

Interaction of Aqueous Polyethylene Glycol Solutions with Iodine

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An experimental study of the interaction of iodine with the ether linkage of some polyethylene glycols was made. The conditions for producing 1:1 complexes of

$\begin{array}{c} -\text{CH}_2 \\ \diagdown \\ \text{O} \\ \diagup \\ -\text{CH}_2 \end{array} \cdot \text{I}_2$ were determined. Some qualitative observations are presented on the effects of polymer weight, polymer-iodine ratios in solution, and on the behavior of these complexes in analytical reactions.

SINCE the turn of the century (1) it has been known that iodine solutions in pure solvents are either violet or brown. Violet solutions are formed in such solvents as carbon disulfide, carbon tetrachloride, and simple aliphatic hydrocarbons. In these solvents the iodine has an absorption spectrum similar to that which it has in the gaseous state with an absorption maximum in the vicinity of 518 to 520 μ , and with a molar absorptivity of about 1000 (2). Brown solutions are formed when the iodine is dissolved in alcohols, ethers, ketones, organic acids, and basic nitrogenous solvents. Hildebrand and Glascock (3) showed that, at least in alcohols and ethers, 1:1 complexes were formed, and later Mulliken (4) showed by means of molecular orbital argumentation, that iodine would bind to the oxygen of an ether at right angles to the plane of the molecule. These solutions have an absorption maximum around 450 to 460 μ with a molar absorptivity a little bit less than that in the violet solution.

The blue form of iodine which is observed in the starch reaction or in the reaction of iodine with the cyclodextrins, benzonitrile, and coumarin complexes appears, from the X-ray diffraction studies of Cramer (5) to be due, not to the normal diatomic iodine form, but instead to a polymeric blue modification kept inside the channels within these inclusion compounds. Hence, these compounds are quite different from the ether-iodine complexes discussed here.

It is a well known phenomenon that the brown solutions tend to become violet when heated, reverting to their original color on cooling. Also it has been observed that in the case of the violet color of the carbon disulfide solution this may be shifted to the brown color as the solution is cooled in a dry ice-ether bath. Beckman (6) by means of precise molecular weight determinations in

both the violet and the brown solutions established that the iodine is present in the diatomic state in both instances. Thus, the current view is that when the iodine forms a weak coordination complex the brown color is observed, but these complexes may be easily dissociated merely by heating.

In this paper it is our intention to report some phenomena which were observed when we attempted to do iodometric titrations in the presence of aqueous solutions of some polyethylene glycol polymers¹ (PEG). Their structures may be written as $\text{HOCH}_2 \cdot (\text{CH}_2\text{OCH}_2)_n \cdot \text{CH}_2\text{OH}$, where the average n varies from 7.2 to 8.1 in the case of PEG 400, from 20.1 to 22.3 for PEG 1000, and from 67.0 to 83.0 in the case of PEG 4000. The authors have written the formula this way instead of the usual way, *viz.*, $\text{H}(\text{OCH}_2\text{CH}_2)_{n+1}\text{OH}$, because we wish to stress the polyether character of these molecules. From the work of a group of investigators and inventors (8), it is well known that iodine forms complexes with such polymeric materials, but it seemed to us that a qualitative description of what we observed plus some of the quantitative measurements which were made would provide the analyst with an understanding of what occurs in the above-mentioned solutions.

EXPERIMENTAL, RESULTS, AND DISCUSSION

To study the quantitative aspects of the interaction of polyethylene glycols with iodine, it was decided to work with the higher molecular weight PEG 4000 which had qualitatively been observed to yield solid, filterable precipitates with KI_3 solutions. It was anticipated that a PEG which yields a precipitate with iodine in aqueous solutions would permit an evaluation of the limiting molar ratio I_2 -PEG in the complex. To make this evaluation it would be necessary to form the precipitates in solutions with large excesses of KI_3 relative to the

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PEG. For this purpose the concentration of PEG 4000 is expressed as molarity of $-\text{CH}_2\text{OCH}_2-$ (mol. wt. = 44), and the contribution of the end $-\text{CH}_2\text{OH}$ groups to the molecular weight is neglected.

In the experiment, 10.0 ml. or less of an appropriately diluted stock solution of PEG 4000 was pipeted into ground-glass-stoppered flasks, enough water was added to make 10.0 ml., and then 10.0 ml. of 0.0554 *M* KI_3 solution was added. The mixtures were swirled and set aside in a dark place for from 3 to 6.5 hr., after which time the suspension was vacuum filtered through a membrane filter. An aliquot of each filtrate was pipeted into a flask, about 5 ml. of 1 *N* H_2SO_4 and 10 ml. of H_2O were added, and the solution was titrated to a colorless end point. The amount of unprecipitated iodine in the 20.0-ml. of reaction mixture thus is determined, and by difference the amount of complexed and precipitated iodine is known.

