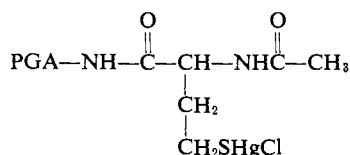


transition is quite sharp at about pH 5.8, but in 0.2 *M* sodium chloride the transition is shifted to approximately pH 5.2.

Poly-L-glutamic acid (DP 530) as the sodium salt was purchased from Pilot Chemical Co. Sodium chloride, mercuric chloride, sodium hydroxide, and potassium hydrogen phthalate were purchased as analyzed reagents from the Baker Chemical Co. The N-acetyl-DL-homocysteine thiolactone was obtained from Professor L. Stryer of Stanford University. The  $^{35}\text{Cl}$  line-width measurements were made on a Varian Model V-4300 nmr spectrometer at 4.3 Mc using 500-cycle modulation and lock-in-detection to stabilize the base line.

Poly-L-glutamate was labeled at the terminal amide function by reaction with N-acetyl-DL-homocysteine thiolactone using the method reported by Benesch and Benesch.<sup>6</sup> The solutions measured were made using a sodium hydroxide-potassium hydrogen phthalate buffer over a pH range from 4 to 8. All solutions were 1.00 *M* in sodium chloride,  $1.0 \times 10^{-4}$  *M* in mercuric chloride, and 0.18% poly-L-glutamate by weight. On mixing the labeled poly-L-glutamate with the mercury solution, the mercury adds to the -SH group so that the total molecule observed may be represented as



Although the mercury(II) is in approximately a tenfold excess, the line broadening caused by  $10^{-4}$  *M* mercury(II) in 1.0 *M* sodium chloride is less than 2 cps.<sup>7</sup> Under these conditions the probabilities of the chloride being at each site are a constant from one solution to the next so that any change in line width reflects only changes in the correlation time of the mercury site induced by the variations of pH. The experimental results are summarized in Figure 1.

The detailed features of the experimental curve are in excellent agreement with those reported by Idelson and Blout for optical rotation as a function of pH for a 0.2% solution of poly-L-glutamate in 0.2 *M* sodium chloride.<sup>4</sup> In that plot, however, there was a maximum at about pH 4.6 and the authors suggested that the decrease from the maximum rotation associated with the helical form could be caused by a contraction of the helix resulting from protonation of the carboxyl groups. While such a maximum is consistent with the data in Figure 1, the data are also consistent with a straight line of zero slope. This indicates that a change in the correlation time for the helix associated with such a contraction is on the order of the experimental error for this technique. These results demonstrate that the halogen ion probe is a sensitive technique for the investigation of structural properties and gross behavior of large molecules in solution.

(4) M. Idelson and E. R. Blout, *J. Am. Chem. Soc.*, **80**, 4631 (1958).

(5) P. Doty, A. Wada, J. T. Yang, and E. R. Blout, *J. Polymer Sci.*, **23**, 851 (1957).

(6) R. Benesch and R. E. Benesch, *Biochim. Biophys. Acta*, **63**, 166 (1962).

(7) At high pH the  $\text{OH}^-$  ion interferes with the chloride exchange at the mercury site; however, below pH 9 the exchange is unaffected: R. Bryant, unpublished results.

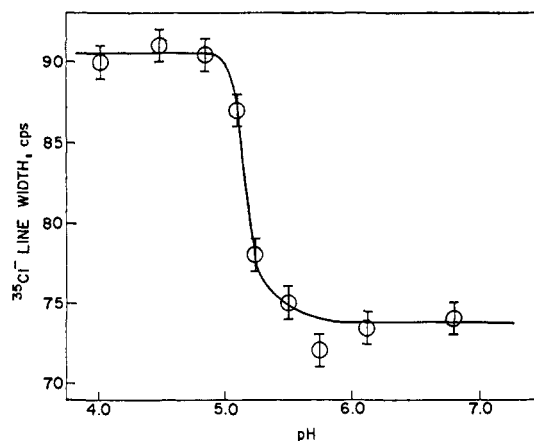


Figure 1.  $^{35}\text{Cl}$  line width as a function of pH for 0.18% poly-L-glutamic acid in 1.0 *M* sodium chloride showing the poly-L-glutamic acid helix-coil transition at pH 5.2.

