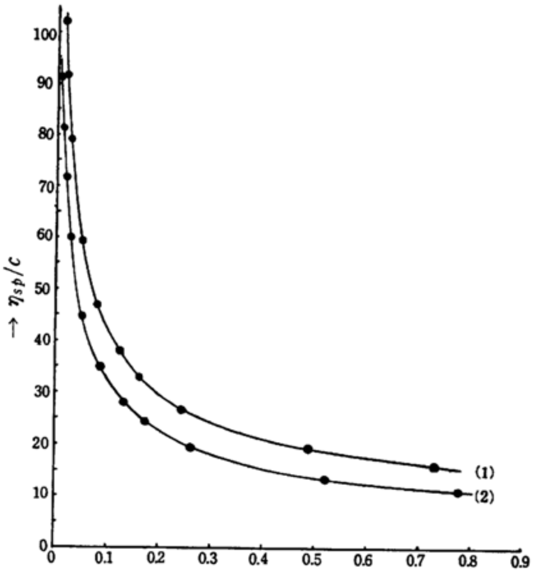


Fig. 2. Reduced viscosity vs. concentration curves.
curve (1) for PSA-100
〃 (2) for PSA-R

Considering that the reduced viscosity is a measure of the extention of a polymer coil in solution, the curves show that the size of a polymer becomes larger upon dilution. This phenomenon is generally explained as follows. As the concentration of PSA decreases, the negative net charge on a polyanion increases as a result of increasing dissociation of sulfonic acid groups, and so polymer chains extend more and more, due to the enhanced intramolecular repulsive force between like charges.

The relation between reduced viscosity and concentration of PSA is satisfactorily described by the formula

$$\frac{\eta_{sp}}{c}=\frac{A}{1+B\sqrt{c}} \qquad (1)$$

proposed by Fuoss[7,8]. Here, A and B are empirical constants. A has a meaning of intrinsic viscosity $[\eta]$, and B is a constant dependent on inter-ionic forces. The agreement of the experimental data with Eq. 1 is shown in Fig. 3. The value A is 400 for both PSA samples. The value B is

28 for PSA-100 and
41 for PSA-R

That the two PSA samples of different degrees of sulfonation have the same A value (400) is understandable by recalling that both PSA samples were prepared from the same polystyrene as a starting material and by assuming that no chain scission or cross-link formation through a

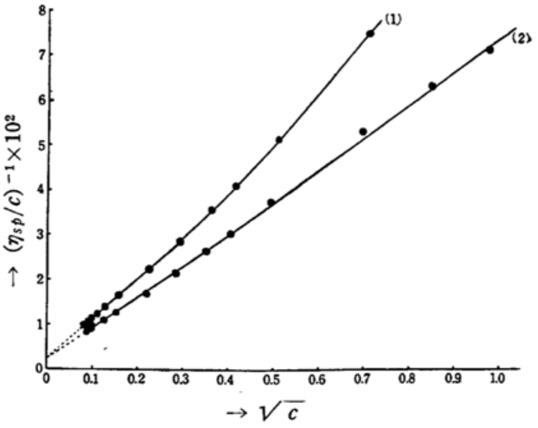


Fig. 3. Reciprocal reduced viscosity vs. $\sqrt{c}$ curves (Fuoss plot).
(1): for PSA-100
(2): for PSA-R

---

*,**) Samples from Koppers' polystyrene (viscosity-average molecular weight 3×10^5). Sulfonation for two weeks at room temperature. Degree of sulfonation 36.8 %. Viscosity measurement at 25°C.

[7] R. M. Fuoss and G. I. Cather, *J. Polymer Sci.*, **4**, 97 (1949).

[8] R. M. Fuoss, ibid., **3**, 603 (1948).

sulfone bridge during the course of sulfonation reaction occurred.

Water-Dioxane Mixed Solvent. — Viscosity data of PSA-R for water-dioxane mixed solvent of various mixing ratio are shown in Fig. 4.

