transferred by means of an engraving pantograph onto the bottom of a small cylindrical aluminum cup (Fig. 3); the cup was inserted in a hole bored through the rotor parallel to the axis of rotation, 2.170 inches from the axis and displaced 90° from the analytical cell hole. The hole was counterbored from the top to leave a supporting shoulder of metal in such a position that the exponential aperture would be at the median plane. The cup was pressed down to the shoulder where it is held in alignment by friction. A similar but blind hole was bored in the symmetric position to maintain proper mass distribution. This assembly has been successfully operated at angular speeds up to 56,100 r.p.m.

We wish to thank Mr. G. Harris and Mr. Wm. Scheulke of the Chemistry Division's workshop for their contributions to the solution of problems encountered in the design and construction of the aperture assemblies.

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PASADENA, CALIFORNIA

[CONTRIBUTION FROM CLARKSON COLLEGE OF TECHNOLOGY]

Influence of Electrolytes on the Light Scattering of Inorganic Compounds. Light Scattering of Phosphotungstic Acids[1]

BY E. MATIJEVIĆ[2] AND M. KERKER

RECEIVED OCTOBER 4, 1958

A light scattering investigation of 9-phosphotungstic acid and 12-phosphotungstic acid in aqueous solution and in the presence of various concentrations of added electrolyte was carried out. The apparent molecular weight in aqueous solution was lower than the formula molecular weight, but it increased with increasing salt concentrations and eventually reached values higher than the formula molecular weight.

The study of solutions of electrolytes by light scattering is beset by numerous difficulties. On the one hand, simple electrolytes, which are amenable to theoretical treatment at moderate concentrations, have low ionic weights and therefore do not scatter light sufficiently intense for quantitative work. On the other hand, there is no satisfactory theoretical treatment for high ionic weight electrolytes such as proteins, micelles and polyelectrolytes, and even an adequate physical model for these is frequently lacking. Intermediate between these two classes of electrolytes are the isopoly and heteropoly compounds and other polynuclear inorganic complexes. They are strong electrolytes of moderately high molecular weight whose kinetic units are fully defined and they can be studied by light scattering.[3-5]

In this paper we will present light scattering data for 9-phosphotungstic acid, $H_6P_2W_{18}O_{62}$, (9-PTA), and 12-phosphotungstic acid, $H_7PW_{12}O_{42}$, (12-PTA), in aqueous solution and in the presence of added electrolyte. Earlier work has established the above molecular formulas and demonstrated that these substances are practically completely ionized in dilute solutions.[3,6,7]

Experimental

Materials. 1. **12-Phosphotungstic Acid.**—The reagent grade acid available from J. T. Baker Company was purified by the following procedure. One hundred g. was dissolved in 75 ml. of water and transferred to a separatory funnel. A few drops of concd. HNO_3 were added and the phosphotungstic acid was extracted with ether. The acid-ether complex (the lowest of the three layers) was separated, washed several times with 2 *N* HCl, then with water and again extracted with ether. The ether was finally evaporated *in vacuo* with mild heating on a water-bath, the crystals dried *in vacuo* and ground. The moisture was determined by drying to constant weight at 200°.

2. **9-Phosphotungstic Acid.**—This was prepared as described by Wu[8] and modified by Souchay[9] and Kerker, *et al.*[3] First the ammonium salt was obtained and purified by several precipitations with ammonium chloride and then the free acid was prepared by dissolving the salt in HCl (1:1) and extracting with ether. Several subsequent extractions were performed to secure a pure and salt-free 9-phosphotungstic acid. The ether complex was freed from ether by evaporation and drying *in vacuo*.

Both phosphotungstic acids gave clear solutions even when dissolved in very high concentrations. On the other hand, solutions of the unpurified commercial 12-PTA were quite turbid and could only be clarified by filtration with considerable difficulty.

3. Nitric acid and potassium chloride were of the highest purity grade commercial chemicals. The latter was recrystallized before use. Water was distilled twice, the second time from an all-Pyrex still. All glassware was thoroughly cleaned and steamed before use.

