

The Molecular Weight of a Sodium Lignosulfonate in Dimethylsulfoxide and in Aqueous 0.1M Sodium Chlorine

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Synopsis

Values of the weight-average molecular weight for a high molecular weight lignosulfonate were found to be nearly equal in aqueous sodium chloride and in DMSO. Prolonged storage in DMSO produced no perceptible change in molecular weight. The results indicated that the lignosulfonate macromolecule was a truly covalent species and was not an aggregate comprised of many low molecular weight units held together by association forces.

INTRODUCTION

Several authors have reported that lignins undergo molecular association when dissolved in certain solvents. From conductometric evidence, Gardon and Mason¹ suggested that the low molecular weight lignosulfonates associate in aqueous solution to give micellar-like aggregates. Gross et al.² found that the number-average molecular weight M_n for various organosol lignins measured in dioxane or tetrahydropyran was higher by a factor of between 2 and 4 than molecular weights obtained using ethylene carbonate as a solvent. Brown³ noted similar effects when the molecular weight of a kraft lignin was measured by vapor pressure osmometry in dimethylsulfoxide (DMSO) and dioxane; M_n increased by a factor of two in the latter solvent. From an infrared study, Lindberg⁴ has suggested that thiolignins in dioxane solution form aggregates held together by hydrogen bonds. Marton and Marton⁵ have developed a calibration procedure using lignin model compounds to compensate for association in the determination of the molecular weight of lignins by vapor pressure osmometry. Most of the association effects reported thus far for lignin solutions have two common characteristics. Firstly, organosolv lignins of comparatively low molecular weight (≈ 1000) have been involved. Secondly, the increase of molecular weight on association is not very great, usually only twofold.

Some fractions of lignin, particularly lignosulfonates in aqueous solution, are found to have rather high molecular weight ($\approx 100,000$). An interesting question is whether or not these large molecules are truly covalent

species or, instead, are aggregates of much smaller molecules held together by hydrogen bonds or hydrophobic interactions. Recent experiments reported by Benko⁶ have a direct bearing on this question. Benko measured, by a diffusion technique, the relative molecular weights of kraft lignins and lignosulfonates. In some cases he found very large differences in the molecular weights measured in aqueous and organic solvents. For example, a polymerized hardwood lignosulfonate gave an apparent molecular weight of 50,000 in 0.1*N* aqueous KCl which decreased to about 2000 when measured in DMSO. Clearly, this effect seems to be an order of magnitude greater than the type of association reported by other workers and, if found to be of general occurrence, will have important implications for both lignin utilization and chemical pulping.

Accordingly, it was decided to measure M_w for a high molecular weight lignosulfonate in an aqueous and an organic solvent. The sedimentation equilibrium technique was used. The solvents were 0.1*M* aqueous NaCl and DMSO. The latter was chosen expressly because both Benko⁶ and Brown³ obtained low molecular weights for their lignins dissolved in DMSO.

EXPERIMENTAL RESULTS

The sodium lignosulfonate used was sample RAS-II, prepared in 1964 for a study of lignin gelling reactions.⁷

DMSO was "Baker Analyzed Reagent," quoted as having a density of 1.095 and a water content of 0.027%.

The weight-average molecular weight M_w was determined by the short column sedimentation equilibrium technique in a Spinco Model E analytical ultracentrifuge.⁸ Measurements were made at several solute concentrations and rotor speeds and M_w was obtained by extrapolation to zero field and concentration as described previously.⁹ Examples of the extrapolation procedures for lignin sample RAS-II in DMSO are given in Figure 1.