η_{sp}/c vs. c relation in all the solvents studied is well described by Fuoss' Eq. 1 (cf. Fig. 5). The values A and B obtained are summarized in Table II together with the dielectric constant ε of the solvents. Values of ε of the mixed solvents are those borrowed from the published data on the ε-mixing ratio relationship by G. Åkerlöf and O. A. Short⁹⁾.

From Fig. 4 it is seen that the reduced viscosity decreases with the decrease of dielectric constant of solvent. This may be explained as follows. The dissociation $-SO_3H \rightarrow -SO_3^- + H^+$ is diminished as ε decreases, and consequently the negative net charge on a polyanion decreases, so that the polymer coil becomes more contracted in a low ε solvent than in a solvent of high ε. As the dioxane content in water increases, the Coulombic repulsive force between charged groups becomes stronger due to the decrease of dielectric constant of the medium. This effect to expand a polymer coil, however, may be less dominant than the effect of diminished dissociation of the sulfonic acid group.

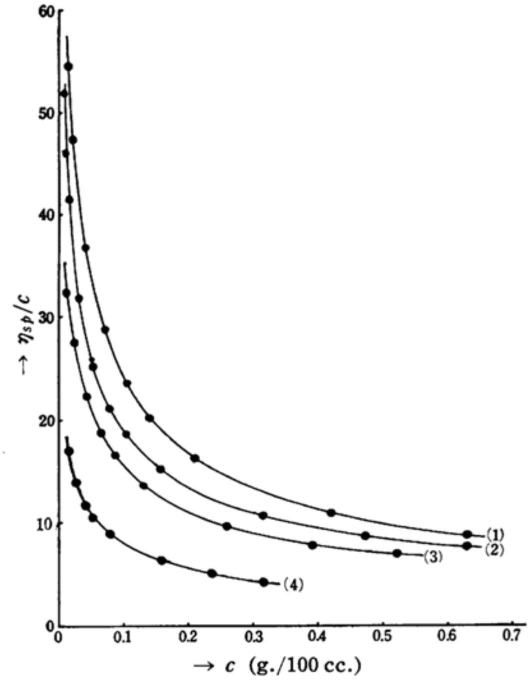


Fig. 4. Effect of dielectric constant of solvent on reduced viscosity.

PSA-R
(for $\varepsilon=76.7$ see Fig. 2)
(1) $\varepsilon=58.9$
(2) $\varepsilon=40.9$
(3) $\varepsilon=32.4$
(4) $\varepsilon=16.9$

TABLE II

ε	B	A	$1/\varepsilon^2\times10^3$
16.9	147	400	3.50
32.4	74.6	400	0.952
40.9	68.6	400	0.598
58.9	59.6	400	0.288
76.7	41.3	400	0.170

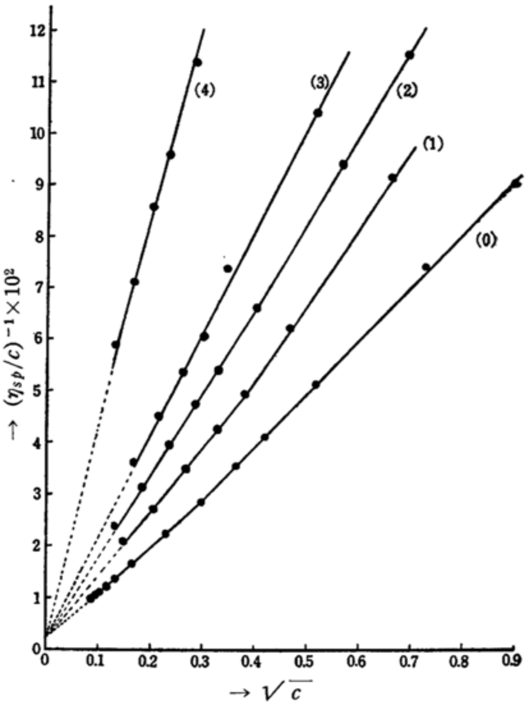


Fig. 5. Fuoss plot for the curves of Fig. 4.