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## Oxidation of Radon in Aqueous Solutions

Sir:

We have observed an apparent oxidation of radon in aqueous oxidizing solutions under certain conditions. Previously, Fields, Stein, and Zirin reported that a radon fluoride of low volatility was formed when radon and fluorine were heated to  $400^\circ$ ,<sup>1</sup> but research on the chemistry of radon has been limited because of the short half-life and high specific activity of radon, a radioactive daughter of radium.

In our experiments,  $10^{-7}$  *M*  $\text{RaBr}_2$  solutions were allowed to remain in contact with various aqueous, oxidizing solutions for a period of 23 days or longer (six half-lives of radon). These solutions were then extracted with equal amounts of hexane. The relative amounts of radon in the two phases were determined by counting the 0.35-Mev  $\alpha$  activity of a subsequent daughter,  $^{214}\text{Pb}$ . The samples were counted after a 2-hr aging period which was sufficient time to essentially establish a state of secular equilibrium between the  $^{222}\text{Rn}$  and the  $^{214}\text{Pb}$ . The ratios of the  $^{214}\text{Pb}$  counting rates in the two phases are given in Table I as the distribution ratio of radon between hexane and the various aqueous solutions. The error given is the standard deviation of the 6-12 trials run on each particular aqueous phase. A change from a nonpolar species in water to a polar or ionic species in oxidizing solutions is apparent. This behavior is not due to merely the influence of electrolyte in the aqueous phase. Tatsuya

(1) P. R. Fields, L. Stein, and M. H. Zirin, "Noble Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago, Ill., 1963, pp 113-119; *J. Am. Chem. Soc.*, **84**, 4164 (1962).

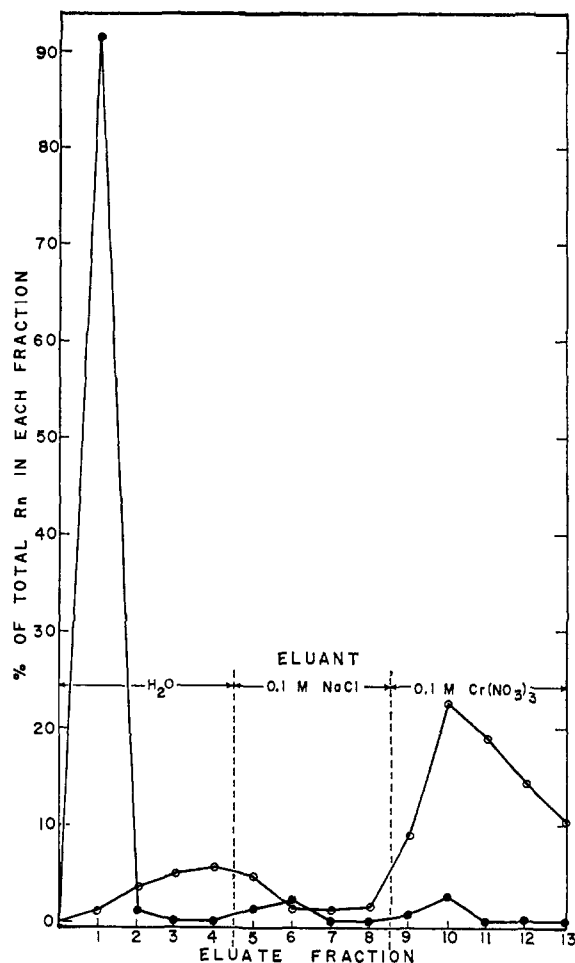


Figure 1. Anion exchange of nonoxidized Rn (●) in H<sub>2</sub>O and oxidized Rn (○) in 0.1 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, made strongly alkaline with NH<sub>4</sub>OH.

and Yamasaki<sup>2</sup> have shown that addition of strong electrolyte to water lowers the solubility of radon in that phase, whereas in our experiments, the opposite effect was observed in that the distribution ratio for extraction was diminished when oxidizing electrolytes were present in the aqueous phase.