Experimental Technique.—The solutions of phosphotungstic acid used for measurements were obtained either by direct weighing of the solid substance or by dilution of a stock solution of high concentration with water or with a solution containing added electrolyte (KCl, HNO_3) of the same concentration as the stock solution.

In order to obtain optically clear, dust-free solutions, they were filtered through an ultrafine glass filter (Pyrex UF) under pressure of nitrogen. Firstly an aliquot of the solution was filtered several times and discarded, and then the main portion of the solution was filtered through the same filter directly into the light scattering cell. In a number of cases the filtrate was quantitatively analyzed and no loss during the filtration could be found. When solutions were prepared by dilution, the filtration was not always necessary as the filtered stock solution was diluted carefully with the filtered solvent and no contamination by dust or lint permitted during the operation of dilution.

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[1] Supported by U. S. Atomic Energy Commission Contract No. AT (30-1)-1801.

[2] On leave of absence from the Faculty of Science, University, Zagreb, Yugoslavia.

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TABLE I

12-Phosphotungstic acid (12-PTA)				9-Phosphotungstic acid (9-PTA)			
Solvent	n_0	dn/dc	$H \times 10^6$	Solvent	n_0	dn/dc	$H \times 10^6$
H_2O	1.33986	0.1040	2.951	H_2O	1.33986	0.1195	3.896
0.01 N HNO_3	1.33994	.1040	2.951	0.05 N KCl	1.34021	.1195	3.898
.05 N HNO_3	1.34029	.1046	2.987	.10 N KCl	1.34074	.1195	3.906
.10 N HNO_3	1.34070	.1050	3.011	.50 N KCl	1.34485	.1195	3.925
.30 N HNO_3	1.34237	1055	3.048	10 N HNO_3	1.34052	1195	3.899

The readings were taken with an Aminco light scattering microphotometer at wave length λ 436 mμ and angle $\theta = 90°$. The instrument was calibrated with the purest redistilled toluene and benzene for which the absolute turbidities were taken from the literature.[10] The photometer scale was standardized before each reading with a toluene solution sealed in a light scattering cell. Toluene is convenient as a standard for it scatters approximately as strongly as the most concentrated solutions of phosphotungstic acid used in these experiments.

For the measurements, a 24 × 24 mm. rectangular cell was used which was thoroughly cleaned, steamed in acetone or ethanol and dried before use.

The refractive index data were obtained with a Brice-Phoenix differential refractometer which was calibrated using sucrose solutions of different concentrations. The instrument was thermostated at 25°.

Light scattering data obtained with solutions of 9-PTA had to be corrected for consumptive absorption. This compound is yellow and absorbs somewhat at 436 mμ.

When the effect of time on the scattering values was explored the solutions were kept in the same cell covered with a glass cover in an atmosphere saturated with the vapor of a solution of identical composition.

Results

One important question had to be answered before undertaking these experiments and that was the problem of stability of the phosphotungstic acid solutions. Souchay[11] has claimed that 12-PTA is unstable in neutral solution and decomposes if not strongly acidified with mineral acids. Furthermore, earlier work indicated that the light scattering of the 12-PTA solutions increases with time.[3] However, our recent coagulation experiments with heteropoly compounds have revealed that the stability of the solutions of heteropoly compounds depends on their purity.[6] Very carefully purified materials remained stable in acid and in neutral solutions and gave reproducible results even though the same solutions were used over a long period of time. For this reason the purification of heteropoly compounds seemed to be the pertinent step in obtaining stable solutions.

Light scattering values of solutions prepared from purified materials as described above were time independent. In several cases the scattering of some solutions was followed through long periods of time (up to 4 days) and no change could be noticed. These results show again that the stability of heteropoly compounds in solutions depends definitely on the purity of the materials. The change in scattering with time, as observed before with unpurified materials,[3] is probably due to the slow coagulation of colloidal contaminations by the heteropoly ions since we have already shown that these are extremely powerful coagulators.