The data obtained are plotted in Fig. 1, with the ordinate representing the number of mmoles

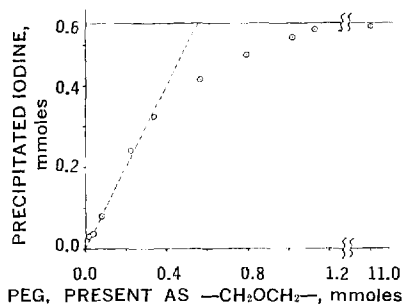


Fig. 1.—Precipitation of I_2 by PEG 4000.

of iodine precipitated and the abscissa representing the mmoles of $-\text{CH}_2\text{OCH}_2-$ added. It will be observed that at high ratios of iodine to ether, *i.e.*, where very small quantities of $-\text{CH}_2\text{OCH}_2-$ were added, each mole of $-\text{CH}_2\text{OCH}_2-$ added precipitated 1 mole of I_2 . Thus, initially the points fall on the straight dotted line with a slope of unity. In the light of Hildebrand and Glascock's experimental observations and Mulliken's calculations, cited previously, this is exactly what one would expect.

As the amount of PEG added increases so that the iodine remaining in solution is depleted, a deviation from the straight line is observed, and the experimental points form a curve which asymptotically approaches the limiting value of 0.0554. This can be understood in terms of the competing equilibria in these solutions, the iodine being complexed by both the ether and the iodide ion present in solution. If the iodine-ether complexation constant was very much larger than that of the triple iodide ion, the experimental points would remain on the straight line right up to the limiting value of 0.0554. The fact that they do not merely indicates that they are approximately of the same order of magnitude. The value for the reaction ($\text{I}^- + \text{I}_2 \rightleftharpoons \text{I}_3^-$) is about 725 (9) at 25°.

In the course of the above experiment some interesting qualitative observations were made. These observations concern the color and character of the

precipitates. In those solutions where the residual iodine concentration was high, the precipitates were dense and dark black with a submetallic lustre resembling that of iodine itself. On the other hand, where the mole ratio of ether to iodine was large, *i.e.*, 10 and higher, the precipitates were very much more voluminous and were light reddish-brown in color, becoming lighter as the ratio was increased.

Thus, it is apparent that when every ether oxygen is coordinated with iodine, a precipitate resembling iodine crystals in color and lustre is observed, but when the coordination is made to every tenth oxygen or less, the color of the precipitate appears more like that of a dilute ether solution of iodine. It was also evident that only a small fraction of the ether linkages had to be coordinated before the solubility of the PEG was reduced so that precipitation occurred.

Another interesting phenomenon was observed when precipitates with low iodine: $-\text{CH}_2\text{OCH}_2-$ ratios were washed with distilled water. These light reddish-brown precipitates immediately became much darker in color, and their appearance changed to that of the precipitates with the I_2 : $-\text{CH}_2\text{OCH}_2-$ ratios of approximately 1. This occurred whether they were washed by decantation or directly on filter paper. In addition it was observed that there was a substantial reduction in the volume of the precipitate. Furthermore, the filtrate or the supernatant from such a washing has a light but definite yellow color. A possible explanation of this phenomenon follows.

The PEG 4000 precipitate can be assumed to have the iodine randomly distributed among its ether oxygens, but weighting each individual molecule sufficiently so that it is made insoluble. However, not every oxygen position is coordinated with iodine as evidenced by the light color of the precipitate. On washing, however, disproportionation occurs with iodine from some of the molecules being transferred to others, producing complexes that have a higher I_2 : $-\text{CH}_2\text{OCH}_2-$ ratio and ones which have a much lower ratio. The former of these which approach the 1:1 complex are dark and insoluble, whereas the latter having a relatively small number of ether oxygens complexed with iodine, are light colored and water soluble. The effect is indeed a very striking one to observe.

Additional Qualitative Observations.—In light of the phenomena which have been described above, it was thought appropriate to make a qualitative comparison between the interaction of the KI_3 solutions with PEGs of various molecular weights. Those available were PEG 400, 1000, and 4000. The purpose of this study was to determine the relative ease of precipitating the lighter and heavier PEGs, using minimal amounts of iodine to accomplish that objective. The actual experiment performed was to dissolve 6.0 Gm. of each of the PEGs in 10.0 ml. of water. This makes a solution which is 13.6 *M* in ether linkages. Again the terminal $-\text{CH}_2\text{OH}$ groups are ignored. These 10.0-ml. portions of PEG solutions were titrated dropwise with an 0.0554 *M* KI_3 solution with continuous agitation. In all 3 cases, as the first drop and each successive drop of KI_3 was added, a reddish-brown precipitate formed in the area where the drop initially contacted the solution. However, it dissolved with agitation to give a yellow solution

