NOTES

Velocity Ultracentrifugation and Diffusion of Silicotungstic Acid

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One of the most important techniques for investigating the molecular weights of large molecules in solution is the velocity ultracentrifuge method. In usual practice, this method requires the independent determination of the sedimentation and diffusion coefficients s_0 and D_0, extrapolated to infinite dilution, of a solute in a given solution, and the application of the familar Svedberg equation: $M = RTs_0/D_0(1 - \bar{V}\rho)$.[1] Despite long usage, this technique has not been subjected to critical and accurate tests, particularly for solutes whose molecular dimensions approach those of the solvent. This is primarily due to a scarcity of solutes which fulfill all the requirements for such a test. Some of the saturated inorganic heteropoly acids would seem to be eminently suitable: (a) they are small molecules, with molecular weights in the range 1000–3000; (b) since they are very dense, they have relatively large and accurately determinable sedimentation coefficients[2]; and (c) they are well-defined pure compounds whose molecular weights are accurately known and whose crystalline structures have been determined.[3,4] We have investigated the sedimentation and diffusion behavior of silico-12-tungstic acid, $H_4SiW_{12}O_{40}{\cdot}xH_2O$, and have obtained the correct molecular weight from the Svedberg equation, within the experimental errors.

Materials and Methods.—C.P. silicotungstic acid was obtained in hydrated form from Fischer. It was stored over anhydrous $CaCl_2$ to constant weight, and was then analyzed for its residual water of hydration as follows. A solution of the dried acid was precipitated with cinchonine,[5] the precipitate heated to 400° and weighed as $WO_3 + SiO_2$. The water of hydration remaining in the dried sample was calculated from this data, and the dried acid was thus shown to have the average composition $H_4SiW_{12}O_{40}{\cdot}14H_2O$.

Ultracentrifuge and diffusion experiments, and partial specific volume determinations were all carried out in a sodium acetate–acetic acid buffer, *p*H 4.58, ionic strength 0.2. In this buffer silicotungstic acid exists as the $SiW_{12}O_{40}^{-4}$ ion (see below), and the ionic strength of the buffer is large enough to make negligible any electric potentials which might be produced during sedimentation and diffusion of the anion.

Ultracentrifuge experiments were performed near 25° in a Spinco Model E instrument, in conjunction with the synthetic boundary cell.[6] s was determined from a plot of log x against time, x being the distance of the mean ordinate of the sedimenting boundary from the axis of rotation. The usual viscosity and density corrections to water at 25° were made,[1] taking the temperature of the rotor to be 0.8° lower than the average of the temperatures before and after a run,[7] due to the adiabatic expansion of the rotor upon acceleration. The estimated precision measure of the extrapolated sedimentation coefficient is ±3%.

Differential diffusion coefficients were determined using the Gouy interferometric technique. This method has been completely described[8,9] and slight variations in technique used in this Laboratory have been reported.[10] The diffusion data for this system were quite precise with the drift in C_t over 85% of the gradient curve being less than 0.2%. This indicates that the diffusing species was homogeneous. The diffusion coefficients were computed from the lower fringe position measurements and have an estimated precision of better than ±0.2%. The usual viscosity correction[1] to water at 25.0° was applied.

Density measurements on solutions of $H_4SiW_{12}O_{40}{\cdot}14H_2O$ in the acetate buffer were carried out at 25° in calibrated 20-ml. pycnometers. $\bar{V}$ of the anhydrous acid is 0.140_9 cc./g. It was calculated,[1] knowing the residual water of hydration in the dried acid. Although $\bar{V}$ is thus given for the neutral acid, whereas only the silicotungstate ion is the kinetic unit in solution, no significant ambiguity exists since only the difference of four ionizable H atoms is involved. It is estimated that the term $(1 - \bar{V}\rho)$ is known with a precision of better than ±0.3%.