Figure 1 represents excess turbidities (τ) of solutions of 12-PTA in water and in 0.01, 0.05, 0.10, 0.30 N nitric acid. Nitric acid was employed since potassium chloride, usually used in such experiments, gives an insoluble salt with 12-PTA. For comparison, the data obtained previously by Kerker, *et al.*,[3] for aqueous solutions of 12-PTA are given in the same diagram and denoted with squares.

Figure 2 represents the turbidities of solutions of 9-PTA in water, 0.05, 0.10 and 0.50 N KCl. In this case the potassium chloride could be used since the potassium salt of the 9-PTA is very soluble. The scattering of both, the 12-PTA and 9-PTA, shows a great dependence on the addition of simple electrolytes throughout the whole concentration region of the scattering compound.

In order to establish whether the nitric acid exerts only an electrolyte effect upon the light scattering of 12-PTA or also shows some common ion effect we have compared the turbidities of 9-PTA in equal concentrations of KCl and HNO_3 (0.10 N) in Fig. 3. In the low concentration region of 9-PTA (up to 0.03 g./ml.), both turbidities obtained upon addition of HNO_3 and KCl are exactly the same, giving the same molecular weight. Although in the higher concentration region the solutions with HNO_3 are somewhat less turbid, it appears that the influence of the HNO_3 is primarily an electrolyte rather than a common ion effect.

For these data the apparent molecular weight has been obtained in the usual way by plotting Hc/τ against the concentration c. H is a constant for a certain system and is given by the expression

$$H = \frac{32\pi^3 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2}{3\lambda^4 N} \qquad (1)$$

where n_0 is the refractive index of the solvent, dn/dc the change of the refractive index of the solution with concentration, λ the wave length employed and N Avogadro's number. The apparent molecular weight is the reciprocal of the Hc/τ value at intercept $c = 0$. The values for n_0, dn/dc and H used in this work for the calculation of molecular weights are given in Table I.

The apparent molecular weights as calculated from the turbidities in Figs. 1-3 and the values given in Table I are plotted in Fig. 4. The values are strongly dependent upon the added salt concentration, increasing from 1000 to 5200 for 9-PTA and from 1400 to 3800 for 12-PTA. This compares with the formula molecular weights of 4369 and 2916. The values corresponding to the formula molecular weights were obtained experimentally at electrolyte concentrations of 0.05 N HNO_3 for 12-PTA and 0.1 N KCl for 9-PTA.

Although the general trend of the curves in Fig. 4 is similar, it would appear that the detailed variation of the apparent molecular weight with salt concentration would have to be worked out for each compound individually.

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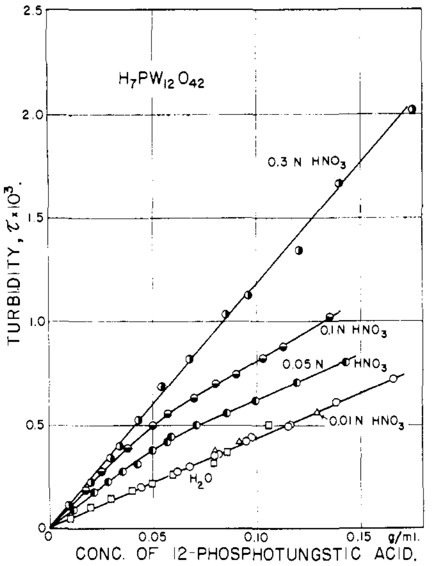

Fig. 1.—Turbidity of 12-PTA in the presence of various HNO_3 concentrations. In the lowest curve squares represent data of Kerker, Lee and Chou[3] in water, circles represent our data in water and triangles our data in 0.01 *N* HNO_3.