TABLE I.—ASSAY RESULTS WITH POLYETHYLENE GLYCOLS

PEG	ml. KI ₃ to Achieve Precipitation	mole Ratio, —CH ₂ OCH ₂ — KI ₃	I ₂ % Easily Titratable
400	8.5	290	98
1000	4.2	585	43
4000	3.5	713	...

which became more and more wine-red in color as more KI₃ was added. Finally, as the titration continued, there came a point at which the reddish-brown turbidity persisted, and further addition of KI₃ only increased the amount of turbidity. The second column of Table I lists the ml. of titrant required just to reach the point of permanent turbidity for each of the PEGs.

It will be seen that as the molecular weight of the PEG increases, the amount of KI₃ needed decreases. In the third column of Table I this is further illustrated by presenting the mole ratio of ether linkages to the KI₃ at that point. After the point of permanent turbidity had been reached, enough additional KI₃ was added to bring the volume of that reagent to 10.0 ml. The precipitates obtained were watched for the next 1.5 hr. to observe alterations in their characteristics. In the case of the PEG 400, the solution initially had a reddish-brown suspension in it, but with time and occasional swirling of the flask, this precipitate coalesced to give a few drops of a dark black liquid. When the supernatant liquid was decanted, these globules collapsed and appeared to wet the glass. The thin films formed in this way were dark red by transmitted light.

In the case of PEG 1000, as the precipitate aged, a dark black portion of liquid material similar to that observed with the PEG 400 and some light reddish-brown wax-like solids were observed. In the case of the PEG 4000, the changes which occurred were not very striking, except that the very light brown precipitates that formed initially appeared to get darker with time and to diminish to some extent in volume. After about 15 min. this precipitate had settled out, leaving a very lightly straw-colored solution above it.

The situation obtained in these solutions after the rapid addition of the additional KI₃ to make the final 10.0 ml. is one where the mole ratio of ether oxygens to iodine is still quite high, being about 246. It is evident for precipitation to occur under such circumstances, that the iodine be concentrated on some molecules, rendering them insoluble, while the bulk of the remaining molecules have so few iodine atoms on them that they remain in solution. This is the final situation which prevails after a period of time sufficiently long to bring the system to equilibrium.

When the lower molecular weight PEG is used, the iodine concentrates on the precipitated molecules to give them an iodine-ether ratio close to unity as evidenced by their dark color. With the higher molecular weight polymers a lower ratio leads to precipitation.

The changes that occurred with time are those associated with bringing the system to this disproportionate equilibrium and to coalescence of

the liquid-like product from the lower polymers, and perhaps some aging of the higher polymer precipitates.

Several interesting additional observations were made. The first is concerned with the relative ease of dissociating these precipitated complexes. This was studied by titrating the iodine with standard Na₂S₂O₃, employing moderate agitation of the solution during the titration. The titrations were performed rapidly, *i.e.*, in a matter of several minutes, to see how quickly the iodine became available. The titrant was added until the supernatant was just colorless. The per cent recovery of the iodine is given in the fourth column of Table I. In the case of the PEG 400, nearly all of the iodine was recovered immediately, and with vigorous and prolonged agitation, the small residual amount of dark material could be brought into solution with all of the iodine being recovered. With PEG 1000, however, this is not so easily accomplished. The iodine is tenaciously retained by the precipitate and only 43% could be readily recovered. With the PEG 4000, recovery was essentially zero or very little, and also the precipitate interfered with the end point detection.

A second observation, relating to the dissociation of these complexes was made when a solvent like propylene glycol was added. If it was added to the extent of about 50 vol. %, precipitation of the iodine-PEG complexes was avoided completely. If the propylene glycol was added with heating after precipitation had been effected, the precipitates redissolved, and quantitative recovery of the iodine was achieved. The explanation here, of course, is that an additional coordinating reagent has been added which is competing nearly as strongly as the PEG itself for the iodine. Consequently, the PEG coordinates only a small fraction of the iodine, insufficient in amount to achieve precipitation. Furthermore, this alcohol has a greater solvent effect than water, for both the PEG and the PEG-iodine precipitate.

Two additional observations of interest were the following: aqueous solutions of the PEGs can extract, to a degree, the iodine present in the violet-colored chloroform and carbon tetrachloride solutions, and the vapor pressure of iodine over well-dried PEG-iodine precipitates was significantly lower than that of iodine itself. If the PEG 1000-iodine precipitate was heated on a spatula, the iodine could be driven off, but the reaction was slow and the temperature had to be in excess of 100°.

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