Table I. Distribution Ratios for Extraction of Radon into Hexane from Aqueous Solution

Aqueous phase (all contained RaBr <sub>2</sub> )	Distribution ratios (hexane/aqueous)
H <sub>2</sub> O	33.2 ± 6.3
5% H <sub>2</sub> O <sub>2</sub>	10.4 ± 1.5
5% H <sub>2</sub> O <sub>2</sub> -1 N HNO <sub>3</sub>	7.0 ± 0.9
25% H <sub>2</sub> O <sub>2</sub>	4.3 ± 1.8
25% H <sub>2</sub> O <sub>2</sub> -1 N HNO <sub>3</sub>	3.4 ± 1.5
0.5 M K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	7.3 ± 0.8
0.2 M KMnO <sub>4</sub>	2.6 ± 0.8
0.1 M K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.2 ± 0.1

This apparent oxidation of radon is substantiated by the results of flushing the aqueous solutions with air or argon. Five times the amount of radon was removed from a nonoxidizing solution as was removed

(2) S. Tatsuya and A. Yamasaki, *Bull. Chem. Soc. Japan*, **38**, 1110 (1965).

from an oxidizing solution after 1 hr of bubbling air through the solutions. Further argon flushing of the nonoxidizing solution removed an additional small amount of radon, while further flushing of the oxidizing solution produced no additional loss.

Ion-exchange experiments were conducted with the radon from the 0.1 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and the 25% H<sub>2</sub>O<sub>2</sub> solutions. They have shown the oxidized radon species to be nonionic in a neutral or acidic solution and to be negatively charged in a strongly alkaline solution. The resins used were 100-200 mesh Dowex 1-X8 anion exchanger (Cl<sup>-</sup> form) and Dowex 50-X8 cation-exchange resin (H<sup>+</sup> form). The anion-exchange resin bed was washed exhaustively with sodium hydroxide to convert the resin to the hydroxide form. The various radon solutions were allowed to flow through the particular resin at a rate of 1 ml/min. The elution process then consisted simply of passing the desired eluent through the column at the same rate and collecting the eluate in 5-ml fractions. The amount of radon in each fraction was then determined in the previously described manner. The eluents consisted of water, 0.1 M NaCl, and 0.1 M Cr(NO<sub>3</sub>)<sub>3</sub>, consecutively. Oxidized radon in solutions that had been made strongly alkaline with ammonium hydroxide (trials at pH 11.4, 11.8, and 12.5) was retained on the anion-exchange column. Elution was not accomplished with water or chloride ions, but the radon was removed by elution with nitrate ions (see Figure 1). Oxidized radon in a neutral or acidic solution, when passed through the anion-exchange column, could be eluted with water. The same was found for oxidized radon, regardless of acidic or basic conditions, when passed through the cation-exchange resin. Nonoxidized radon produced from radium decay in water was not retained on either the cation- or anion-exchange resin regardless of the pH of the radon solution. Figure 1 gives an example of nonoxidized radon passed through an anion-exchange resin.

Oxidized radon in neutral or acidic solutions behaved as a polar but nonionic species. It was non-extractable into hexane, and, when it was passed through either an anion- or cation-exchange column, a larger volume of water (ca. 25 ml) was required for elution than was required for the elution of the nonoxidized form (ca. 5 ml).

If an analogy is drawn between radon and xenon,<sup>3,4</sup> the oxidized radon species could be RnO<sub>3</sub> below a pH of 11 and HRnO<sub>4</sub><sup>-</sup> above a pH of 11. However, further work is required to reveal the extent to which any such analogy can be made.

The oxidation of radon has been accomplished only in solutions in which <sup>222</sup>Rn has been allowed to come to secular equilibrium with <sup>226</sup>Ra. Attempts at oxidizing elemental radon, which had previously been separated from its parent radium, have been unsuccessful.<sup>5</sup>

(3) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(4) H. H. Claassen and G. Knapp, *ibid.*, **86**, 2341 (1964).

(5) This work was supported by the Atomic Energy Commission, Contract AT(11-1)-584.

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