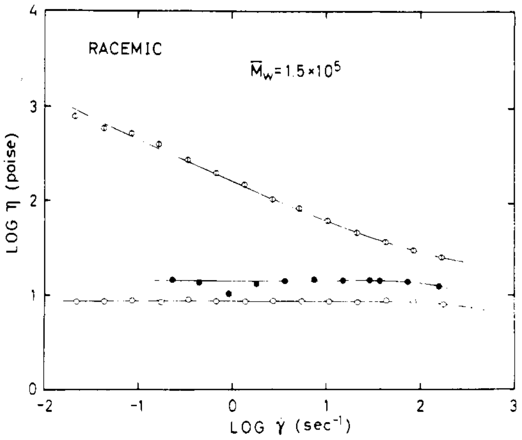

Figure 10. Apparent viscosities as a function of shear rate ($\dot{\gamma}$): (○) 20%; (●) 30%; (◐) 40%.

tions would be observed. The decrease in the apparent viscosity for a 40% solution with increasing shear rate may arise from plastic flow of piled domains, each of which has a very high yield value. On the contrary, the yielding of domain in 20 and 30% solutions may occur at so small a stress that it cannot be detected. From the above results system a 40% solution, we conclude that domains in concentrated solutions are smaller and more stable than those in less concentrated solutions. The higher mechanical stability of the domains in a 40% solution is also considered to be responsible for the decrease of transmission of light with increasing shear rate due to dynamic scattering, as mentioned earlier.

We point out that no long-range orientation would be expected, so long as polydomain flow takes place. To attain uniform molecular orientation throughout a sample, one must find conditions where a continuous monodomain phase truly exists. Piled polydomain will be transformed to a monodomain continuous phase by shear or other external field. To obtain a highly oriented system (i.e., to obtain an oriented monodomain continuous phase), one must induce the domains to coalesce and grow larger. For this purpose, the applied stress (or strain) must be delivered effectively to individual domains. Consequently, to get a highly oriented sample, it is necessary to take into account the mode of deformation, including the geometry of the apparatus as well as the size and stability of domains, which probably depend on molecular weight, concentration, temperature, pressure, and so on.

The above results show that domains for higher concentration are small and mechanically stable and that a higher shear rate (or larger stress) is required to obtain an oriented monodomain continuous phase. On the other hand, for lower concentrations only a low shear rate (or small stress) is required because domains are large and unstable, provided all other conditions such as geometrical conditions of the apparatus, temperature, and so on are the same.

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Some Solution Properties of Polyacrylamide

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ABSTRACT: Six samples of polyacrylamide prepared by radical polymerization in water solution were studied by the methods of sedimentation equilibrium and viscometry. Evaluation of sedimentation equilibrium yielded the molecular weight, the polydispersity parameter, and the second virial coefficient. The intrinsic viscosity increases with increasing concentration of sodium chloride. The parameters of the Mark-Houwink-Sakurada relation $[\eta] = KM^a$ were estimated and compared with the literature data.

Water-soluble polymers are rapidly gaining practical importance as viscosity-enhancing agents, flocculating agents, food additives, etc. However, at present the basic properties of these polymers and their solutions are not known to a satisfactory degree. This situation arises (among other things) from the fact that these polymers exhibit a large number of unwelcome properties. They frequently have broad distribution of molecular weights,

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are extensively branched, exhibit polyelectrolyte effects, and have a tendency toward aging. The term aging embraces a number of ill-understood phenomena such as aggregation, degradation, cross-linking, and slow dissolution.

In the first part of our broader study of water-soluble polymers, we report the results of our measurements on polyacrylamide. Among water-soluble polymers, polyacrylamide is relatively well-behaved. When the polymerization temperature is not too high, the chains are probably strictly linear, there is no sign of bimodality in molecular weight distribution, and the hydrolysis of the amide bonds is usually insignificant (meaning absence of polyelectrolyte effects). The aging of polyacrylamide solutions manifests itself by the generally poor reproducibility of experimental data and by a decrease of the solution viscosity over longer periods of time.

