$$
\begin{aligned}
2^{1/2}B_{50} &= 0\\
2^{1/2}B_{51} &= -\tau_{19}\\
2^{1/2}B_{52} &= 0\\
2^{1/2}B_{53} &= -\tau_{34}\\
2^{1/2}B_{54} &= \tau_{19} + \tau_{34}\\
6^{1/2}B_{60} &= -\tau_{01} + \tau_{02} - \tau_{03}\\
6^{1/2}B_{61} &= \tau_{01} + 3\tau_{19}\\
6^{1/2}B_{62} &= -\tau_{02}\\
6^{1/2}B_{63} &= \tau_{03} - \tau_{34}\\
6^{1/2}B_{64} &= \tau_{34} + 3\tau_{19}\\
B_{ii} &= B_{i,j+5}\ (\text{for } i = \text{a, b, 4 or 5})\\
B_{ij} &= -B_{i,j+5}\ (\text{for } i = \text{c, d, or 6})\\
B_{aj} &= B_{cj}\\
2B_{bj} &= 3^{1/2}B_{dj}
\end{aligned}
$$

and

$$\tau_{kl} = 1/r_{kl}$$

The potential function for the out-of-plane vibrations was chosen to be

$$
\begin{aligned}
2V = {}& H\Omega(\Omega_0 + \Omega_5^2) + H_\theta\,[(\theta_{14} + \theta_{24})^2 + (\theta_{69} + \theta_{79})^2]/4\\
&+ H_1''(\beta_{346}^2 + \beta_{891}^2) + H_2''[(\theta_{39} + \theta_{29})^2 + (\theta_{84} + \theta_{74})^2]/4
\end{aligned}
$$

Here H_Ω and H_θ are the force constants for the out-of-plane skeletal deformation and for the O–H torsion, respectively. The elements of the potential energy matrix expressed in terms of the symmetry coördinates are

$$
\begin{aligned}
F_{aa} &= 3H\Omega/8\\
F_{bb} &= 2H\theta/3\\
F_{44} &= 2H_2''/3\\
F_{55} &= H_1''\\
F_{cc} &= 3H_\Omega/8\\
F_{dd} &= H_\theta/2 + H_1''/6 + H_2''/18\\
F_{d6} &= -H_1''/18^{1/2} + 2^{1/2}H_2''/9\\
F_{66} &= H_1''/3 + 4H_2''/9
\end{aligned}
$$

and all other cross terms are equal to zero.

The approximate calculation of the low frequency vibrations may be made by the use of the **G** and **F** matrices now derived. For the calculation, the **G** matrix elements G_{44}, G_{45}, G_{55} and G_{66} were modified[8,20] so that they were in accord with the rigid monomer model, while the corresponding **F** matrix elements were used without modification. The rigid monomer model is physically equivalent with the assumption of infinite values for the force constants H_Ω and H_θ. The **F** matrix elements for the low frequency vibrations necessarily do not contain these constants.

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BERKELEY, CALIF.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

The Molecular Weight of Insoluble Sodium Metaphosphate[1]

BY ULRICH P. STRAUSS AND JEAN W. DAY

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The molecular weight of an "insoluble" sodium metaphosphate, $NaPO_3$ II, was determined from intrinsic viscosity measurements in aqueous lithium bromide. The necessary intrinsic viscosity–molecular weight relationships were obtained from viscosity measurements of several potassium Kurrol salts whose molecular weights ranged from 220,000 to 1,320,000. The results establish $NaPO_3$ II as a long-chain polyphosphate with a molecular weight of at least 280,000.

While much work has been done on the $NaPO_3$ system[2] there are considerable gaps in our knowledge of these compounds. X-Ray and microscopic studies have established the existence of at least three forms of crystalline $NaPO_3$ which are characterized as insoluble.[3] Two of these forms, $NaPO_3$ II and $NaPO_3$ III, have been denoted as Maddrell salts, and another form, $NaPO_3$ IV, has been called Kurrol salt. The Maddrell salts are believed to be high polymers[2,4]; however, proof of their structure is incomplete and their molecular weights apparently have not been determined.

This paper describes the determination of the molecular weight of $NaPO_3$ II. The problems were to identify the sample,[5] to select a solvent and to determine the molecular weight by means of viscosity measurements.