The refractive index increment, dn/dc , was measured with a Zeiss diffusion interferometer¹⁰ and the partial specific volume \bar{v} was determined in Lipkin pycnometers.¹⁰ Great care was taken to avoid water uptake by the

TABLE I
Values of dn/dc , \bar{v} , and M_w for Sodium Lignosulfonate
(Sample RAS-II) in Various Solvents

Solvent	dn/dc , ml g ⁻¹	\bar{v} , ml g ⁻¹	M_w
0.1 <i>M</i> NaCl (1964 data)	0.197 ^a	0.61 ^a	60000
0.1 <i>M</i> NaCl (present data)	0.200	0.61 ^a	52000
DMSO	0.117	0.59	43000

^a Not measured on RAS-II, but a mean derived from measurements on several similar samples.

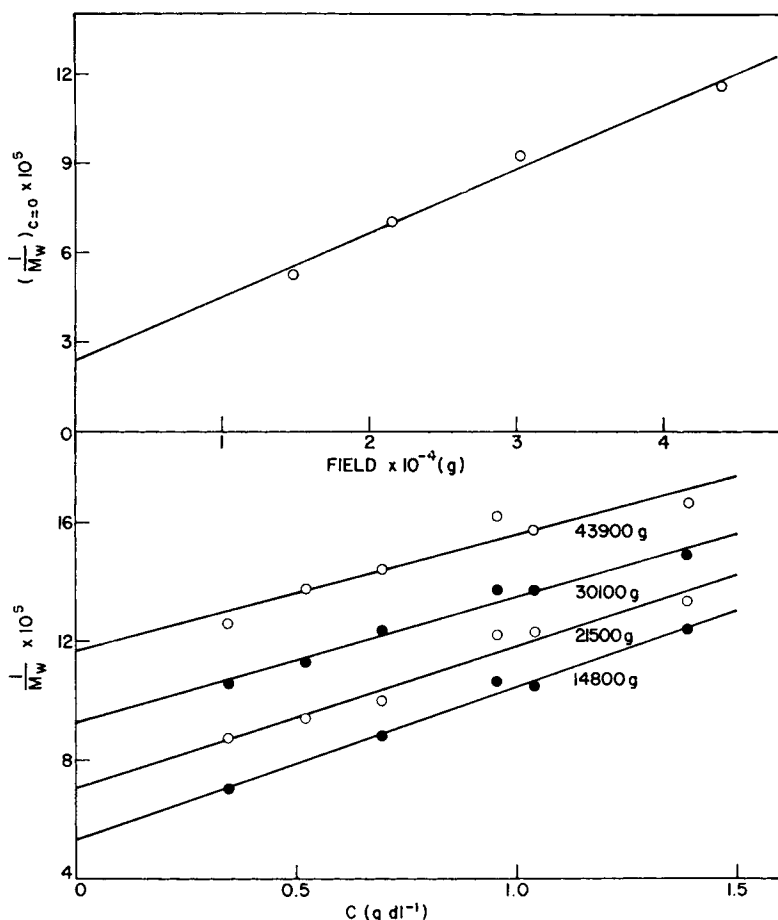


Fig. 1. $1/M_w$ vs. C (lower graph) and $(1/M_w)_{c=0}$ vs. field (upper graph) for sodium lignosulfonate dissolved in dimethyl sulphoxide.

DMSO during these measurements. With DMSO, it was found that the only way to obtain reproducible values of dn/dc was to effect solution or storage in sealed glass tubes.^{11,12}

The results for dn/dc , \bar{v} , and M_w are given in Table I. The original measurement of the molecular weight of RAS-II is included⁷ to be compared with the more recent determination after four years of dry storage at 3°C.

TABLE II
Methoxyl and Sulfur Contents of Sodium Lignosulfonate
Before and After Solution in DMSO

Sample	Methoxyl, %	Sulfur, %
Original	12.41	5.55
Recovered from DMSO	12.34	5.67

The effect of storage was also tested on the molecular weight of lignosulfonate dissolved in DMSO. Several portions of a 1% solution of RAS-II in DMSO were sealed in glass tubes and stored at room temperature for times up to 42 days. Molecular weights measured at the single rotor speed of 20,410 rpm are shown in Figure 2. It is quite apparent that M_w is independent of the time of storage of the solution.