PSA-R
(0) $\varepsilon=76.7$
(1) $\varepsilon=58.9$
(2) $\varepsilon=40.9$
(3) $\varepsilon=32.4$
(4) $\varepsilon=16.9$

Furthermore B vs. $1/\varepsilon^2$ plot is approximated by linear relation (cf. Fig. 6).

The parameter A has the same value 400 in any solvent. This may indicate that PSA molecule has the same size at infinite dilution in any solvent studied here.

In Sodium Chloride Aqueous Solution.—Plot of η_{sp}/c vs. c is shown in Figs. 7 and 8 for

---

9) G. Åkerlöf and O. A. Short, *J. Am. Chem. Soc.*, **58**, 1241 (1936).

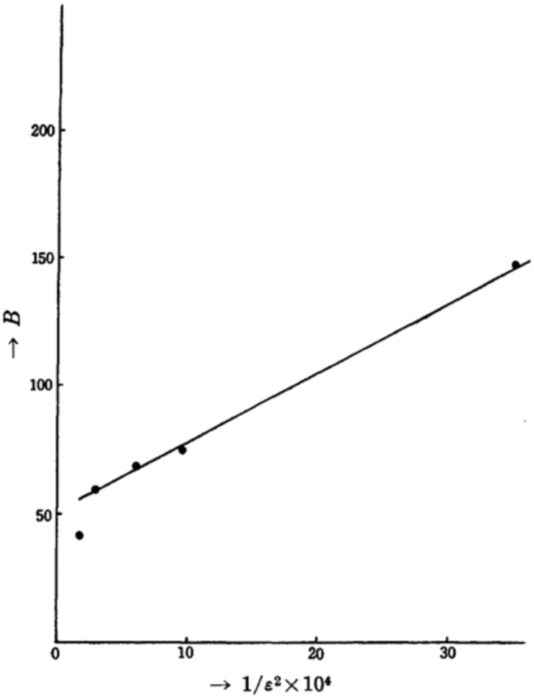


Fig. 6. Constant B of Fuoss' formula plotted against $1/\varepsilon^2$.

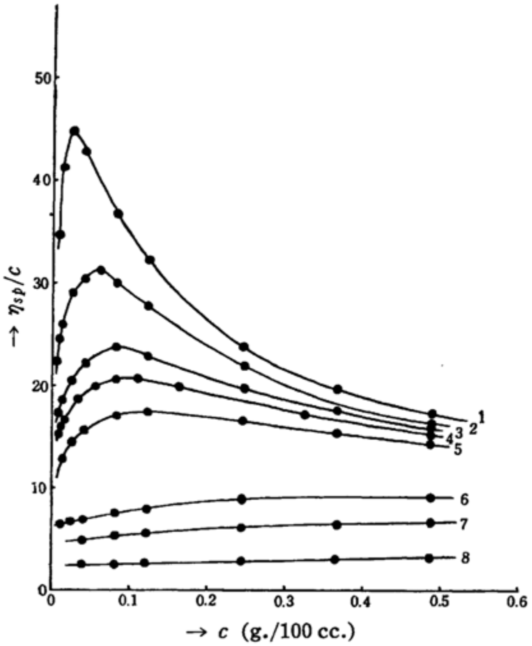


Fig. 7. Effect of salt on reduced viscosity. (PSA-100)

1) 0.000126 N NaCl aq. soln.
2) 0.000314 〃
3) 0.000628 〃
4) 0.000840 〃
5) 0.00126 〃
6) 0.00628 〃
7) 0.0126 〃
8) 0.0628 〃

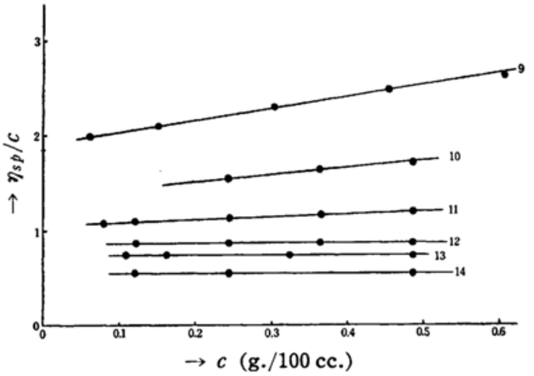


Fig. 8. Effect of salt on reduced viscosity. (PSA-100)