Experimental Results

The results of 13 independent sedimentation experiments with concentrations, c, of from 1 to 9 weight per cent. $H_4SiW_{12}O_{40}{\cdot}14H_2O$ in acetate buffer, *p*H 4.58, ionic strength 0.2, are given in Table I. The least-squares straight line through these data satisfies the relation: $s_{25}^{W} = (4.56 - 0.16c)$ svedbergs.

Table I

Sedimentation Data for Silicotungstic Acid

Wt. % acid	s_{25}^{W} (svedbergs)	Wt. % acid	s_{25}^{W} (svedbergs)
0	4.56^{a}	3.622	4.0_3
1.150	4.3_8	3.622	4.0_7
1.150	4.4_8	5.407	3.5_8
2.046	4.1_8	5.407	3.7_4
2.046	4.3_6	7.048	3.2_9
2.430	4.0_6	7.048	3.3_0
2.430	4.1_3	9.149	3.0_9

[a] Extrapolated.

In order to determine that charge effects were negligible in this buffer, two sedimentation experiments were performed in acetate buffers of the same *p*H but different ionic strengths. At ionic strength 0.30, c = 4.72 wt. %, $s_{25}^{W} = 3.86$ *S*; at ionic strength 0.10, c = 4.58 wt. %, $s_{25}^{W} = 3.64$ *S*. From the least-squares relation above, the values at ionic strength 0.2 are $s_{25}^{W} = 3.80$ and 3.83 *S*, respectively. Therefore, within experimental errors, no significant effect of ionic strength under these conditions is observed.

The results of four independent diffusion experiments at average concentrations from 1 to 6 weight

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[1] T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Oxford Univ. Press, London, 1940.

[2] S. J. Singer and J. L. T. Waugh, *Proc. Nat. Acad. Sci.*, **38**, 1027 (1952).

[3] J. F. Keggin, *Proc. Roy. Soc.* (*London*), **144A**, 75 (1934).

[4] R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934).

[5] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Second Ed., The Macmillan Co., New York, N. Y., 1948, p. 729.

[6] E. G. Pickels, W. F. Harrington and H. K. Schachman, *Proc. Nat. Acad. Sci.*, **38**, 943 (1952).

[7] (a) D. F. Waugh and D. A. Yphantis, *Rev. Sci. Instr.*, **23**, 609 (1952); (b) A. Biancheria and G. Kegeles, This Journal, **76**, 3737 (1954).

[8] L. G. Longsworth, *ibid.*, **69**, 2510 (1947).

[9] G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

[10] P. A. Lyons and C. L. Sandquist, *ibid.*, **75**, 3896 (1953).

per cent. are listed in Table II. The relationship $D_{25}^{W} = (4.515 + 0.134c) \times 10^{-6}$ cm.²/sec. fits the data.

TABLE II

DIFFUSION DATA FOR SILICOTUNGSTIC ACID

Wt. % acid	0	0.964	1.957	4.695	6.192
$D_{25}^{W} \times 10^6$, cm.²/sec.	4.515[a]	4.635	4.769	5.140	5.307

[a] Extrapolated.

It remains to prove the stability of the $SiW_{12}O_{40}^{-4}$ anion in these solutions. Silico-12-tungstic acid is stable at *p*H values more acid than 6, according to the titration data of Malaprade[11], which we have essentially confirmed. Furthermore, we have measured the *p*H of several solutions of the acid in the acetate buffer used in these experiments. If the change of the *p*H of the solution from that of the buffer is attributed to the effect of the liberation of H ions from the silicotungstic acid upon the acetate–acetic acid equilibrium, a simple calculation gives the number, *n*, of such H ions per molecule of the silicotungstic acid. This number is close to 4, as is seen in Table III, in agreement with the above formulation of the anion.

TABLE III

Wt. % $H_4SiW_{12}O_{40}$	*p*H of buffered soln.	*n*[a]
0	4.58	..
1.966	4.49	4
3.122	4.40	4
5.154	4.33	4
8.116	4.28	3

[a] Number of protons ionized per molecule of silicotungstic acid, see text.