Haas and MacDonald[1] studied the stability of polyacrylamide in solution up to 50 days. They found that damage can result from two sources: (1) the growth of microorganisms, which may be suppressed by antimicrobial agents (they recommended an addition of 3% 2-propanol); (2) traces of initiator ($K_2S_2O_8$) in the product which cause slow degradation. Effect 2 may be suppressed by some reducing agents ($NaNO_2$); it is absent in a polymer initiated by biacetyl.

Kulicke and Klein[2] have similarly observed the stabilizing effect of 2-propanol. In addition, polyacrylamide is more stable in nonaqueous solvents such as formamide or ethylene glycol than in water. These authors explained the aging and the stabilization through the changes of chain conformation of single molecules based on hydrogen bonds.

The molecular weight of polyacrylamide samples has been measured by a combination of diffusion and sedimentation velocity measurements,[3] by light scattering,[4-9] and from the analysis of the polymerization kinetics.[10] These studies led to a number of relations between the intrinsic viscosity $[\eta]$ and the molecular weight. Scholtan[3] obtained the relation

$$[\eta] = 6.31 \times 10^{-3} M^{0.80} \qquad (1)$$

for polyacrylamide dissolved in water at 25 °C. The molecular weight is the diffusion-sedimentation average measured on fractionated samples.

The relation

$$[\eta] = 3.73 \times 10^{-2} M^{0.66} \qquad (2)$$

was reported by American Cyanamid Co.[4] for polyacrylamide in 1.0 M $NaNO_3$ at 30 °C; the molecular weight was measured by light scattering. This relation is widely used in the literature. However, we have been unable to obtain the original bulletin.

The relation of Korotkina et al.[7]

$$[\eta] = 2.5 \times 10^{-2} \bar{M}_n^{0.70} \qquad (3)$$

refers to intrinsic viscosities in 10% aqueous NaCl and to number-average molecular weights $\bar{M}_n$ calculated by light-scattering techniques from the limiting tangent at high scattering angles. Their fractions were very broad and the results were scattered.

The relation

$$[\eta] = 3.02 \times 10^{-3} M_w^{0.82} \qquad (4)$$

is based on light-scattering measurements in 1% aqueous NaCl.[8] Unfortunately, the original paper[8] was not available to us.

Recently, Klein and Conrad[9] measured the molecular weight of unfractionated polyacrylamide and reported the relations

$$[\eta] = 4.9 \times 10^{-3} M_w^{0.80} \qquad (5)$$

for water at 25 °C,

$$[\eta] = 7.19 \times 10^{-3} M_w^{0.77} \qquad (6)$$

for 0.5 M aqueous NaCl at 25 °C, and

$$[\eta] = 1.36 \times 10^{-1} M_w^{0.54} \qquad (7)$$

for ethylene glycol at 25 °C. In the region of molecular weights covered in these experiments,[9] the intrinsic viscosity in solutions of NaCl according to eq 5 and 6 seems to be about 5–15% lower than in water.

Finally, Collinson et al.[10] based the relation

$$[\eta] = 6.8 \times 10^{-2} \bar{M}_n^{0.66} \qquad (8)$$

on the kinetic analysis of their polymerization experiments.

While Klein and Conrad[9] found that the intrinsic viscosity of polyacrylamide decreases slightly with increasing concentration of NaCl, Eliassaf and Silberberg[11] reported that the specific viscosity of a sample of polyacrylamide at 30 °C is not influenced by addition of up to 3.66 N NaCl, of up to 4.72 N LiCl, or of up to 7.32 M urea. Addition of ethanol reduced the specific viscosity; at higher concentrations of ethanol the polymer precipitated.

Silberberg et al.[5] measured light scattering and intrinsic viscosity of a single sample of commercial polyacrylamide in water as a function of temperature. The intercept of the plot of the light-scattering quantity Kc/R_{90} was independent of temperature, suggesting the absence of aggregation and degradation in the temperature region up to 50 °C. The second virial coefficient was extremely high and increased with increasing temperature. The intrinsic viscosity increased steeply with temperature; however, at temperatures higher than about 40 °C the reduced viscosity η_{sp}/c decreased with increasing concentration.