9) 0.0942 N NaCl aq. soln.
10) 0.2573 〃
11) 0.500 〃
12) 1.00 〃
13) 1.33 〃
14) 2.00 〃

solutions of PSA-100 in various concentration of aqueous sodium chloride in the range of 0.000126 to 2.00 N. Reduced viscosity is strongly affected by the presence of sodium chloride and diminished as the sodium chloride content in solution increases. When the sodium chloride concentration is small, the curves exhibit a maximum, which vanishes, however, with the increasing content of sodium chloride and the curves approach those for ordinary non-polar polymers. These behaviors of PSA are characteristic of many other polyelectrolytes. The qualitative explanation was given above. (See, for example, references 10 and 11).

Sodium chloride normality x and PSA normality c_m at the maximum of reduced viscosity are shown in Table III. PSA normality is greater by 10^1 than sodium chloride normality.

Values of intrinsic viscosity and sodium chloride concentration x (mol./l.) in solution are summarized in Table IV.

TABLE III

c at $(\eta_{sp}/c)_{\max}$ (g./100 cc.)	$(\eta_{sp}/c)_{\max}$	$x\times10^3$	$c_m\times10^3$
0.022	45.0	0.126	1.13
0.061	31.3	0.314	3.14
0.081	23.8	0.628	4.16
0.090	20.7	0.840	4.63
0.10	17.3	1.26	5.14

---

10) R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 602 (1948).

11) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.* **71**, 433 (1952),

TABLE IV

x	$[\eta]$	x	$[\eta]$	x	$[\eta]$
0.000126	25.0	0.00628	6.10	0.500	1.05
0.000314	18.0	0.0126	4.80	1.00	0.86
0.000628	15.7	0.0628	2.30	1.33	0.75
0.000840	13.3	0.0942	1.90	2.00	0.55
0.00126	8.82	0.2573	1.36		

$[\eta]$ values for low sodium chloride concentration are unreliable due to difficulty in extrapolating to zero concentration.

The relation between $[\eta]$ and x can be approximately described by the formula

$$[\eta]^{1/3} = a + \frac{b}{\sqrt{x}}$$

presented by Fuoss and Strauss[10] in the range of comparatively high sodium chloride concentration (Fig. 9).

In the Hermans-Overbeek theory[12] the polyion is considered as a sphere in which the separate charges are replaced by a continuous charge distribution, and the small ions are assumed to be governed by the Poisson-Boltzmann equation. Applying the result of the theory to the case in which the polymer coil is free-draining and the added salt concentration is not so low, it is concluded that $[\eta]$ vs. $1/\sqrt{x}$ relation is linear[11]. For the PSA sample a linear relation between $[\eta]$ and $1/\sqrt{x}$ is obtained in the range of concentration above ca. 0.006 N (Fig. 10).

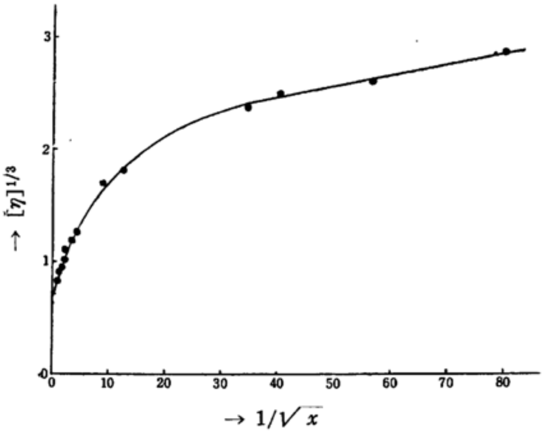


Fig. 9. Effect of salt concentration on the intrinsic viscosity (1).