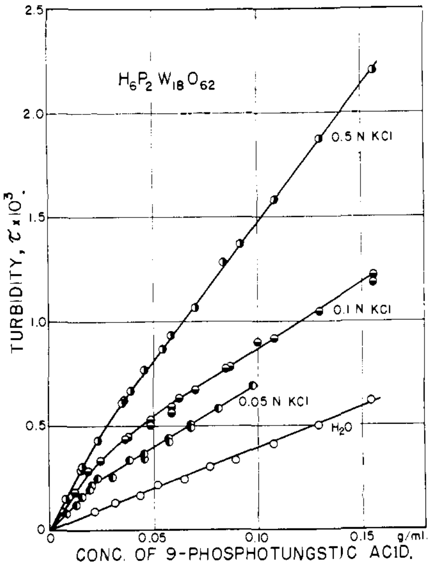

Fig. 2.—Turbidity of 9-PTA in the presence of various KCl concentrations.

Discussion

The light scattering equation for a two component system is given by

$$Hc/\tau = \frac{1}{M_2}(1 + c \, \mathrm{d} \ln \gamma_2/\mathrm{d}c) \qquad (2)$$

where γ_2 is the activity coefficient of the solute. The usual extrapolation of Hc/τ *vs.* c will give an intercept corresponding to the molecular weight only when d ln γ_2/dc is independent of concentration over the range from $c = 0$ to the lowest experimentally determined concentration. If the light scattering data is extended to sufficiently low concentrations, then Hc/τ will always extrapolate to the inverse molecular weight.

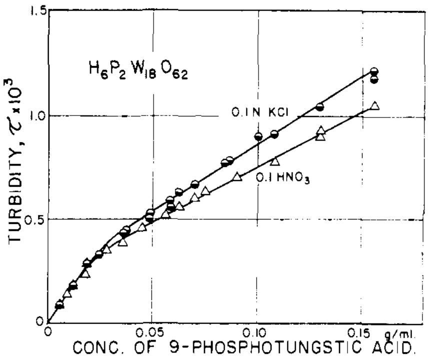

Fig. 3.—Comparison of the turbidity of 9-PTA in presence of 0.1 *N* KCl with that in 0.1 *N* HNO_3.

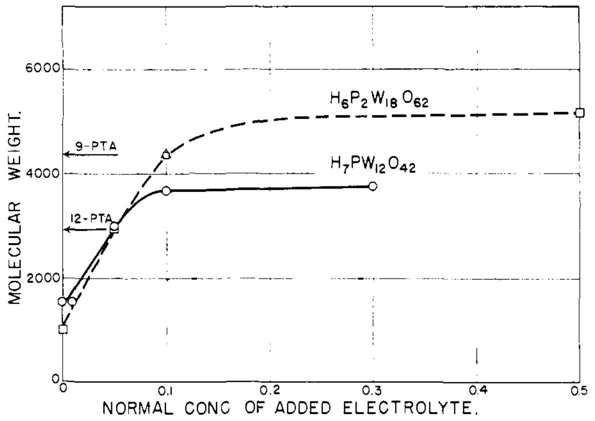

Fig. 4.—Apparent molecular weights of 9-PTA and 12-PTA as a function of added electrolyte concentration.

This was not the case for our salt-free solutions where the apparent molecular weight was much lower than that corresponding to the molecular formulas of the phosphotungstic acids. This means that for the phosphotungstic acids, it is necessary to go to concentrations even lower than 0.01 g./ml. which was our lowest value. However, for such low concentrations, the excess turbidity is so small a fraction of the solvent scattering that it becomes exceedingly difficult to obtain significant data. Kronman and Timasheff have recently obtained data for silicotungstic acid at sufficiently low concentrations to indicate this expected trend.[12]

In the presence of added electrolyte, the scattering is described by multicomponent theory[13-15] which is dependent upon detailed knowledge of the thermodynamic interactions among the various species. Since this thermodynamic data is presently lacking, we can at least qualitatively consider that the effect of the added electrolyte is to influence d ln γ_2/dc in equation 2. As the electrolyte concentration increases, the apparent molecular weight also increases from a value which is lower to one which is higher than the formula weight. This corresponds to d ln γ_2/dc changing from positive to negative values.