Results and Discussion

Identification of Sample.—The X-ray diffraction pattern identified the water-insoluble fraction, which constituted 95% of the sample, as $NaPO_3$ II.[6] No attempt was made to identify the water-soluble constituents. Six-tenths of a per cent. of the sample was volatile when it was heated at 600° for 18 hr. The sample was converted to the water-soluble Graham salt by heating at 600°,[7] and the Na/P ratio was determined by titrating the aqueous solution obtained to the first equivalence point[8]; the Na/P ratio was 1.03. The sample contained 9.69 meq. of phosphorus per gram of polymer,[9] calculated on a dry basis. The theoretical value for a sodium metaphosphate of this composition is 9.72. The agreement is within the accuracy attainable with the analytical technique.

Solubility Characteristics.—While the sample was insoluble in water it could be dissolved in aqueous LiBr. The dissolution probably involves an ion-exchange mechanism similar to that encountered with potassium Kurrol salt.[10]

Determination of Molecular Weight.—Several potassium Kurrol salts whose molecular weights ranged from 220,000 to 1,320,000 were used to prepare a calibration curve to estimate the mo-

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(1) The contents of this paper are contained in a thesis to be submitted by Jean W. Day to the Graduate School of Rutgers University in partial fulfillment of the requirements for the degree of Master of Science. This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1) 1018.

(2) B. Topley, *Quart. Revs.* (*London*), **3**, 345 (1949).

(3) E. P. Partridge, *Chem. Eng. News*, **27**, 214 (1949).

(4) E. Thilo, G. Schulz and E. Wichmann, *Z. anorg. allgem. Chem.*, **272**, 182 (1953).

(5) The sample was commercial IMP produced by Monsanto Chemical Co. (G. E. Taylor and A. G. Erdman, U. S. Patent 2,356,799, May 27, 1943).

(6) ASTM 2412, d, 2-0766.

(7) E. P. Partridge, V. Hicks and G. W. Smith, THIS JOURNAL, **63**, 454 (1941).

(8) U. P. Strauss and T. L. Treitler, *ibid.*, **77**, 1473 (1955).

(9) This was determined by potentiometric titration of the hydrolyzed polymer using NaOH as described by J. R. Van Wazer, *et al.*, *ibid.*, **72**, 639, 644, 647, 655, 906 (1950).

(10) R. Pfanstiel and R. K. Iler, *ibid.*, **74**, 6059 (1952).

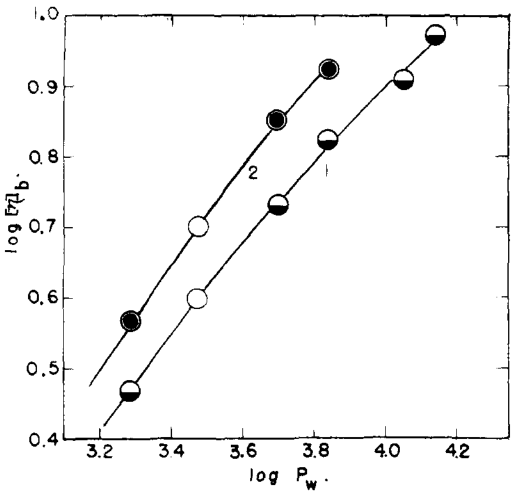

Fig. 1.—Log $[\eta]_b$ *vs.* log P_w for potassium polyphosphates in: (1) 1.35 *N* LiBr; (2) 1.06 *N* LiBr. The open circles mark the values obtained for $NaPO_3$ II.

lecular weight of the $NaPO_3$ sample. Their intrinsic viscosities in 1.35 *N* aqueous LiBr were determined and a double logarithmic plot of P_w the weight average number of PO_3 units per molecule, against $[\eta]_b$[11] was made. The log $[\eta]_b$ of the $NaPO_3$ in 1.35 *N* LiBr was 3.96. Interpolation of the graph in Fig. 1-1 indicates a molecular weight of 290,000.

The molecular weights of the potassium Kurrol salts were determined from specific viscosity–molecular weight relationships obtained with samples of sodium polyphosphate. These samples had been prepared in this Laboratory by ion exchange of potassium Kurrol salts and their molecular weights had been determined by light scattering.[12] Their molecular weights ranged from 11,000 to 1,250,000. Reduced viscosities for 0.1 *N* solutions of the sodium polymers were determined in an aqueous solution, 0.25 *N* in NaBr and 0.1 *N* in KBr, and a double logarithmic plot of P_w *vs.* η_{sp} was made. The specific viscosities of 0.1 *N* solutions of the potassium polyphosphates were determined in an aqueous solution of 0.35 *N* NaBr,[13] and their molecular weights were obtained by interpolation from the graph.