At The University of Texas, we have been using the method of sedimentation equilibrium for measurement of molecular weight and other thermodynamic properties in highly nonideal polymer solutions.[12-14] Recently we have extended the method also for a study of polydispersity and have shown that the method is applicable to solutions of polyacrylamide.[15] In the present study, we measure the sedimentation equilibrium data for six samples of polyacrylamide, correlate them with intrinsic viscosities, and compare the results with the older measurements. We also study the effect of the concentration of NaCl on the intrinsic viscosity of polyacrylamide. In addition, we have measured the partial specific volume and refractive increment of polyacrylamide in water and in aqueous NaCl solutions.

Experimental Part

Polymerization of Acrylamide. Polyacrylamide was prepared by polymerization of a 5% aqueous solution of acrylamide (10% solution for the highest molecular weight sample W24392) at 50–60 °C, using the radical initiator $K_2S_2O_8$ (10–100 mg/L). After 4 h the conversion was essentially quantitative. The samples W24243, W24245, and W24392 were dehydrated after polymerization by addition of 10 volumes of methanol to 1 volume of the reaction mixture. The other three samples were first diluted by water to form a 1–2% polymer solution and then precipitated by a tenfold excess of methanol. The samples were dried overnight under vacuum at 60–80 °C. The residual content of water was measured by drying the samples at 120 °C for 4 h and also by an elemental analysis for nitrogen. The water content was 7–11% by weight, in good agreement with the value 2–9% found by

Kulicke and Klein.[16] Drying at higher temperatures was avoided because it led to the cross-linking of the polymer. The residual content of monomer was under 0.1%; the degree of hydrolysis (carboxyl groups) estimated by colloid titration[17,18] was about 0.3%.

Specific Volume of Polyacrylamide. The density measurements were made at 20 °C by using a DMA 02C Digital Precision Density Meter manufactured by A. Paar, K. G., Austria. The two polyacrylamide samples with the lowest molecular weights (W25651, W25499) were dissolved in water and in 0.2 M aqueous NaCl. Two solutions ($c \sim 0.010$, $c \sim 0.005$ g/mL) were prepared from each sample in each solvent; each solution was measured twice. The partial specific volume $\bar{v}$ was calculated by the expression

$$\bar{v} = [1 - (\rho - \rho_s)/c]/\rho_s \qquad (9)$$

where ρ and ρ_s are the density of solution and the density of the solvent mixture, respectively. Concentration c (in g/mL) was corrected for the water content of the samples. For each solvent, the eight experimental values of $\bar{v}$ differed only by a few units in the third decimal place. The values (reported in a later section) represent the averages of these eight measurements.

Refractive Increments of Polyacrylamide. For the measurement of the refractive increment at 20 °C the same solutions were used as for the density measurement; again, each solution was measured twice. A Brice-Phoenix Model BP-2000-V differential refractometer equipped with an R-101-4 special glass cell was employed for this measurement at two wavelengths (mercury lines at 546 and 436 nm). Within each set of eight measurements, the values differed by a few units in the third decimal place; the averages are reported in a later section.

Using the diffusion technique in the ultracentrifuge described earlier,[19] we have also measured the refractive increments of polyacrylamide at constant chemical potential $(\Delta n/c)_\mu$ at 20 °C. The sample W25651 was measured in water and in 0.2 and 1.0 M aqueous NaCl. The measurement in each solvent was repeated 3 or 4 times. Again the scatter was in the third decimal place; we report the average values.