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The added electrolyte can also be thought of as influencing the system by "screening" the repulsive electrostatic interactions among the heteropolyanions. This reduces the ordering effect of these interactions which in turn results in greater scattering and correspondingly higher apparent molecular weights. One would then expect, in the limit of "swamping" electrolyte, to obtain the formula molecular weight.

Doty and Steiner[16] have given a quantitative treatment for solutions of macro-ions in the presence of additional electrolyte using this point of view. In their theory, the quantity $(HcM_2/\tau - 1)$ can only take on positive values, corresponding to apparent molecular weights either less than or equal to the formula molecular weight. Our results show that this quantity takes on negative values with high concentrations of added electrolyte, where the apparent molecular weight is greater than the formula molecular weight, showing that this theory cannot represent the behavior of the phosphotungstic acids under these conditions.

For the practical problem of determining the molecular weight of compounds like the phosphotungstic acids, it is not enough merely to add a quantity of *swamping electrolyte.* From Fig. 4, it can be seen that the apparent molecular weight increases with added salt to an upper limit appreciably greater than that corresponding to the molecular formula. Therefore, the light scattering data should be obtained at more than one salt concentration. This will lead to an upper limit for the molecular weight. Since, for heteropoly compounds, the empirical formula weights are usually known, the light scattering measurements in combination with other techniques may serve to establish the molecular species. For example, with 12-PTA the upper limit of 3800 is only consistent with monomeric molecules, since the empirical formula weight is 2916.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Ketene[1]

BY W. B. GUENTHER AND W. D. WALTERS

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The thermal decomposition of ketene has been studied in a static system at 396–563° with most of the work in the region 498–550° at pressures near 100 mm. In addition to carbon monoxide, ethylene and methane reported in the earlier work as major products, carbon dioxide and allene (under some conditions) were found in large amounts. Methane appears to be produced mainly in secondary reactions. The percentages of ketene determined by analysis had no simple relationship to the pressure change. Data from experiments with initial pressures of 44–329 mm. at 520° indicated that the rate of formation of carbon dioxide has a second-order dependence on the initial pressure. Likewise the order of ketene disappearance with respect to the initial pressure at 520 and 550° is almost two. The process for formation of carbon monoxide appears to be complex. Addition of allene and its products increased the rate of carbon monoxide formation.

In view of the importance of ketene in the thermal decompositions of acetone,[2] acetic acid,[3] acetic anhydride,[4] cyclobutanone,[5] methyl acetate[6] and ethyl acetate[6] and its lesser occurrence in other thermal reactions, it seemed important to investigate further the behavior of ketene alone. Since the ketene formed in the pyrolyses of acetone,[2] biacetyl[7] and methyl ethyl ketone[8] has been found to undergo subsequent reactions during the course of the decomposition, additional information concerning ketene would be of interest in the consideration of the products and mechanisms of these other decompositions.

From experiments with ketene in a flow system at 1150° Muller and Peytral[9] reported the following major products: CO, 66%; C_2H_4, 20%; CH_4, 8%. However, in a static system at 540° Williamson[10] found that methane was considerably more important than ethylene. In contrast to the earlier work[9,10] carbon dioxide was observed by Akeroyd[11] to be another major product at 570°. Allene was postulated, but not detected experimentally.[11] From pressure measurements Williamson[10] concluded that the order of the ketene decomposition in the initial stages is approximately 1.5. He reported an abnormal retardation of the reaction after 5–6% pressure increase. It was assumed that this pressure increase corresponded to 10–12% reaction. One of the purposes of the present study was to obtain analyses for the unreacted ketene as well as the products, during the reaction in a static system.

Experimental

Materials and Apparatus.—For the first half of the experiments in this research ketene from the pyrolysis of acetone in a "ketene lamp"[12] was used after fractionation in a low temperature Podbielniak column (90 cm., Heli-Grid packing). The boiling point for samples distilled at 75 cm. pressure was −50 to −51°.[13] By reaction with water

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(1) Abstracted from the Ph.D. thesis of W. B. Guenther, University of Rochester, 1954. This work was supported by a grant from the Celanese Corporation of America.

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