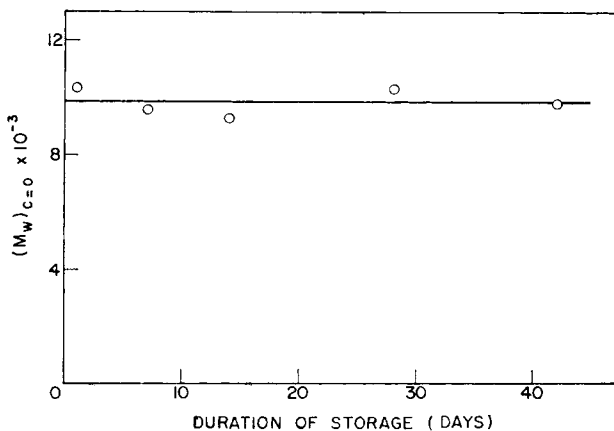


Fig. 2. Variation of $(M_w)_{c=0}$ with time of storage for sodium lignosulfonate dissolved in DMSO. $(M_w)_{c=0}$ was measured at a constant field of 30,100 g.

The lignosulfonate dissolved in DMSO was recovered by precipitation with ethyl acetate which was removed by washing with petroleum ether. No significant changes were noted when the infrared spectrum of the recovered sample was compared with that of the original. Similarly, the original methoxyl content of 12.4% and the sulfur content of 5.6% were virtually unchanged by solution and recovery in the organic solvent (Table II).

DISCUSSION

Perhaps the first consideration is the validity of the experimental approach. After four years of storage, the weight-average molecular weight measured in 0.1M aqueous NaCl had decreased about 13%. Such a difference is within the experimental error of the short column method, as used in the present work. In addition, the internal consistency of the data for each solvent was fairly high. The standard error of deviation of $1/M_w$ in the plots of $1/M_w$ versus c was 0.3×10^{-5} which fell to 0.2×10^{-5} for $1/M_w$ versus field. Further confidence in the experimental framework is provided by the recovery and characterization of the lignosulfonate solute from DMSO. No evidence of marked chemical change was found.

Next we should consider what magnitude of molecular weight change was expected. If the high molecular weight of the lignosulfonate in aqueous

solution is due to the association of many smaller molecules, one might anticipate a manifold decrease in M_w when the lignosulfonate is dissolved in DMSO. The results in Table I show no such decrease. A small reduction in M_w was noted in DMSO, but this was not far outside the possible experimental error. Furthermore, storage in DMSO at room temperature for times of up to 42 days produced no change in molecular weight (Fig. 2). Clearly, our high molecular weight lignosulfonate was not breaking down in DMSO to yield low molecular weight units. In accord with this is the result of a previous experiment⁹ in which an aqueous solution of sodium lignosulfonate was heated in a sealed light-scattering cell to temperatures as high as 120°C. No significant decrease in molecular weight could be detected even though the light-scattering measurements were made at 95°C. Thus neither solvent-induced or heat-induced dissociation of high molecular weight lignosulfonate into smaller fragments is indicated by these experiments.

Further support for the essentially covalent nature of high molecular weight lignins comes from the work of Sokolov and Bogomolov¹³ who used the ultracentrifuge to determine the molecular weight of sulfate and soda lignins in both DMSO and pyridine. Molecular weight ranged from 73,000 to 3,500 and for any one fraction nearly identical values were found in the two solvents. From an investigation of the gel filtration of milled wood lignin, native lignin, and dioxane lignin in DMSO, Ekman and Lindberg¹⁴ have concluded that the fractions obtained are composed of real macromolecular species and not of molecular aggregates held together by association forces.

In the opinion of the present authors, the evidence, on balance, supports the concept of a covalent species for high molecular weight lignosulfonates. The difficulty of interpreting the results of porous-disk diffusion experiments on a polydisperse polyelectrolyte system probably led to the opposite conclusion being drawn in previous work.⁶

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