We have also performed sedimentation and diffusion experiments with phospho-12-tungstic and phospho-12-molybdic acids in the same acetate buffer.[12] With these acids, however, *p*H measurements on the solutions confirm earlier titration studies[11] in indicating that the acids are decomposed at *p*H 4.58. Ultracentrifuge experiments in solutions sufficiently acid to ensure the stability of the $PW_{12}O_{40}^{-3}$ and $PMo_{12}O_{40}^{-3}$ ions have been impractical because of reaction of the metal in the ultracentrifuge synthetic boundary cells. The experiments with these unstable acids at *p*H 4.58, while not of use for the purposes of this paper, are of interest, however, in connection with the chemistry of these compounds, but this will not be discussed here.

From the constants characterizing the silico-12-tungstic acid, we may calculate the molecular weight of the anhydrous anion $SiW_{12}O_{40}^{-4}$ from the Svedberg equation. The parameter s_0 is the least precise quantity in the equation, and the calculated molecular weight is estimated to have a precision measure of ±3%. The calculated value is 2.91×10^3, and the agreement with the formula weight 2875.1 is excellent. Should it become possible to determine *s* with a precision comparable to that of *D* and $(1 - \bar{V}\rho)$, a still more sensitive test of the Svedberg equation would be possible.

From the friction coefficient per mole, $f = (1 - \bar{V}\rho)/s_0$, and the friction coefficient of the equivalent sphere, $f_0 = 6\pi\eta N(3M\bar{V}/4\pi N)^{1/3}$, where η is the solvent viscosity and N is Avogadro's number, we find that the friction ratio[1] $f/f_0 = 1.0$. Such a value indicates that the solute molecule is indeed effectively spherical and unhydrated in solution. The effective hydrodynamic diameter, *d*, calculated from the relation $d = 2(3M\bar{V}/4\pi N)^{1/3}$, is about 11 Å. On the other hand, X-ray studies of crystalline silico-12-tungstic acid[4] show that the molecule conforms to a cuboöctahedron, which may be considered effectively spherical. The unit cell dimension of the pentahydrate of the acid is 12.1 Å., which is consistent with the hydrodynamic diameter obtained above.

With these results, the Svedberg equation has been subjected to the most critical experimental test as yet applied, so far as we are aware. These results, together with the derivation of the Svedberg equation from irreversible thermodynamics,[13] should help to confirm its general validity in the determination of molecular weights in solution.

Silicotungstic acid, and related substances, may also be of use in calibrating other methods of molecular weight determination, such as light scattering, and as model substances for investigating various problems of molecular hydrodynamic behavior.

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[11] L. Malaprade, *Ann. Chim.*, [10] **11**, 159, 172 (1929).

[12] Unpublished experiments.

[13] G. J. Hooyman, H. Holtan, P. Mazur and S. R. deGroot, *Physica*, **19**, 1095 (1953).

On the Dielectric Constant of Liquid Hydrogen Cyanide

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The dielectric constant of hydrogen cyanide is noteworthy in that it varies from 206 at −13.3° (m.p.) to 106 at 25.7° (b.p.). Pauling[1] has pointed out that the value at room temperature is about three times larger than expected empirically for a normal liquid with the same molecular dipole moment; for a model of straight chain polymers the factor three is the average degree of polymerization. Coates and Coates[2] in reporting their dielectric constant results further remark that the rapid decrease with temperature indicates a decreasing degree of polymerization at higher temperatures. It is the purpose of this note to present a more quantitative discussion on the basis of the linear chain model and the dielectric constant theory of Kirkwood.[3]

We assume the series of equilibria $(HCN)_n$ +

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[1] L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1939, p. 275.

[2] G. E. Coates and J. E. Coates, *J. Chem. Soc.*, 77 (1944).

[3] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).