Intrinsic Viscosity. The viscosities were measured by a Fica Viscomatic automatic viscometer at 20 °C. The concentration of the starting (undiluted) solution was chosen so as to obtain the relative viscosity $\eta_{rel} = 1.3$–2.0. Five concentrations were measured with the following fraction of the starting concentration: 1, $^2/_3$, $^1/_2$, $^1/_3$, $^1/_6$. Within this concentration region, the plots of $\ln \eta_{rel}/c$ against c exhibited good linearity; the values of intrinsic viscosity $[\eta]$ and Huggins' constant k_H were obtained from these plots in the usual way.

Intrinsic viscosities were measured in three solvents: water, 0.2 M aqueous NaCl, and 1.0 M aqueous NaCl. The growth of microorganisms was prevented by adding 0.002 M sodium azide to all solutions.

To achieve satisfactory results we had to allow the samples enough time for complete dissolution. For the low molecular weight samples, 2–3 days was sufficient. However, the high molecular weight samples required up to 3 weeks for complete dissolution, as judged visually by the disappearance of gellike particles. Even with these precautions we found poor reproducibility of the intrinsic viscosity. The spread of values in repeated experiments was typically about 10% but occasionally (for the higher molecular weights) even 25%. The reproducibility was much worse for solutions in water than for solutions in either 0.2 or 1.0 M aqueous NaCl. The measurements on the high molecular weight sample W24392 were especially difficult. The values of intrinsic viscosity in mL/g and Huggins' constant k_H, which we are reporting, are in most cases averages from two or more experiments. The data were not corrected for the non-Newtonian behavior.

Sedimentation Equilibrium. The sedimentation equilibrium experiments were performed at 20 °C in a Spinco Model E ultracentrifuge equipped with an electronic speed control, the ANJ heavy rotor, a Kel-F coated aluminum double-sector centerpiece, sapphire windows, and schlieren and interference optics. The interference photographs were evaluated by using an automated plate reader as described in our previous papers.[12-14]

For the sedimentation experiments, we selected as a solvent 0.2 M aqueous NaCl. The presence of the salt helps to stabilize the run against convection in the meniscus region. About 0.15 mL of the solution (concentration about 6×10^{-4} g/mL) was injected into the solution compartment, creating a column about 4.5-mm high. For the high molecular weight sample W24392, we have used 0.07 mL (~2.0-mm column) and a concentration about 3×10^{-4} g/mL. The rotor velocity was adjusted according to the molecular weight of the sample, being 8000 rpm for the lowest sample and 2800 rpm for the highest. At these velocities, the meniscus region was almost completely depleted of polymer. The residual concentration at the meniscus was under 10 μm of the fringe displacement. The duration of the runs was about 6 days. For each sample we did two equilibrium experiments (three for sample W24392).

Table I
Specific Volume and Refractive Increment of Polyacrylamide at 20 °C

solvent	$\bar{v}$, mL/g	$\Delta n/c^a$ 546 nm	$\Delta n/c^a$ 436 nm	$(\Delta n/c)_\mu{}^b$ 546 nm
water	0.696	0.182	0.185	0.173
0.2 M NaCl	0.687	0.182	0.186	0.172
1.0 M NaCl				0.175

[a] From the differential refractometer. [b] From the diffusion experiment in the ultracentrifuge.

Results and Discussion

Our experimental values of the specific volume and refractive increment are collected in Table I. Our value of $\bar{v}$ is significantly smaller than the value 0.769 reported for water solutions by Scholtan.[3] If Scholtan's and our values of $\bar{v}$ are both used for the evaluation of the same sedimentation experiment (either equilibrium or velocity), Scholtan's value would yield molecular weights about 30% higher than ours.

Our refractive increment is slightly lower than the value 0.187 reported for water solutions at 25 °C by Klein and Conrad;[9] it is slightly higher than the value 0.17 for 10% NaCl solutions at 20 °C as given by Korotkina et al.[7] The values for water solutions given by Cantow[6] (0.163 at 25 °C) as well as by Silberberg et al.[5] (0.149) seem to be too low. All the above literature values refer to the wavelength 546 nm.

Our values of the refractive increment measured under the condition of constant chemical potential are about 5% lower than the values measured in the differential refractometer. This difference is observed even in water solutions, where preferential adsorption cannot play any role. We do not know the source of this discrepancy.