To test whether the $NaPO_3$ II behaved like other long chain polyphosphates in solution, the work was repeated in 1.06 *N* LiBr in which $[\eta]_b$ of $NaPO_3$ II was 5.01. By interpolation of curve 2 in Fig. 1 one obtains a molecular weight of 270.000, in good agreement with that obtained at the higher lithium bromide concentration.

These results indicate that the $NaPO_3$ II consists of very long polyphosphate chains.[14] Since there may be some degradation during the dissolution process, the molecular weight of the chains in the crystal may be even larger than the average value of 280,000 obtained by us.

Experimental Methods

X-Ray Instrumentation.—The Debye–Scherrer pattern was obtained with a North American Phillips camera of 114.6 mm. diameter using Cu Kα radiation and a nickel filter. The sample was placed on a Vaseline-tipped glass fiber and was exposed for 8 hours. The interplanar spacings were determined by the Straumanis self-calibration technique[15]; the spacings were measured with a steel millimeter rule. The intensities were estimated visually, assigning 10 to the most intense line.

Dissolution of Samples.—The concentrations of the aqueous LiBr solutions were determined by potentiometric titration with silver nitrate.

All of the polymers were dissolved in 1.06 and 1.35 *N* aqueous LiBr. The solutions of the potassium Kurrol salts ranged from 0.19 to 1.1 g./100 cc. Solutions of the $NaPO_3$ ranged from 0.46 to 1.0 g./100 cc.

Since the $NaPO_3$ dissolved very slowly and since there was danger of the sample degrading while it was going into solution, a study to determine the optimum dissolution time was undertaken. Relative viscosities of three solutions ranging from 0.46 to 1.0 g./100 cc. were determined after shaking periods ranging from 6 hours to 6 days. NaOH was added to each solution to minimize degradation[16-20]; generally, the *p*H was raised from 5.8 to 7. The samples shaken for 24 hr. gave the highest and most consistent viscosities. The amount of polymer undissolved at this time was always less than 3%.

Viscosity.—Viscosities were measured at 25.00° in two Bingham viscometers[21] operating at driving pressures from 35 to 118 g./cm.^{2}. The viscometer constants for 1.35 *N* LiBr at 200 seconds, $(pt)_{200}$, were 11,552 and 15,487. Relative viscosities determined in the two viscometers were identical.

The viscosities of the potassium Kurrol salts were measured within 6 hr. after the solvent was first introduced. The $NaPO_3$ solutions were measured within 8 hr. of the completion of a 24-hour shaking period. During this interval they were kept in the refrigerator to minimize degradation. The specific viscosity of a typical solution kept in the refrigerator for 10 days decreased only 4%.

Water-soluble Content.—The per cent. water soluble was determined by shaking the $NaPO_3$-sample in water for 19 hr. after its *p*H was raised to minimize degradation. The sample was centrifuged twice in the ultracentrifuge. An aliquot of the supernatant liquid was taken and the amount of phosphate in solution was determined colorimetrically,[22] measuring the intensity of the yellow color formed by treating the hydrolyzed phosphate with vanadomolybdate reagent.

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[11] $[\eta]_b = \lim_{N \to 0} \eta_{sp}/N$, where η_{sp} is the specific viscosity and *N* the normality of the polymer. It has been shown in this Laboratory by P. L. Wineman that $[\eta]_b$ of a polyphosphate in an aqueous solution containing a swamping electrolyte is independent of the cation of the polyelectrolyte.

[12] U. P. Strauss and P. L. Wineman, THIS JOURNAL, **80**, 2366 (1958).

[13] This work was done by R. Hubbard in this Laboratory.

[14] While the possibility of a few branch-points is not ruled out, the Na/P ratio of 1.03 makes their presence extremely unlikely.[8,10]

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[21] E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922.

[22] Method of C. J. Barton, *Anal. Chem.*, **20**, 1068 (1948), as modified by J. Beukenkamp, W. Rieman, III, and S. Lindenbaum, *ibid.*, **26**, 505 (1954). We used the Lumetron 402E made by Photovolt with a filter whose maximum transmission is at 390 millimicrons.