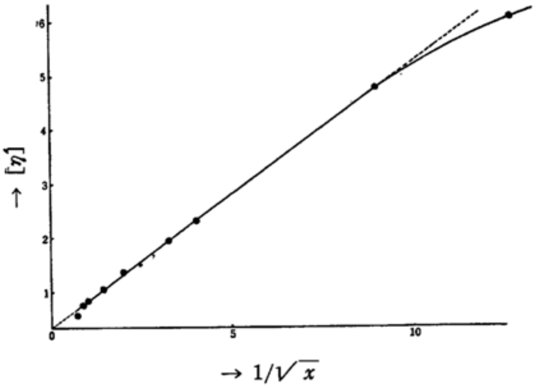


Fig. 10. Effect of salt concentration on the intrinsic viscosity (2).

In Sodium Bromide and Sodium Sulfate Aqueous Solution.—In sodium bromide and sodium sulfate aqueous solution the viscosity behavior of PSA-100 is nearly the same as in sodium chloride aqueous solution.

The effect of viscosity depression, i. e. the effect for inducing the contraction of polymer coil is strong in the order NaCl $>$NaBr$\approx Na_2SO_4$, although the difference is very slight (Table V). No distinct lyotropic effect is observed here.

TABLE V. INTRINSIC VISCOSITY OF PSA-100 IN VARIOUS SOLVENTS

Solvent			$[\eta]$
Na_2SO_4	1.491 N	aq. soln.	0.81
〃	0.745	〃	1.06
〃	0.373	〃	1.31
NaBr	2.93 N	aq. soln.	0.39
〃	1.46	〃	0.82
〃	0.73	〃	1.23
NaCl	2.00 N	aq. soln.	0.55
〃	1.33	〃	0.75
〃	1.00	〃	0.86
〃	0.50	〃	1.05

Part II. Viscosity Equation for PSA

As was stated in the previous part, PSA behaves like ordinary non-polar polymers in its viscosity character when the concentration of the added salt in the solution is high; here η_{sp}/c vs. c relation becomes linear. Hence in this circumstance it is possible to obtain Sakurada-Houwink's viscosity equation for PSA.

In this part it is aimed to prepare various PSA samples of the same charge density and different degrees of polymerization and to obtain the viscosity equation which holds between their degree of polymerization and their intrinsic viscosity in 0.52 N hydrochloric acid and 0.5 N sodium chloride aqueous solution.

For the preparation of PSA samples,

---

[12] J. J. Hermans and J. Th. G. Overbeek, ibid., 67, 761 (1948).

TABLE VI

PSA	[η] of PS before sulfonation in benzene soln. at 25°C	P	[η] of PSA in 0.5 N NaCl	[η] of PSA in 0.52 N HCl
From Fract. 2	1.025	2534	1.41	1.64
〃 〃 4	0.672	1421	0.84	0.89
〃 〃 5	0.544	1063	0.61	0.67

polystyrene (average molecular weight= 180,000; American Bakelite Company) was fractionated into several fractions and these were sulfonated under the same condition as was described above.

As the authors have some evidence from the previous experiments (Part I) that neither chain scission nor sulfone bridge formation occurs during the course of sulfonation, the degree of polymerization of the fractionated polystyrenes before and after sulfonation was assumed to be unchanged. The degree of polymerization of the fractionated polystyrenes was determined from the viscosity measurement in benzene solution at 25°C.

Experimental Results

Fractionation of Polystyrene.—30 g. of polystyrene pellets was dissolved into 1.2 l. of methyl ethyl ketone in a 2 l. flask and the solution was filtered with a No. 4 glass filter. At room temperature, methanol was slowly added to the solution with stirring until the solution became turbid and then an additional 6 cc. of methanol was added. The flask was set in a thermostat and the bath temperature was raised up until the solution became clear. Then the bath was gradually cooled to the room temperature with stirring. At the room temperature the mixture was allowed to come to equilibrium, and the precipitate was separated by decantation and then an additional 11 cc. of methanol was added to the solution. This process was repeated six times. The amount of methanol used in each precipitation process was 6, 11, 16, 26, 40 and 150 cc., respectively. Each fraction was redissolved into toluene and reprecipitated by a great excess of methanol and finally dried up to a constant weight in vacuo at 50°C.