The sedimentation equilibrium experiments were evaluated by a method reported in another paper.[15] That method is based on the assumption that the distribution of the molecular weights in the polymer sample is unimodal and can be reasonably described by the Schulz–Zimm distribution function. It is also assumed that the thermodynamic apparent molecular weight M_{app} can be described as

$$M_{app}^{-1} = \bar{M}_w^{-1}(1 + \alpha \bar{M}_w c)^2/(1 + \beta \bar{M}_w c) \qquad (10)$$

where the parameters α and β are related to the second virial coefficient as

$$A_2 = \alpha - \beta/2 \qquad (11)$$

In eq 10, M_{app} and $\bar{M}_w$ refer to the local values within the cell. The method[15] allows for calculation of the molecular weight average $\bar{M}_w$ of the *original* sample, of its polydispersity parameter $u \equiv \bar{M}_z/\bar{M}_w - 1$, of the second virial coefficient A_2, and of the ratio β/α. It should be noted that, for samples which are not strongly nonideal, the computer program often sets $\beta/\alpha = 0$.

Table II
Molecular Weight, Polydispersity, and Thermodynamic Parameters from Sedimentation Equilibria of Polyacrylamide in 0.2 M Aqueous NaCl at 20 °C

sample	run	$10^{-3}\bar{M}_w$	u	$10^4 A_2$	β/α
W25651	1	263	0.42	3.21	0.00
	2	246	0.46	2.91	0.00
W25499	1	581	0.55	3.03	0.00
	2	651	0.68	3.59	0.28
W24243	1	952	0.68	2.93	0.00
	2	1074	0.66	3.30	0.27
W24245	1	2759	0.78	3.10	0.42
	2	2100	0.67	2.70	0.30
W25655	1	2831	0.53	2.78	0.15
	2	2664	0.50	2.83	0.23
W24392	1	10000	0.46	2.03	0.27
	2	8124	0.57	2.24	0.26
	3	15487	0.83	2.31	0.42

Table III
Molecular Weights, Intrinsic Viscosities, and Huggins' Constants of Polyacrylamide Samples at 20 °C

		H_2O		0.2 M NaCl		1.0 M NaCl	
sample	$10^{-3}\bar{M}_w$	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
W25651	255	132	0.41	133	0.38	150	0.38
W25499	616	242	0.40	268	0.41	296	0.37
W24243	1010	330	0.28	379	0.40	404	0.36
W24245	2430	494	0.17	640	0.34	673	0.37
W25655	2750	743	0.39	752	0.38	803	0.39
W24392	11200	1600	0.37	1500	0.40	1790	0.35

In Table II are collected the results of this evaluation. We report the values obtained from each equilibrium run. For most samples, duplicate runs yield values differing 10% or less. However, the difference is larger for the sample W24245 and especially for the high molecular weight sample W24392. The discrepancy seems to be a manifestation of the generally poor reproducibility of the measurements on polyacrylamide solutions due to possible degradation and/or incomplete dissolution.

The process of radical polymerization with disproportionation leads under ideal conditions to the Schulz–Zimm distribution function of molecular weights with the parameter $z = 1$. This corresponds to our parameter $u = 0.5$. When the conditions during polymerization are not strictly ideal, the distribution function gets broader and u increases. A loss of low molecular weight molecules during precipitation may cause a slight narrowing of the distribution. Thus, our values of u seem to be quite reasonable. They also agree well with the value $\bar{M}_w/\bar{M}_n = 2.5$ reported for unfractionated polyacrylamide by Kulicke and Klein;[16] this value corresponds to $u = 0.67$.

The second virial coefficient A_2 seems to decrease slowly with increasing molecular weight; this is in agreement with most theories of polymer solutions. The value of A_2 is of the same order of magnitude as the typical values of other polymers in good solvents. Thus, the observation of Silberberg et al.[5] that the second virial coefficient of polyacrylamide in water at room temperature is about 40×10^{-4}, i.e., about 15 times larger than our values, was not confirmed. On the other hand, our values are in good agreement with the value 2.6×10^{-4}, which is the value reported by Cantow[6] after conversion to the standard units.

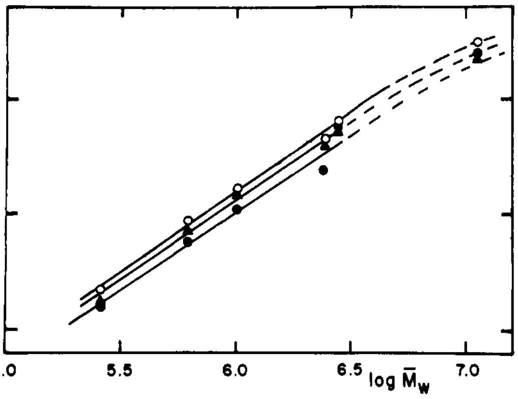

Figure 1. Logarithmic plot of the dependence of the intrinsic viscosity of polyacrylamide samples on their molecular weight $\bar{M}_w$: (●) in water; (▲) in 0.2 M aqueous NaCl; (○) in 1.0 M aqueous NaCl.

Our experimental values of intrinsic viscosity and Huggins' constant k_H are collected in Table III together with values of $\bar{M}_w$, which were averaged from Table II. For a given sample of polyacrylamide the intrinsic viscosity increases with the concentration of sodium chloride. The increase is about 10% for 0.2 M solution and another 10% for 1.0 M solutions, well above the experimental error in most cases. This result contrasts with the report by Eliassaf and Silberberg[11] that the intrinsic viscosity is not influenced by the concentration of either NaCl, LiCl, or urea. Equations 5 and 6 of Klein and Conrad[9] imply that in our region of molecular weights there is a slight decrease of intrinsic viscosity in 0.5 M NaCl. Our observation that intrinsic viscosity increases with increasing ionic strength implies that the polyelectrolyte effect in our solutions (i.e., the hydrolysis of amide bonds in our samples) is negligible. At any rate, sodium chloride seems to increase the solvent power of water for polyacrylamide. This effect may be caused by some rearrangements in the hydrogen bonds within the solution (the hydrogen bonds are responsible for the solubility of polyacrylamide in water) or it may be a result of the generally observed enhancement of solvent power in mixed solvents.[14] At this moment, we have insufficient information and we prefer not to advance any hypothesis.

In Figure 1 we have plotted the intrinsic viscosity of our samples vs. molecular weight in a logarithmic scale. In the region of the highest molecular weight, the curves seem to be bending down. This may be caused either by the experimental error in the measurement of molecular weight and/or viscosity or, more probably, by not taking into account the non-Newtonian behavior of the solutions. The non-Newtonian behavior should be prominent for sample W24392; the required value at zero-velocity gradient would be probably higher than the value obtained in a standard Ubbelohde viscometer. For molecular weights less than about 3×10^6 the plots in Figure 1 are linear; we obtained from them the relations

$$[\eta] = 3.09 \times 10^{-2}\bar{M}_w^{0.67} \quad (12)$$

for polyacrylamide in water,

$$[\eta] = 3.02 \times 10^{-2}\bar{M}_w^{0.68} \quad (13)$$

for polyacrylamide in 0.2 M aqueous NaCl, and

$$[\eta] = 2.88 \times 10^{-2}\bar{M}_w^{0.69} \quad (14)$$

for polyacrylamide in 1.0 M aqueous NaCl.