Sulfonation. — Silver sulfate and concentrated sulfuric acid were added to each fraction in the proportion polystyrene : Ag_2SO_4 : conc. $H_2SO_4 = 10 : 0.2 : 110$ by weight. Each mixture was put into a conical flask, which was compactly sealed to prevent the entrance of moisture. The flask was set in a thermostat at 50°C. The following procedure was the same as described in Part I.

It was expected that PSA's, of the same degree of sulfonation would be obtained, but this was unsuccessful. This may be ascribed to the fact that the texture or structure of the precipitated mass is different for each fraction. (There was no regularity between their reactivity and their molecular weight.) Only the PSA's prepared from Fractions No. 2, 4 and 5 had about the same degree of sulfonation, 85%, so that these PSA's were used for viscosity measurement. The viscosity data obtained are shown in Table VI and Fig. 11.

Viscosity Equation.—Molecular weight M of the fractionated polystyrene (before sulfonation) was determined by the viscosity formula by C. Bawn et al.[13]

$$[\eta]=1.13\times10^{-4}\cdot M^{0.73}$$

(in benzene at 25°C, c in g./100 ml.)

which seems to be most reliable.

The relation between $\log[\eta]$ and $\log P$ of PSA is well approximated by a straight line and we obtained the following viscosity equations (cf. Fig. 11).

$$[\eta]=6.35\times10^{-4}\cdot P \quad \text{(in 0.52 N HCl aq.)} \qquad (2)$$

$$[\eta]=5.75\times10^{-4}\cdot P \quad \text{(in 0.50 N NaCl aq.)} \qquad (3)$$

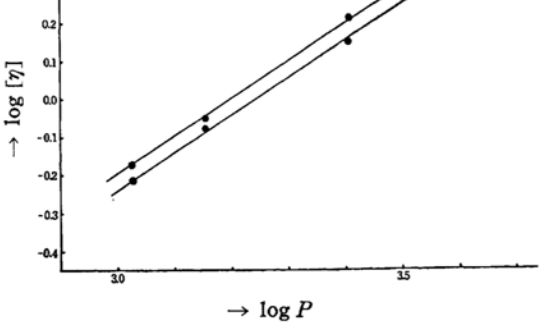


Fig. 11. Intrinsic viscosity vs. polymerization degree relation in salt solution.
1) in 0.52 N HCl
2) in 0.50 N NaCl

---

[13] C. Bawn, R. Freeman and A. Kamaladin, *Trans. Faraday Soc.*, **46**, 1107 (1950).

Here P is the degree of polymerization of PSA. Eq. 2 is for $0.52\,\text{N}$ HCl aqueous solution, and Eq. 3 for $0.50\,\text{N}$ NaCl aqueous solution.

It is noticeable that $[\eta]$ is directly proportional to the first power of the degree of polymerization.

Calculating the degree of polymerization by Eq. 2 from the viscosity data obtained by Mock and Marshall[14] for vinyltoluene-styrene copolymer sulfonic acid ($P=2036$ by osmotic measurement in methyl ethyl ketone; $[\eta]=1.58$ in $0.54\,\text{N}$ HCl at 25°C), $P=2490$ is obtained.

If the authors calculate the degree of polymerization of PSA-R used in the present study ($P=1730$ by viscosity measurement in benzene solution at 25°C before sulfonation; $[\eta]=1.07$ at 25°C in $0.5\,\text{N}$ NaCl aq. soln.; degree of sulfonation$=85\%$) by Eq. 3, $P=1860$ is obtained.

Hence Eq. 2 or 3 may be used for calculating roughly the degree of polymerization of highly sulfonated polystyrenesulfonic acid from its intrinsic viscosity in $0.5\,\text{N}$ HCl or $0.5\,\text{N}$ NaCl aqueous solution.

The cost of this research has been partly defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

---

[14] R. A. Mock and C. A. Marshall, *J. Polymer Sci.*, **13**, 263 (1954).