In Figure 2 we have plotted our values of $\bar{M}_w$ and $[\eta]$ for polyacrylamide in water together with the relationships found in the literature (eq 1–5 and 8). The lines in Figure 2 are drawn taking into account the range of molecular weights reported in the literature (except for line 4 for which this information is missing). There seems to be good agreement between our data and the relation of American Cyanamid Co.,[4] eq 2. However, this relation refers to 1.0 M aqueous $NaNO_3$. Our data for 1.0 M aqueous NaCl give values of $[\eta]$ about 20% higher. The relation of Korotkina et al.[7] for 10% aqueous NaCl, eq 3, gives an almost perfect

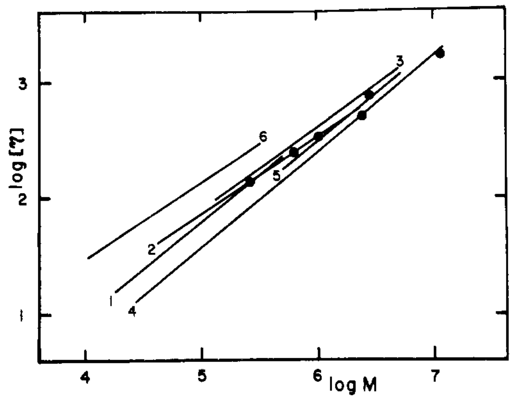

Figure 2. Dependence of the intrinsic viscosity of polyacrylamide on its molecular weight: (1) relation of Scholtan,[3] eq 1; (2) American Cyanamid Co.,[4] eq 2; (3) Korotkina et al.,[7] eq 3; (4) Myagchenkov et al.,[8] eq 4; (5) Klein and Conrad,[9] eq 5 (the line for eq 6 is indistinguishable on the plot of this scale); (6) Collinson et al.,[10] eq 8. Points represent our experimental values in water.

fit with our data in 1.0 M aqueous NaCl. Of course, Korotkina et al.[7] constructed their relation by using the number-average molecular weights $\bar{M}_n$ obtained from the asymptotic tangent to the light-scattering envelope. We feel that this could have been a misinterpretation. If their solutions contained a small amout of microgel, the initial tangent to the envelope (their $\bar{M}_w$ value) would represent the microgels. The tangent at higher angles is then the contribution of the single molecules and should be interpreted as $\bar{M}_w$, not as $\bar{M}_n$. This would also explain why Korotkina et al.[7] obtained the implausibly high value of $\bar{M}_w/\bar{M}_n$ = 3–15 for fractionated polymers.

The relation of Collinson et al.,[10] eq 8, is reported for the number-average molecular weight obtained from the polymerization kinetics; it has almost the same slope as our relation, eq 12. The fit would be almost perfect if we assume that the polydispersity ratio for their samples had the very reasonable value $\bar{M}_w/\bar{M}_n = 2.8$.

The relations of Scholtan,[3] eq 1, and of Klein and Conrad,[9] eq 5, which both have the rather high Mark–Houwink–Sakurada exponent 0.80, while differing from each other by 30%, still give a reasonable fit to our data in the region of molecular weights covered by the respective relations. Finally, the relation of Myagchenkov et al.,[8] eq 4, is quite different from all the other relations. As we were not able to obtain and study the original paper, we do not know the reason for this discrepancy.

In summary, we believe that our measurements are in reasonable agreement with the older measurements; the value of the Mark–Houwink–Sakurada exponent is in the region 0.66–0.70 for various concentrations of salt.

Conclusions

The good agreement between our dependence of the intrinsic viscosity on the molecular weight and the critically reviewed older data serves as a proof that our method of evaluation of the sedimentation equilibria is reasonably reliable. Our data together with the older ones yield the Mark–Houwink–Sakurada exponent in the region 0.66–0.70 for all aqueous mixtures. Relations 12–14 perform well up to a molecular weight of at least 3×10^6. For higher molecular weights the extrapolation to vanishing shear stress would be advisable when measuring the intrinsic viscosity.

The reproducibility of our measured values of both molecular weight and intrinsic viscosity was about 10% deteriorating to about 25% for the very high molecular weights. The water content of the "dry" polymer should be taken into account when evaluating intrinsic viscosity, specific volume, refractive increment, etc.

The intrinsic viscosity of polyacrylamide samples increases with the concentration of sodium chloride. The increase is moderate but beyond the experimental error.

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